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Solubility of Ethylene, 1-Butene and 1-Hexene in Polyethylenes

by

Mark Henry Mulder

A thesis submitted to the Faculty of Graduate Studies and Research in
partial fulfillment of the requirements for the degree of
Master of Science in Chemical Engineering

Department of Chemical and Materials Engineering

Edmonton, Alberta

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ABSTRACT

In this thesis a description of the procedures and equipment for measuring the solubility of ethylene, 1-butene and 1-hexene in polyethylene at pressures up to 3500 kPa and temperatures ranging from 30 to 90°C are presented. The method chosen to measure the weight change of the gases sorbed into the polyethylene was a gravimetric method using a Cahn D110 microbalance. The required buoyancy correction was determined by measuring the volume change of the polyethylene at the various pressures and temperatures of this study with a cathetometer. The crystallinity of the polyethylene samples was measured by x-ray diffraction and the density was measured using Archimedes principle.

Results of the volume change measurements for four polyethylene samples having crystallinities from 19 to 70% and the ethylene solubility for a sample with 47% crystallinity are presented. For ethylene sorption, the swelling varied linearly with ethylene pressure and was not very sensitive to temperature in the 30 to 90°C range. Volume changes at about 3500 kPa ethylene pressure varied from 0.5 to 2.2% for changes in polyethylene crystallinity from 70 to 19%. The ethylene solubility followed Henry's law; the solubility coefficients at 30, 50 and 70°C were 0.0559, 0.0528 and 0.0501 (mg C_2H_4)/(g PE $atm_{C_2H_4}$), respectively.

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NOMENCLATURE

2θ	x-ray diffraction angle
α_a	weight fraction of amorphous polyethylene
α_T^{Po}	thermal expansion coefficient
β_P^{Po}	pressure expansion coefficient
χ	Flory-Huggins interaction parameter
ΔH_c	enthalpy of condensation
ΔH_m	enthalpy of mixing
ΔH_s	enthalpy of solution (sorption)
$\frac{\varepsilon}{k}$	Lennard-Jones force constant
λ	x-ray wavelength
μg	microgram
μm	micrometer
ν	volume fraction
ρ_f	density of a fluid
ρ_s	density of a solid material
ω	acentric factor
a	activity
atm	atmosphere
A_{110}	uncorrected area under the 110 crystalline peak
A_{200}	uncorrected area under the 200 crystalline peak
A_{210}	uncorrected area under the 210 crystalline peak

A_{A1}	uncorrected area under the first amorphous peak
A_{A2}	uncorrected area under the second amorphous peak
as_{110}	atomic scattering correction factor for the 110 crystalline peak
as_{A1}	atomic scattering correction factor for the first amorphous peak
Al	aluminum
Au	gold
B	Bunn factor
cm	centimeter
C	concentration
^{o}C	degrees Celsius
C_{110}	overall correction for the 110 crystalline peak
C_{200}	overall correction for the 200 crystalline peak
C_{210}	overall correction for the 210 crystalline peak
C_{A1}	overall correction for the first amorphous peak
C_{A2}	overall correction for the second amorphous peak
d	density
d_a	density of 100% amorphous polyethylene
d_c	density of 100% crystalline polyethylene
dc	direct current
D	diffusion constant
f_t	temperature correction factor
f_{t110}	temperature correction factor for the 110 crystalline peak
f_{tA1}	temperature correction factor for the first amorphous peak

g	grams
Hg	mercury
HDPE	high-density polyethylene
In	length increase of the polyethylene sample
IUPAC	International Union of Pure and Applied Chemistry
kg	kilogram
k_H	Henry's Law coefficient
kmol	kilogram moles
kPa	kilopascal
K	Kelvin
L	length of the polyethylene sample
L_0	initial length of the polyethylene after cell had been evacuated
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
Lp	Lorentz-Polarization correction factor
Lp_{110}	Lorentz-Polarization correction factor for the 110 crystalline peak
Lp_{A1}	Lorentz-Polarization correction factor for the first amorphous peak
L_P^{Po}	length of the polyethylene at pressure, P
L_0^{Po}	length of the polyethylene when the cell is evacuated
L_T^{Po}	length of the polyethylene at temperature, T
$L_{T_b}^{Po}$	length of the polyethylene at some base temperature
m	meters
mg	milligrams

mm	millimeters
mV	millivolts
P	pressure
P_l^o	vapor pressure
Pa	pascal
P_c	critical pressure
P_m	Permeability constant
P_r^o	reduced vapor pressure
R	universal gas constant
s	seconds
slpm	standard liter per minute
S	solubility
S_c	solubility coefficient
STP	standard temperature and pressure (0°C and 101.325 kPa)
T	temperature
T_c	critical temperature
TEA	Thermal Evolution Analyzer
T_r	reduced temperature
UNIFAC	universal functional group activity coefficient
v	volts
v_s	specific volume
V	volume
V_m	partial molar volume

$V_{T.P}^{Po}$	volume of the polyethylene at some temperature and pressure
w	watt
W_a	weight of a substance in air
WAXS	wide angle x-ray scattering
W_s	weight of a substance when it is submerged in a liquid
X	crystallinity
X_C	corrected crystallinity
X_{UC}	uncorrected crystallinity

1. INTRODUCTION

Polyethylene is a polyolefin, which is represented by the formula $CH_3(C_2H_4)_nCH_3$. This formula, however, is inadequate in describing the wide variety of structurally different forms of polyethylene. The three main types of polyethylene are high-density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE). These three types of polyethylene have different molecular structures. HDPE has virtually no side branches; LLDPE has short side branches and LDPE has long and short side branches as illustrated below in Figure 1.1.

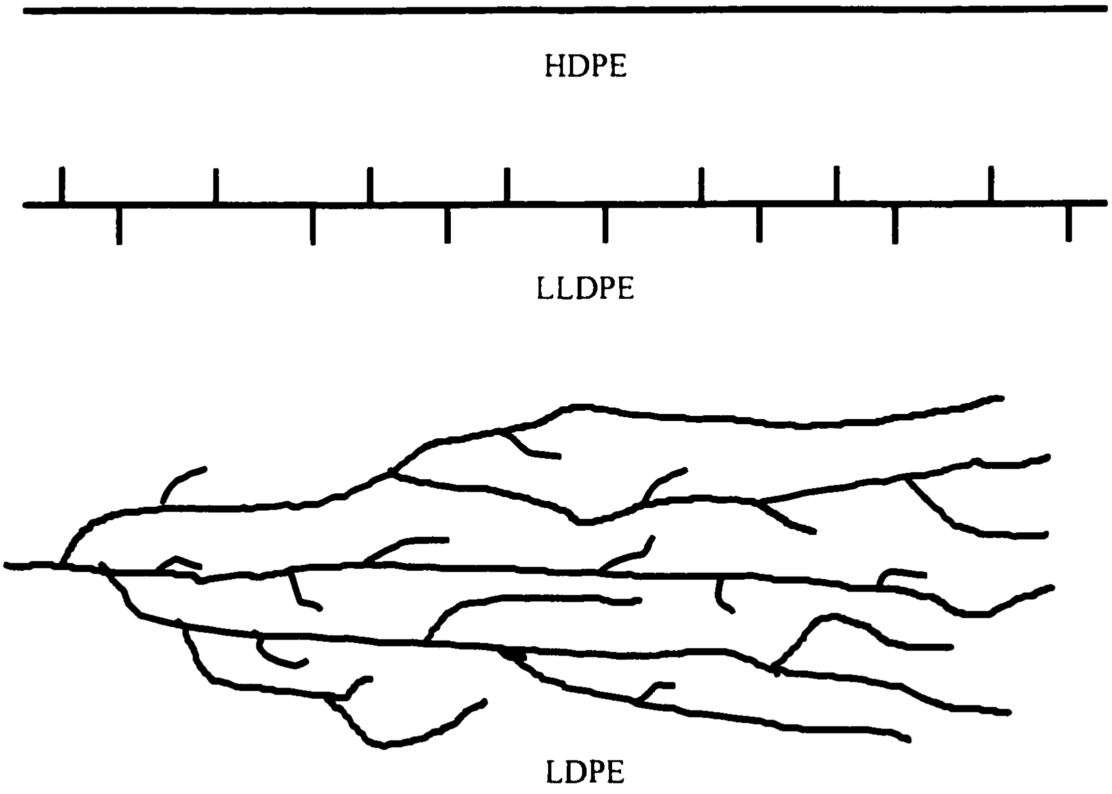


Figure 1.1 Structure of HDPE, LLDPE and LDPE

A number of different monomers are used to produce polyethylene. A monomer is a molecule, which combines with other molecules of the same or different type to form a polymer. In this study the solubility of the monomers: ethylene, 1-butene and 1-hexene in polyethylene were examined. Properties of these monomers are shown in Table 1.1 below.

Table 1.1 Properties of Ethylene, 1-Butene and 1-Hexene

Monomer	Molecular Weight kg/kmol	Critical Temp (K)	Critical Pressure (kPa)	Liquid Molar Volume (m^3/kmol)	Acentric Factor (1)	Flammability Limits (2) (vol %)
Ethylene	28.054	282.3	5031.8	0.0492	0.0852	2.7 to 36
1-Butene	56.107	419.5	4019.6	0.0896	0.1867	1.6 to 9.3
1-Hexene	84.161	504.0	3140.0	0.1261	0.2800	1.2 to 9.2

Notes:
1. The acentric factor is calculated from the accepted vapor pressure and the definition $\omega = -\log_{10}(P_r^o)_{Tr=0.7} - 1.000$ where $(P_r^o)_{Tr=0.7}$ is the reduced vapor pressure at a reduced temperature of 0.7
2. The flammability limits are the boundary-line mixtures of vapor or gas with air, which if ignited will just propagate flame. They are given in terms of percentage by volume of gas or vapor in the air.

Solubility is the amount of one substance that will dissolve into a given amount of another substance at equilibrium and at a given temperature.

It is important to know the solubility of monomers in polyethylene for a number of reasons. One reason is to properly design purge systems to recover monomers and prevent fires after the polyethylene has been produced. Polyethylene is produced by solution, slurry or gas-phase processes and these processes leave some monomer in the freshly produced polyethylene which evolves out by a diffusion-controlled mechanism. The evolved monomer and the air surrounding the polymer pellets can form a combustible mixture. According to Beret et al. (1977) bin fires due to the inadequate purging of freshly produced polyethylene and ethylene-vinyl acetate copolymers have occurred. Ignition is usually caused by sparks from static electricity generated during pneumatic conveying of the polyethylene pellets. Because the monomers and an ignition source can be assumed present any time freshly produced polyethylene is handled, it is essential that the production facilities be designed to prevent the formation of a combustible mixture. Rational design and operation of purge systems for polyethylene production requires quantitative data on the level of residual monomer in the resin and rate at which the monomer evolves from the resin. Quantitative information about the solubility of ethylene and comonomers in polyethylenes is also required to properly model the kinetics of polyethylene polymerization in gas-phase and slurry processes.

It is surprising that very little information on the solubility of olefins in polyethylenes is available in the open literature and discussions with polyethylene producers indicates that even the amount of proprietary data on olefin solubility in polyethylenes is very limited. It is the objective of this work to develop methods for the measurement of olefin solubility in polyethylenes and to provide data on these solubilities.

2. LITERATURE REVIEW

The intent of this section is to give an overview of the published research papers on the measurement of the solubility of gases in solid polyethylene and when those gases are ethylene, 1-butene or 1-hexene details of the results will be reported. The articles are arranged in chronological order and if the method of solubility has already been described in an earlier article the method is not described again, but the name of the method is mentioned and the conclusions determined by the researchers are presented. The description of the solubility measurement method is restricted to the description supplied by the research paper, which in some cases was extremely limited. A brief summary of the conclusions reached, by the researchers, pertaining to the solubility of gases in polyethylene is also included

In 1958 Michaels and Parker from Massachusetts Institute of Technology determined the solubility of oxygen and nitrogen in polyethylene by a pressure decay method. A quantity of 150 g of polyethylene pellets was placed in a glass sample bulb, which was attached to the measurement system by a ground glass joint. The sample was allowed to come to equilibrium with the test gas at atmospheric pressure at 25°C. After equilibrium the system was exhausted rapidly by way of a large-bore stopcock and a Megavac pump. A pressure of less than 0.05 mm Hg was easily attained in a one minute pumping interval. After pumping, the sample bulb and associated tubing was sealed and allowed to come to final pressure equilibrium. The initial and final pressures were used to determine the solubility of the gas in the polyethylene by a simple material balance. This procedure required a small correction for the gas lost (<5%) during the rapid evacuation period. The amount of gas lost was estimated from diffusion experiments performed earlier by others on similar materials. Michaels and Parker (1958) believed that their method of solubility measurement was useful for studying any gas-solid system where the solubility constant and the diffusion constant for the gas in the solid are small.

In 1959 Michaels and Parker determined the solubility of carbon dioxide in polyethylene by the same method and concluded:

(1) The solubility of nitrogen, oxygen and carbon dioxide in polyethylene is dependent on the volume fraction of amorphous polymer. This relationship indicates that gas is insoluble in the crystalline fraction of the polymer for the gases studied. Analytically their finding may be expressed as:

$$S_c = \alpha_a S_0 \tag{2.1}$$

Where S_c is the solubility coefficient (weight of gas/weight of polymer x pressure), α_a is the weight fraction of amorphous polyethylene and S_0 is the solubility coefficient at a 100% amorphous condition.

(2) The temperature dependence of the solubility coefficient from 10-50°C obeyed the van't Hoff relationship of

$$S_c = S_0 e^{-\frac{\Delta H}{RT}} \tag{2.2}$$

where S_c is the solubility coefficient (cm^3 of gas at STP/ cm^3 of polyethylene – atm) S_0 is a constant, ΔH is the apparent enthalpy of solution, R is the gas constant and T is the absolute temperature of the measurement.

Rogers et al. (1960) from Syracuse University measured the solubility, diffusion and permeation of methyl bromide, ethyl bromide, isobutylene, n-pentane, n-hexane, n-heptane, n-octane, cyclohexane, benzene, toluene, ethyl benzene, p-xylene, chloroform, and carbon tetrachloride in polyethylene by means of a quartz helix microbalance. The basic apparatus was modified slightly in design to allow the portion of the glass tube containing the film sample suspended on the helix to be surrounded by a constant temperature bath so that measurements at below room temperature could be made. The measurements were conducted at temperatures of −8 to 30°C and at pressures up to the vapor pressures of the gases studied.

Rogers et al. concluded that:

(1) At lower concentration the sorbed penetrants obeyed Henry's law

$$C = k_H P \tag{2.3}$$

where k_H is the Henry's law coefficient, C is the gas concentration in the polymer and P is the gas pressure in contact with the polymer.

(2) For higher concentrations of sorbed penetrants, the solubility deviated from Henry's law, but could be represented by

$$S_c = S_0 e^{GV_m} \tag{2.4}$$

where S_c is the solubility coefficient, S_0 is the solubility coefficient at zero concentration for a penetrant of zero molar volume, G is a constant and V_m is the partial molar volume of the condensed vapor.

(3) There is a linear dependence of the solubility of the gases studied on the degree of crystallinity of the polyethylene with solubility increasing with decreasing crystallinity.

(4) The solubility coefficient increases as the molar volume of the condensed vapor increases. However, there are two general classes, the straight chain paraffins and the

more spherical aromatic and halogen compounds. The paraffins had a lower solubility then the aromatic and halogen compounds at the same molar volume.

(5) Solubility of the gases decreased with increasing temperature.

(6) The presence of the crystalline regions in polyethylene imposes a constraint on the polymer chains of the amorphous region. The crystalline regions act as cross-links restricting swelling of the polyethylene and sorption of the penetrant gas.

In 1961 Michaels and Bixler from Massachusetts Institute of Technology measured the solubility of helium, carbon monoxide, argon, methane, ethane, allene, propylene, propane, sulfur hexafluoride and methyl chloride in polyethylene. The solubility measurement was performed by two different methods. They used the same pressure decay method as Michaels and Parker had used earlier in 1958 and 1959 at atmospheric pressure.

They also used a time lag method where the solubility coefficient is determined indirectly from the equation $P_m = DS_c$ where P_m is permeability constant (flux rate per unit pressure gradient), D is the diffusion constant and S_c is the solubility coefficient. This equation was shown by Michaels and Parker (1959) to be valid for gases that obeyed the arbitrary criteria of permanent gases imposed in their study. These were that (a) the diffusion constant in polyethylene shall be independent of gas concentration, and (b) the solution process be characterized by Henry's Law (solubility proportional to pressure). The time lag method involves measuring P_m and D in a single experiment by bringing gas at a certain pressure in contact with one face on an initially evacuated polyethylene film. Pressures ranging from 0.7 to 107 kPa were used in this study. The pressure build-up due to the flow of gas through the film into a chamber downstream is measured as a function of time. The diffusion constant is derived from the unsteady state portion of the flow process and the permeability constant is calculated from the steady state portion. Michaels and Bixler (1961) found that the time lag method was somewhat less precise than the equilibrium solubility method used by Michaels and Parker (1958, 1959). An error analysis on an average experimental time lag run showed that the precision of solubility constants determined in this manner was ± 9% at the 95% confidence level. The major contribution to error arose from variation of sample thickness.

Michaels and Bixler (1961) concluded that:

(1) The temperature dependence of the solubility coefficients of the gases studied for temperatures from 5 to 55°C obeyed the van't Hoff relationship.

(2) The crystalline phase of polyethylene does not sorb gas molecules to any detectable extent in polyethylene for the gases studied.

(3) Polyethylene is macroscopically homogeneous and isotropic with respect to gas sorption and diffusion and amorphous regions in partially crystalline polyethylene are accessible to molecules at least as large as sulfur hexafluoride.

(4) The solubility coefficient can be correlated with the Lennard-Jones force constant by

$$\ln S_c = 0.022\frac{\varepsilon}{k} - 5.07 \tag{2.5}$$

where S_c is the solubility coefficient and ε/k is the Lennard-Jones force constant of the gas.

(5) The enthalpy of solution (ΔH_s) could be determined by

$$\Delta H_S = 1.75 - 0.0164\frac{\varepsilon}{k} \tag{2.6}$$

Eby (1964) from Dupont measured the solubility and diffusion rate of ethane in polyethylene using a gravimetric technique. Pieces 1.3 cm by 10 cm were cut from 0.2 mm sheets and placed in a Sartorius Electrona microbalance, which was evacuated. When the weight decreased less then 1 μg/h, ethane was admitted to the chamber to a pressure of 50 kPa and the weight was recorded as a function of time at 23°C. The data were corrected for the buoyancy of the counterweights and beam.

Eby concluded that:

(1) The solubility coefficient of ethane varies inversely with the lamella thickness of the polyethylene, suggesting absorption in the lamella boundaries. Lamellae were proposed to be relatively perfect crystals and the lamella boundaries to be less perfect and less dense.

In 1967 and 1968 Robeson and Smith from Union Carbide Corporation measured the solubility and diffusion of ethane-butane mixtures in polyethylene at atmospheric pressure by a unique method. A polyethylene film was placed in a copper desorption chamber and then the chamber was evacuated. The gas mixture was then introduced into the evacuated cylinder until the pressure reached atmospheric pressure. Sufficient time was allowed for the polyethylene and gas mixture to reach equilibrium and then the cylinder was quickly evacuated with a vacuum pump and flushed with a small controlled air leak for 15 seconds. After 15 seconds the cylinder was connected to the trapping system, which in turn was connected to a vacuum pump, and a controlled air leak was set to maintain the cylinder pressure at 0.13 to 0.27 kPa. Each glass trap was used for a predetermined time interval during desorption, so that desorbed gas composition data as a function of time could be obtained. After desorption was complete a sample from each tube was injected into a gas chromatograph for analysis. From the volume calculation for each trap and the gas chromatograph analysis the amount of both butane and ethane trapped during each time interval was calculated. The amount desorbed during the 15 second evacuation period was calculated from the experimentally determined diffusion coefficients.

Robeson and Smith (1967, 1968) discovered that:

(1) At 20 and 30°C the solubility constant for both penetrants increased with increasing butane concentration, while at 40, 50 and 60°C the solubility of both gases obeyed Henry's law. It is believed that increased concentrations of the penetrant gas plasticize the polyethylene, resulting in increased solubility constants.

(2) The solubility of both ethane and butane decreased as the temperature of the experiment was increased.

Lowell and McCrum (1967) of Oxford University determined the solubility of cyclopropane in polyethylene by a gravimetric technique. The solubility was measured with a Sartorius vacuum microbalance. The measurement was performed at a pressure of 27 kPa, a temperature of 80°C and the polyethylene was between 70 to 80% crystalline.

Lowell and McCrum found that:

(1) In all the measurements Henry's law was obeyed

(2) The solubility coefficient increases as the amorphous fraction in polyethylene increases.

Stern et al. (1969, 1972, 1983a, 1983b, 1986) of Union Carbide Corporation studied the solubility and permeation of gases in polyethylene. They measured the solubility and permeation of carbon dioxide in polyethylene using a modified time lag method. Stern et al. (1969, 1972, 1983a, 1983b, 1986) also examined some of the existing data on the solubility of gases in polyethylene and discovered two main trends.

(1) The solubility of gases in polyethylene increases as the critical temperature of the gas increases as long as Henry's law is valid.

(2) The pressure at which deviation from Henry's law becomes appreciable decreases as the critical temperature of the solute increases. A plot of the log of the solubility coefficients versus $(T/T_c)^2$ for twenty-eight different substances, having solubility coefficients spanning five orders of magnitude and having critical temperatures in the range of 5.20 to 619.6 K delineated a single straight line, which lead to the equation:

$$\log S_c = -5.64 + 1.14\left(\frac{T}{T_c}\right)^2 \tag{2.7}$$

where S_c is the solubility coefficient in units of moles of solute per grams of amorphous polyethylene, T is the temperature of interest in Kelvin and T_c is the critical temperature of the solute in Kelvin.

In 1969 Li and Long of Esso Research and Engineering Company studied the solubility and permeation of ethylene, methane, nitrogen and mixtures of the same compounds in polyethylene. The solubility of the gases in polyethylene was determined by the quartz spring balance method. This method involves the use of a quartz spring in a high-pressure cell, which has a sight glass. The polymer sample is hung onto the tip of the spring and the solubility of the gas in the polyethylene is determined by measuring the extension of the quartz spring with a cathetometer with the buoyancy effect taken into account. The polyethylene used in this experiment had a crystalline content of 55%. The measurements took place at a temperature of 25°C and the pressures were between 1379 and 9653 kPa.

Li and Long (1969) discovered that:

(1) The solubility of the ethylene ranged from 0.8 g of gas/100 g of polyethylene at 1379 kPa to 6.8 g of gas per 100 g of polyethylene at 8960 kPa.

(2) The ethylene solubility was found to increase exponentially with increasing pressure, whereas the solubility of methane and nitrogen increased asymptotically toward a saturation value. The solubility obeyed Henry's law at low pressures, roughly up to the critical pressure of the gases.

(3) Results of the overall solubilities of methane-ethylene, methane-nitrogen and ethylene-nitrogen mixtures in polyethylene showed a very high plasticizing effect of the preferentially permeating compound. This means that the sorption of the more soluble compound in the polyethylene increased the solubility of the less soluble compound and therefore raised the total solubility of the mixture.

Deas et al. (1972) of Baylor University used a chromatographic method to measure the solubility of hydrogen in polyethylene. The experiments were performed at atmospheric pressure at temperatures ranging from 0 to 45.5°C. Their method included saturating the polyethylene with hydrogen and then after solubility equilibrium was attained the excess hydrogen was swept out of the sample tube by a blast of nitrogen. The tube was left for 24 hours and then connected to a gas chromatograph to measure the amount of hydrogen that was in the polyethylene. The greatest difficulty with this method is that it is necessary to remove all the excess gas from the space around the sample without leaving any residual gas in the tube, while at the same time not removing any gas that was dissolved in the sample.

Deas et al. (1972) determined that the solubility of hydrogen increased linearly as the amorphous fraction in the polyethylene increased, however this was not true for irradiated polyethylene or for a polyethylene containing extended-chain crystals.

In 1974 Kubo and Dole of Baylor University used a chromatographic method similar to Deas et al. (1972) to measure the solubility of hydrogen and helium in polyethylene. The measurements were carried out at 0, 25, 35 and 45°C and at atmospheric pressure.

They found that extraordinarily large amounts of hydrogen and helium were dissolved in the highly crystalline samples of polyethylene, when calculated on the basis of the amorphous content. These extraordinarily large amounts of dissolved gases in the polyethylene based on the amorphous content did not occur until the polyethylene was greater then 85% crystalline. They determined that the lower enthalpy of solution of this interaction was a major factor for the enhanced dissolution.

Takeuchi and Okamura (1976) from Meiji University in Japan measured the solubility and permeability of benzene, cyclohexane, n-hexane and toluene in polyethylene. They used a quartz balance to measure the weight increases of samples hanging in a vapor-laden nitrogen stream. The whole apparatus except the balance was placed in a large heat-insulated container, which assured a constant temperature. The experiments were performed at temperatures of 15 to 50°C and pressures of 1.3 to 9.3 kPa.

Takeuchi and Okamura (1976) confirmed that:

(1) The measured solubilities obeyed Henry's law at the studied pressures and temperatures.
(2) The solubility increased with decreasing crystallinity.
(3) The solubility coefficient decreased as the temperature increased.

Beret and Hager (1979) from Union Carbide measured the solubility and diffusion rates of ethylene in low-density polyethylene (LDPE), ethylene-ethyl acrylate and ethylene-vinyl acetate by a chromatographic method. Spherical pellets of LDPE were placed in a Dupont 916 Thermal Evolution Analyzer (TEA), which was connected to a computer. The pellets were saturated with ethylene by purging with high purity ethylene for more than 48 hours. The diffusion rate measurements began with the ethylene purge being replaced by a nitrogen purge of 1000 cm^3/min, which quickly stripped the ethylene from the sample holder. After 30 seconds the rapid purge was replaced with a high purity nitrogen stream with a volumetric flow rate of 30 cm^3/min. From this point on a flame ionization detector in the TEA continuously monitored the ethylene concentration in the nitrogen stream until the concentration fell below detectable levels. This process required 12-48 hours, depending on the polymer type and the pellet temperature. These measurements were conducted at atmospheric pressure and at temperatures of 23 to 74°C. The solubility of the ethylene in the polymer was determined by measuring the total ethylene evolved over the entire desorption time period.

Beret and Hager (1979) found that for a LDPE that was 48% crystalline the solubility ranged from about 2×10^{-5} moles of ethylene per gram of polymer at 75°C to about 3.4×10^{-5} moles of ethylene per gram of polymer at 23°C.

In 1983 Kulkarni and Stern of Syracuse University measured the solubility and diffusion coefficients of CO_2, CH_4, C_2H_4 and C_3H_8 in 45% crystalline polyethylene (density of 0.918 g/cm^3) by means of a unique volumetric technique. Polyethylene rods were enclosed in an absorption cell and thoroughly evacuated. A known volume of gas at the desired pressure and temperature was allowed to enter the absorption cell, where it is partially absorbed by the polymer sample. The gas pressure was maintained constant during this process by applying a suitable counter pressure through a column of mercury. The temperature of the absorption cell was also maintained constant. The decrease in gas volume due to absorption is accurately measured with a gas buret. The solubility is obtained from the mass of gas dissolved in the polymer when absorption equilibrium is reached. The solubility coefficients were measured at temperatures of 5, 20 and 35°C and at pressures up to 4053 kPa.

Kulkarni and Stern (1983) found that:

(1) The solubility coefficients of ethylene in polyethylene at 5, 20 and 35°C were 0.401, 0.485 and 0.570 cm^3 (STP) of ethylene per cm^3 polyethylene per atmosphere, respectively. The solubility coefficients can be converted to grams of ethylene per

grams of polyethylene per atmosphere, so that they can be compared to the values of Li and Long (1969) and Beret and Hagar (1979). This is accomplished by using the density of the polyethylene and the Peng-Robinson (1976) equation of state at STP to obtain the density of the ethylene. The converted solubility coefficients at 5, 20 and 35°C are 5.51×10^{-4}, 6.66×10^{-4}, and 7.83×10^{-4} grams of ethylene per grams of polyethylene per atmosphere, respectively.

(2) The solubility of all the penetrants was within the limit of Henry's law for the pressures and temperatures used in these experiments.

From 1986 to 1995, Kamiya and co-workers (1986a, 1986b, Hirose et al. (1986), 1988a, 1988b, 1989a, 1989b, Naito et al. (1991), 1992, 1995, Wang and Kamiya (1996)) of the Packaging Materials Division of the Industrial Products Research Institute in Japan wrote numerous papers on the solubility of gases in polymers. They have measured the solubility of ethylene and 1-butene gas in ethylene vinyl acetate; however, their only measurements involving polyethylene have been the solubility of nitrogen and carbon dioxide gas in polyethylene. Their papers are of importance because of the detailed explanations given of the gravimetric method employed in their solubility measurements. These papers go into detail on the buoyancy correction and the method of dilation measurement.

A Cahn model 2000 electrobalance set in a stainless-steel high-pressure chamber was used to measure the solubility of gases in polymers. The apparatus consisted of a high-pressure chamber in a thermostatically controlled air bath connected to a gas supply system. The gas supply system was comprised of gas connections, valves, pressure gauges and a flowmeter, which permitted the evacuation, purging and filling of the pressure chamber to the desired pressure. After calibration of the electromicrobalance, a polymer sample with a buoyancy compensator (Au wire) and a counterbalance (Al rod of 3 mm diameter) were threaded on Nichrome wires and attached to the weighing mechanism. The total volume of the sample film and buoyancy compensator was precisely adjusted to the volume of the counterbalance in order to eliminate the difference in buoyancy between the arms of the electromicrobalance.

The experimental procedure was first to evacuate the sample on the balance to a constant weight by a vacuum pump, then to admit a gas to the chamber stepwise up to 5066 kPa pressure. After the sorption measurement, the pressure was maintained for 24 hours and then the desorption isotherm was measured by decreasing the pressure stepwise to zero. At each step the pressure and weight changes were recorded. Most of the weight change occurred within the first hour of adding or removing the gas and then slow, long continued changes in weight were observed. The experiment was continued until the rate of weight change became less than 0.3% of the total amount of the sorbed gas per hour. The time required to reach equilibrium was usually at least 4 hours. About 15 minutes was needed to change the pressure of the gas at each step in order to avoid shifting the zero position of the electrobalance.

The sorption of CO_2 in polyethylene required that a correction for the buoyancy caused by the volume change of the polyethylene due to thermal expansion and CO2 sorptive dilation be applied to the solubility measurements. The sorptive dilation of the polyethylene was measured by observing the length change of a rectangular polyethylene film, about 45 by 3 mm, during sorption of CO_2 with a cathetometer having a precision of

0.01 mm. In a separate experiment, the thermal expansion coefficient of the polyethylene was determined at a pressure of <0.1 Pa. The system was evacuated by a vacuum pump and dilation was measured at temperatures from 25 to 75°C.

Kamiya and co-workers (1986a, 1986b, Hirose et al. (1986), 1988a, 1988b, 1989a, 1989b, Naito et al. (1991), 1992, 1995, Wang and Kamiya (1996)) concluded that Henry's law described the solubility of nitrogen and carbon dioxide in LDPE for gas pressures up to 5066 kPa.

Castro et al. (1987) of Argentina used an accurate gravimetric method to measure the solubility of n-butane, n-pentane, n-hexane and n-heptane vapors in polyethylene. A Cahn RG electrobalance was used to monitor the weight change. The electrobalance sample tube was immersed in a constant temperature bath and the experiment was performed at temperature intervals of 5°C from −15 to 45°C.

The entire system was completely evacuated before the start of each sorption run. Then the penetrant vapor was admitted into the system until the desired pressure was reached. The pressure in the cell and the weight gain of the sample were measured after no further increase in weight was observed; a process that usually took over two hours. After that more hydrocarbon vapor was admitted. This procedure was repeated until the maximum value of pressure permitted by the experimental system was reached. Upon completion of the sorption run, the vapor was evacuated from the electrobalance to begin the desorption run.

Castro et al. (1987) analyzed the results and determined:

(1) A unique expression to describe the solubility of the hydrocarbon vapors in polyethylene is

$$S = 7.91 \times 10^{-4} a^{1.08} \tag{2.8}$$

where S is the solubility in moles of gas per grams of polyethylene and "a" is the activity of the solvent.

(2) An expression similar to Stern et al. (1969, 1972, 1983a, 1983b, 1986) relating the solubility coefficient (mol/g amorphous polymer-atm) to the reduced temperature of the hydrocarbon vapor was also derived.

(3) The temperature dependence of the solubility obeyed the van't Hoff relationship.

(4) The solubility decreased as the temperature increased for the hydrocarbons studied.

(5) Flory-Huggins interaction parameters for each of the systems studied were obtained from:

$$\ln a = \ln \nu_1 + \nu_2 + \chi \nu_2^2 \tag{2.9}$$

where ν_1 is the volume fraction of penetrant and ν_2 is the volume fraction of polymer and χ is the interaction parameter.

The volume fractions were calculated from the known densities of pure components (liquid solvent) and the volume fraction of amorphous polyethylene assuming that the solvent and polymer volumes are additive on mixing. It was found that at temperatures above 30°C the interaction parameter remained approximately constant, which made it possible to use the Flory-Huggins Equation to calculate the solubility. It was also determined that it was possible to use the Flory-Huggins equation in the pressure range where Henry's law was valid to determine the solubility for the systems studied.

In 1988 Liu and Neogi from the University of Missouri at Rolla measured the solubility of benzene and n-hexane in polyethylene with a Cahn electrobalance that was enclosed within a constant temperature bath. The measurements were conducted at 25, 30, 40, 50 and 60°C and at pressures of between 2 to 7.3 kPa.

Liu and Neogi developed an equation similar to Castro et al. (1987) relating the activity of the gases with the volume fraction of the gas and the volume fraction of the polymer. This modified equation included the modulus of elasticity of the polymer, the universal gas constant and the temperature of the experiment.

Doong and Ho (1991) from Exxon measured the solubility of six aromatic vapors in polyethylene by a modified gravimetric sorption technique. A Cahn 2000 electrobalance was used to monitor the weight change. A flow system was employed in the apparatus so that it could handle the condensable vapors at high temperatures and partial pressures. With the flow system, the electronic components of the balance chamber were purged with an inert nitrogen gas, which exited through the side port of the hang-down tube. Penetrant vapor was carried into the system by nitrogen gas from the bottom of the hang down tube, and the penetrant vapor/nitrogen gas stream exited also through a side port of the hang down tube. For the penetrant stream, one nitrogen stream was bubbled through a liquid penetrant saturator and mixed with a second stream of pure nitrogen gas to give the desired partial pressure of the penetrant. Nitrogen flows were measured and controlled by mass flow controllers. The hang down tube, in which the polymer sample was placed in a pan with a hang down wire connected to the balance, was enclosed in a split tube furnace. All the incoming lines were wrapped with heating tapes to prevent any condensation of vapor. With the heating tapes wrapped around the feed lines, the flow system was capable of operating at penetrant activities (partial pressure/saturation pressure of penetrant at sample temperature) close to 1 and saturator temperatures close to the boiling point of the penetrant liquid. An alternative is to enclose the whole balance in a constant temperature box (Liu and Neogi, 1988). Nevertheless the box temperature cannot exceed the maximum allowable temperature of the electrobalance (usually 60°C). The measured weight change, sample temperature, and system pressure were stored in a computer via a data acquisition system.

The major complexity of the flow system was the hydrodynamic effect, which reduced the weight measured by the microbalance. This was overcome by switching the inlet flow to a bypass exhaust outlet at the end of the sorption equilibrium measurement. The equilibrium weight was then measured without the hydrodynamic effect for a short period of time (less then 0.5 minutes)

Doong and Ho (1991) concluded:

(1) The experimental data could be described by a theoretical model, which takes into account the free energy contributions in the penetrant-polymer system from combinatorial-entropy, free-volume, interactional-enthalpy, and elastic factors. Both UNIFAC group contribution and solubility parameter methods were used to calculate the interactional effects.

(2) The elastic contributions due to the inhibition of chain deformations in amorphous regions from crystalline domains were very significant in determining the temperature dependence of the solubilities. The elastic factor decreased the solubilities more significantly for the bulkier penetrants.

In 1993 Ghosal and Freeman from North Carolina State University reviewed 113 papers on the separation of gases using polymer membranes and concluded the following about the solubility of gases in polymers.

(1) The sorption of gases in polyethylene is similar to the sorption of gases in low molecular weight liquids, and gas concentration in the polymer often obeys Henry's law.

(2) For highly sorbing penetrants such as organic vapors, or gases at high pressures, penetrant concentration in the polymer may deviate from Henry's law. Under these circumstances, penetrant concentration in the polymer can often be satisfactorily represented by the Flory-Huggins equation:

$$\ln a = \ln \nu + (1 - \nu) + \chi(1 - \nu)^2 \tag{2.10}$$

Where "a" is the penetrant activity, v is the volume fraction of penetrant dissolved in the polymer and χ is the Flory-Huggins interaction parameter.

The penetrant activity is equal to P/P_0 for ideal gases. P and P_0 are the penetrant pressure in contact with the polymer and the penetrant vapor pressure, respectively.

(3) Gas solubility in polymers generally increases with increasing gas condensability. Gas critical temperature, normal boiling point or Lennard-Jones force constant are all measures of condensability which correlate well with the solubility coefficients of a range of penetrants in a polymer. For example CO_2 ($T_c = 31^{\circ}C$) is more soluble then CH_4 ($T_c = -82.1^{\circ}C$).

(4) Gas solubility is sensitive to specific interactions between gas and polymer molecules. For example, gases such as CO_2, which has a quadruple moment, are, in general, more soluble in polar polymers.

(5) Increases in temperature can either increase or decrease the solubility of the gas in the polymer depending on the type of gas. The van't Hoff relationship can typically represent the temperature behavior of the solubility of gases in polymers. The dissolution of a gas molecule into a polymer matrix can be viewed as a two-step thermodynamic process. The first step is the condensation of the gaseous penetrant to a condensed density, and the second step is the creation of a molecular scale gap in the polymer of sufficient size to accommodate the penetrant molecule. As a result, the enthalpy of sorption can be written as

$$\Delta H_s = \Delta H_c + \Delta H_m \tag{2.11}$$

where ΔH_c is the enthalpy of condensation, ΔH_s is the enthalpy of sorption and ΔH_m is the enthalpy of mixing.

For low molecular weight, highly supercritical, permanent gases such as H_2 and He, ΔH_c is very small and ΔH_s is governed by ΔH_m. Interactions between polymers and these permanent gases tend to be weak, ΔH_m is positive and therefore, penetrant solubility increases with increasing temperature. For condensable gases and vapors, such as many organic vapors, ΔH_s may be negative due to the large negative contribution of ΔH_c to ΔH_s and the solubility, in turn, decreases with increasing temperature.

(6) Crystalline regions in polymers typically reduce the solubility of gases in polymers.

Lee and Flumerfelt (1995) of Texas A&M University used the gravimetric method to determine the solubility of nitrogen in molten LDPE at temperatures of 121 to 177°C and pressures between 1013 and 12,670 kPa. A Cahn C-1100 pressure balance system, a furnace with a multizone control, a gas flow system and a data acquisition system were used to measure the solubilities.

Lee and Flumerfelt (1995) determined:

(1) The mixing of a gas and a polymer in the pressure range studied is an endothermic process, which is opposite to what is observed for the low-pressure range.

(2) The Flory-Huggins interaction parameter, the solubility coefficient and the activity coefficient of dissolved gases in polyethylene could be correlated to temperature and pressure.

Vittoria (1995) of Universita degli Studi di Salerno in Italy measured the solubility and diffusion of dichloromethane vapor in polyethylene using a quartz spring balance, having an extension of 20 mm/mg. The experiments were conducted at 25°C, from 0.2 to

0.6 of the vapor pressure of dichloromethane. The crystallinity of the polyethylene ranged from 40 to 85%.

Vittoria found that the solubility increased as the amorphous fraction increased.

Castro et al. (1996) reanalyzed the data they measured in 1987 of the solubility of organic vapors in polyethylene to develop another model to predict the solubility of pure compounds and mixtures in polyethylene. They called their new model the UNIFAC-M-H model and is similar to the model developed by Doong and Ho (1991) in that the free energy contributions in the penetrant-polymer system are broken down into combinatorial-entropy, free-volume, interactional-enthalpy, and elastic factors.

Yoon et al. (1996) from Inha University in Korea measured the solubility of 1-butene, 1-hexene and 1-octene in various linear low-density polyethylenes (LLDPE). The solubility of the α-olefin vapor was measured in an airtight cylinder equipped with a quartz spring having 0.5 mm/mg of modulus. The extension of the quartz spring due to the weight change of the samples was monitored with a cathetometer having 10 μm of precision. The buoyancy effect was corrected by calculating the weight of the gas equivalent to the volume of the sample using the Benedict-Webb-Rubin equation. The measurements were performed at temperatures of 70, 75, 80 and 85°C up to a pressure of 100 kPa for 1-butene, 50 kPa for 1-hexene and 20 kPa for 1-octene. The five polyethylene samples tested ranged in crystallinity from 21.9 to 37.8%.

The solubility of 1-butene ranged from about 0.01 to 0.007 grams of 1-butene per gram of amorphous LLDPE at a pressure of 100 kPa depending on the crystallinity of the

LLDPE. The solubility of 1-hexene ranged from about 0.055 to 0.045 grams of 1-hexene per gram of amorphous LLDPE at a pressure of 50 kPa depending on the crystallinity of the LLDPE.

Yoon et al. (1996) concluded:

(1) An increase in the LLDPE crystallinity lowers the solubility of α-olefins, even though the solubility was expressed on the basis of unit weight of amorphous polymer.

(2) Absorption of 1-octene does not alter the crystalline structure of LLDPE. This was determined by soaking a LLDPE for 24 hours in 1-octene and then comparing the wide angle X-ray diffraction pattern of the saturated LLDPE with that of a LLDPE that had not been soaked in 1-octene.

(3) Solubility of 1-butene, 1-hexene and 1-octene deviates from Henry's law at a lower absorption pressure as the molar mass of the α-olefin increases.

(4) That the solubility of the α-olefins in LLDPE deviates from Henry's law, but can be represented by the Flory-Huggins equation, which is:

$$\frac{P_1}{P_1^o} = v_1 e^{\left(v_2 + \chi v_2^2\right)} \tag{2.12}$$

where P_1 is the pressure of the gaseous α-olefins in contact with the LLDPE, P_1^o is the vapor pressure of the α-olefin, v_1 is the volume fraction of the gas dissolved in the LLDPE, v_2 is $(1 - v_1)$ and χ is the Flory-Huggins interaction parameter independent of the actual temperature and absorption pressure.

A summary of the conclusions about the solubility of gases in polyethylene gleaned from the articles written by these 23 research groups are:

1) The solubility of gases in polyethylene increases as the amorphous fraction of the polyethylene increases. This conclusion was reached by Michaels and Parker (1959), Rogers et al. (1960), Michaels and Bixler (1961), Eby (1964), Lowell and McCrum (1967), Deas et al. (1972), Takeuchi and Okamura (1975), Ghosal and Freeman (1993), Vittoria (1995) and Yoon et al. (1996) who measured the solubility of various gases in polyethylene.
2) Henry's law is obeyed up to the critical pressure of a gas or, in other words, as the molar mass or critical temperature of the gas increases, the pressure at which there is a deviation from Henry's law decreases. When the concentration of gases dissolved in the solid polyethylene deviates from Henry's law, the concentration can be represented by Flory-Huggins equation. This conclusion was confirmed by Rogers et al. (1960), Lowell and McCrum (1967), Stern et al. (1969, 1972, 1983a, 1983b, 1986), Li and Long (1969), Takeuchi and Okamura (1975), Kulkarni and Stern (1983), Ghosal and Freeman (1993) and Yoon et al. (1996).
3) The van't Hoff relationship can typically represent the temperature behavior of the solubility of gases in polyethylene. This means that as the temperature increases the solubility of gases in polyethylene can either increase or decrease depending on whether the enthalpy of solution is positive or negative. The enthalpy of solution is usually negative for organic vapors which means the solubility decreases as the temperature increases. The enthalpy of solution is usually positive for permanent gases. This conclusion is mentioned Rogers et al. (1960), Robeson and Smith (1967,

1968), Takeuchi and Okamura (1975), Beret and Hager (1979), Castro et al. (1987), Ghosal and Freeman (1993)

4) Gas solubility in polyethylene generally increases with increasing gas condensability. The critical temperature, the molar volume, the Lennard-Jones force constant and the normal boiling point are all related to gas condensability. This conclusion is confirmed by Rogers et al. (1960), Michaels and Bixler (1961), Stern et al. (1969, 1972, 1983a, 1983b, 1986) and Ghosal and Freeman (1993).

5) Gas solubility in polyethylene can be correlated with a number of the gas properties and other values such as the:

    a) Lennard-Jones force constant as shown by Michaels and Bixler (1961)
    b) Critical temperature as shown by Stern et al. (1969, 1972, 1983a, 1983b, 1986) and Castro et al. (1987)
    c) Gas activity as shown by Castro et al. (1987)
    d) Gas activity, polymer modulus of elasticity, and temperature as shown by Liu and Neogi (1988)
    e) Free energy from combinatorial-entropy, free volume, interactional-enthalpy and elastic factors as shown by Doong and Ho (1991) and Castro et al. (1996)

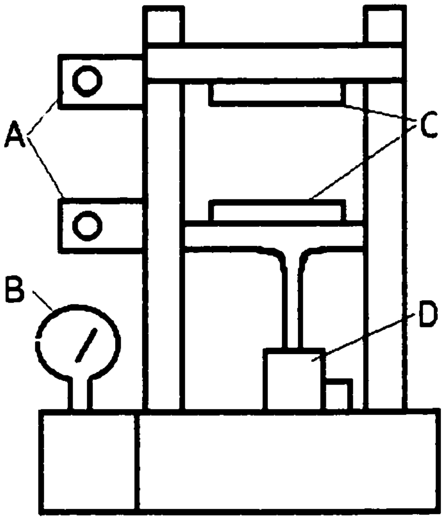
Three research papers; Li and Long (1969), Beret and Hager (1979) and Kulkarni and Stern (1983) recorded the measurement of the solubility of ethylene in polyethylene. The solubility coefficient of ethylene in polyethylene measured by Kulkarni and Stern (1983) at 20°C and up to 4053 kPa is 6.66×10^{-4} grams of ethylene per grams of polyethylene per atmosphere in a 45% crystalline polyethylene. This value is very close to the value measured by Li and Long (1969) of 5.88×10^{-4} grams of ethylene per grams of polyethylene per atmosphere at 25°C and up to 8960 kPa, in a 55% crystalline polyethylene. The above values of Li and Long (1969) were read from a figure in their paper, which makes these values a little more uncertain then those of Kulkarni and Stern (1983) which were values reported in their research paper. The solubility of ethylene in polyethylene measured by Beret and Hagar (1979) at 23°C and atmospheric pressure was 3.4×10^{-5} grams of ethylene per gram of polyethylene per atmosphere in a 48% crystallinity polyethylene. This value is lower than expected when compared to the values of Li and Long (1969) and Kulkarni and Stern (1983). Beret and Hagar (1979) used a chromatographic method to measure the solubility, which means it is highly probable that some ethylene was lost at the beginning of the measurement phase of the experiment and this would account for the lower value of solubility reported here. This analysis shows that the chromatographic method of Beret and Hagar (1979) is not a highly accurate method to determine the solubility of ethylene in polyethylene; however, the methods used by Kulkarni and Stern (1983) or Li and Long (1969) are shown to be accurate methods over a wide pressure range.

The only research paper to record the measurement of 1-butene and 1-hexene in polyethylene is the paper by Yoon et al. (1996). They used a quartz spring method similar to Li and Long (1969) to determine the solubility of 1-butene and 1-hexene in polyethylene up to their vapor pressures. This shows that the gravimetric quartz spring method to measure the solubility of ethylene, 1-butene and 1-hexene at various pressures and temperatures is an excellent choice.

The method chosen to measure the solubilities of ethylene, 1-butene and 1-hexene in this present study was a gravimetric method using a Cahn microbalance and a procedure similar to the work of Kamiya and co-workers (1986a, 1986b, Hirose et al. (1986), 1988a, 1988b, 1989a, 1989b, Naito et al. (1991), 1992, 1995, Wang and Kamiya (1996)). This method was chosen because of the proven accuracy and versatility of the gravimetric method and the excellent description of the procedure given by the many papers written by Kamiya and co-workers (1986a, 1986b, Hirose et al. (1986), 1988a, 1988b, 1989a, 1989b, Naito et al. (1991), 1992, 1995, Wang and Kamiya (1996)).

3. POLYETHYLENE SAMPLE PREPARATION

Various samples of polyethylene were received from polyethylene manufacturers in either pellet or powder form, which were then pressed into flat square sheets on a Carver Laboratory press. A schematic of the press is shown below in Figure 3.1.



A) Temperature Controller

B) Pressure Gauge

C) Hot Plates

D) Hydraulic Press

Figure 3.1 Carver Laboratory Press

The procedure for producing the flat sheets was:

1) The sample mold and press plates were preheated to 170°C.
2) Polyethylene pellets were placed in the mold and preheated for 10 minutes.
3) The polyethylene was pressed at 136 atm pressure for 5 minutes.
4) The polyethylene was then pressed at 318 atm pressure for another 5 minutes.
5) The polyethylene was cooled to 25°C by quenching with water for 5 minutes.
6) The pressure was released and the sample was removed from the mold.

The mold was a 0.5 mm thick piece of brass with a square hole 100 mm by 100 mm.

During the process of making the samples a material was needed to prevent the polyethylene from sticking to the press plates. At first two sheets of 0.0762 mm Mylar were used to prevent the sticking; however, the Mylar was so thin that the roughness of the press plates came through into the pressed polyethylene samples and made it appear as if there were tiny bubbles in the samples. These thin Mylar sheets also melted at temperatures over 170°C. The second material used to prevent the pressed polyethylene sheets from sticking to the press plates were two sheets of Teflon 6 millimeters thick, polished smooth and cut slightly larger then the mold. When the Teflon was used to prevent sticking the polyethylene sheets were smooth, without bubble-like depressions. Also, the Teflon could handle temperatures greater than 170°C.

The finished polyethylene sheets were smooth and had the dimensions of the mold. Two sheets were made from each of the 33 polyethylene samples. A listing of all the pressed samples is given in Appendix A.

4. CHARACTERIZATION OF THE POLYETHYLENE

4.1 Crystallinity

Polyethylene is a semicrystalline material; i.e. it contains both crystalline and amorphous regions. It is believed that the solubility of gases in polyethylene increases with decreasing crystallinity. Thus, the crystallinity of polyethylene is an important characteristic in a study of the solubility of gases in polyethylene.

4.1.1 Method for Measuring Crystallinity

The crystallinity of the polyethylene samples was determined using x-ray diffraction.

A Philips x-ray diffractometer (PW 1050), equipped with a Cu tube, a graphite monochrometer and a vertical goniometer, was used in this study. The diffractometer was operated in the step-scan mode. Step sizes of 0.02° of 2θ with counting of 10 s per step were used. The range of angles measured was from 7° to 35° of 2θ. Angles and intensity measurements were stored in an on-line personal computer. The measurements were performed at the ambient room temperature of about 20°C. A typical plot of the diffracted x-ray intensity versus diffraction angle (°2θ) for a polyethylene that is 50% crystalline (Sample MM003) is shown in Figure 4.1.1.

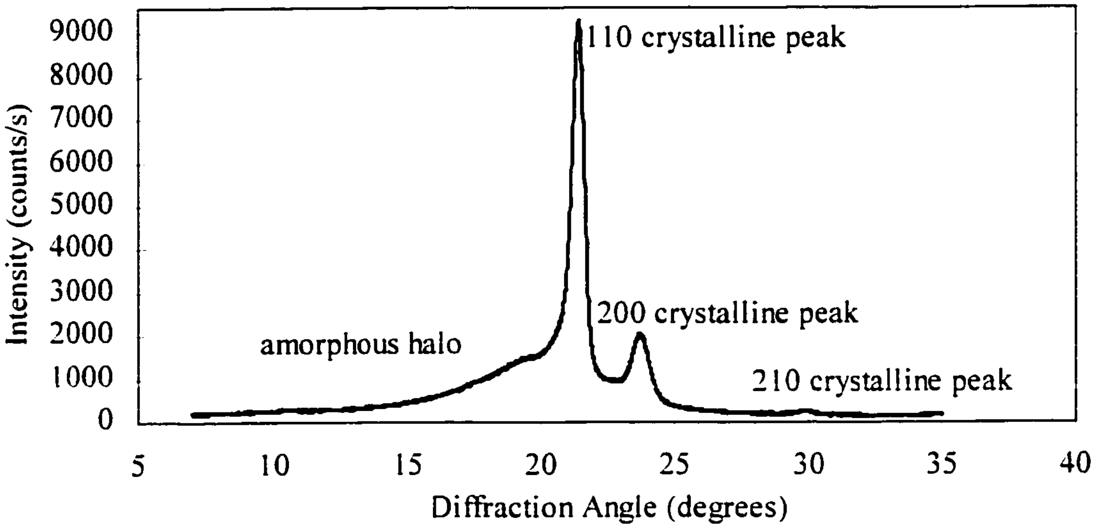


Figure 4.1.1 Plot of Intensity of Diffracted X-rays versus Diffraction Angle 2θ for Sample MM003 - 50% Crystalline Polyethylene

The crystallinity of the polyethylene was determined by calculating the area under the 110, 200 and 210 crystalline diffraction lines and then dividing this area by the combined area of the crystalline and amorphous portions of the plot. This crystallinity was then corrected because of factors that affect the intensity of the diffracted x-ray as discussed in Section 4.1.2. This ratio is the crystalline mass fraction of the polyethylene. A curve-fitting program named Peak-Fit™, from SPSS Science Inc., was used to determine the area under the curves. Butts (1994) investigated the fitting of polyethylene x-ray profiles in an undergraduate research project for the Department of Chemical Engineering at the University of Alberta. He found that good fits were obtained with a linear function for the background, two Gaussian functions for the amorphous halo, one asymmetrical double sigmoidal function for each of the 110 and 200 crystalline peaks, and one Gaussian function for the 210 crystalline peak. In the present study numerous other functions were tried to fit the polyethylene x-ray patterns and it was found that the above functions arrived at by Butts (1994) were the best functions for fitting the diffraction profiles of polyethylene.

4.1.2 Intensity Correction Factors

There are a number of factors that affect the intensity of the diffracted x-ray beam. Some of these factors are dependent on the angle at which the x-rays strike the sample and must be corrected for in order to obtain an accurate measurement of the intensity. All corrections were applied to the calculated crystallinity after fitting the intensity versus diffraction angle with Peak-Fit.

4.1.2.1 Lorentz - Polarization Factor

The Lorentz - Polarization factor is given by

$$Lp = \frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta} \qquad (4.1.2.1)$$

where 2θ is the diffraction angle.

The Lorentz - Polarization factor is a combination of four factors. One part of this equation is known as the polarization factor and is necessary because the incident x-ray beam is unpolarized. Another portion of the equation is from the fact that as a crystal in the sample is rotated through the x-ray beam, more energy is diffracted when the diffraction angle is either small or large. This means that, all things being equal, the diffracted intensity will be greater for large and small values of 2θ than for intermediate values. Also, the fact that the number of particles oriented at or near the Bragg angle is not constant affects the intensity of the diffracted x-ray at varying angles is included in the Lorentz - Polarization Equation. Finally the positioning of the detector and the sample cause the diffraction intensity to be more intense at the low and high angles than the middle angles.

4.1.2.2 Temperature Factor

The thermal vibration of atoms, which increases as temperature increases, causes a decrease in the intensity of the diffracted x-ray beam. Even though the x-ray diffractometer was kept at a constant temperature throughout this study a correction factor known as the temperature factor was applied to the results. This is because the decrease in intensity is a function of lattice spacing, i.e. the temperature factor becomes greater as the ratio u/d increases, where u in the average displacement of an atom from its mean position and d is the plane spacing of the crystal. Reflections at high values of θ involve planes of low d values and therefore the intensity of a diffracted x-ray decreases as θ increases even at a constant temperature.

The equation used to represent the temperature factor was recorded by Aggarwal and Tilley (1955) and is shown here in Equation 4.1.2.2.

$$f_t = e^{-2B} \tag{4.1.2.2}$$

Where f_t is the temperature factor and Bunn (1939) calculated the B factor to be

$$B = \frac{5\sin^2\theta}{\lambda^2} \tag{4.1.2.2.1}$$

Where λ is the wavelength of the x-ray in units of Ångstroms and θ is the diffraction angle divided by 2.

4.1.2.3 Atomic Scattering Factor

The atomic scattering factor is a correction factor that is necessary because x-rays scattered by individual electrons of an atom become more out of phase as the diffraction angles increase. This factor is a function of (sin θ)/λ, where λ is the wavelength of the x-ray in units of Ångstroms and θ is the diffraction angle divided by two.

The atomic scattering correction factor is calculated for polyethylene by squaring the atomic scattering factor for carbon obtained from tables such as Appendix 12 of

Cullity (1978) and the International Tables for Structural Analysis as mentioned by Aggarwal and Tilley (1955).

4.1.3 Procedure to Calculate Crystallinity from the Diffractometer Output

(1) The area under the 110, 200 and 210 crystalline diffraction lines, as well as the amorphous area of the plot was calculated using the computer program Peak-fit.

(2) The uncorrected crystallinity of the polyethylene was calculated using Equation 4.1.3.1.

$$X_{uc} = \frac{A_{110} + A_{200} + A_{210}}{A_{110} + A_{200} + A_{210} + A_{A1} + A_{A2}} \qquad (4.1.3.1)$$

Where A_{110}, A_{200}, and A_{210}, are the areas under the 110, 200 and 210 crystalline peaks, A_{A1}, and A_{A2} are the areas under the first and second amorphous peaks and X_{uc} is the uncorrected crystallinity.

(3) The center diffraction angle of each of the peaks of the plot of intensity versus diffraction angle was determined i.e. 110, 200, 210, first amorphous peak and second amorphous peak. These centers were obtained from the centers of the functions used by Peak-fit to fit the plot.

(4) The intensity correction factors for each peak was calculated using the center diffraction angle of each peak as described in Section 4.1.2 and illustrated in Appendix B.

(5) The overall correction factor for each peak area was calculated using the overall 110-peak area correction as a correction of 1. Equation 4.1.3.2 shows the overall correction factor equation for the first amorphous peak.

$$C_{A1} = \frac{(Lp_{110})(as_{110})(f_{t110})}{(Lp_{A1})(as_{A1})(f_{tA1})} \qquad (4.1.3.2)$$

where C_{A1} is the overall correction factor for the first amorphous area. Lp_{110} is the Lorentz-Polarization correction factor for the 110 peak, as_{110} is the atomic scattering correction factor for the 110 peak, f_{t110} is the temperature correction factor for the 110 peak, Lp_{A1} is the Lorentz-Polarization correction factor for the first amorphous peak, as_{A1} is the atomic scattering correction factor for the first amorphous peak and f_{tA1} is the temperature correction factor for the first amorphous peak.

(6) The corrected crystallinity of the polyethylene was calculated using Equation 4.1.3.3.

$$X_c = \frac{A_{110}C_{110} + A_{200}C_{200} + A_{210}C_{210}}{A_{110}C_{110} + A_{200}C_{200} + A_{210}C_{210} + A_{A1}C_{A1} + A_{A2}C_{A2}} \qquad (4.1.3.3)$$

where A_{110}, A_{200}, and A_{210}, are the uncorrected areas under the 110, 200 and 210 crystalline peaks, respectively and A_{A1} and A_{A2} are the uncorrected areas under the first and second amorphous peaks, respectively. C_{110}, C_{200}, and C_{210} are the overall correction factors to correct the 110, 200 and 210 crystalline areas and C_{A1}, and C_{A2} are the overall correction factors for the first and second amorphous areas.

Detailed sample calculations of all the equations used in this procedure are included in Appendix B.

4.1.4 X-Ray Diffraction Results

The measured x-ray patterns for the four polyethylenes, which were subsequently used for elongation and absorption measurements, are shown in Figures 4.1.4.1 to 4.1.4.4.

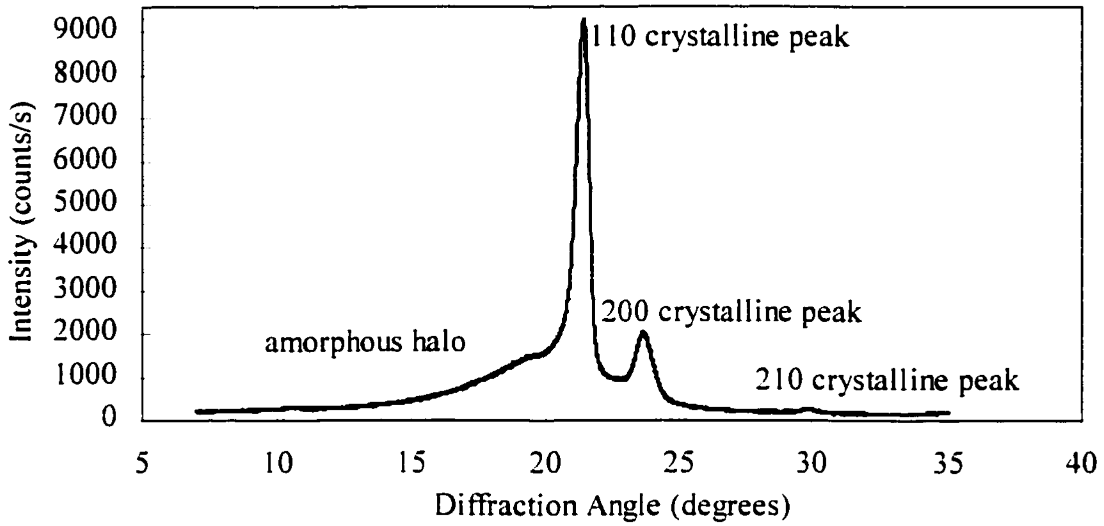


Figure 4.1.4.1 Intensity of Diffracted X-rays versus Diffraction Angle 2θ for Sample MM003

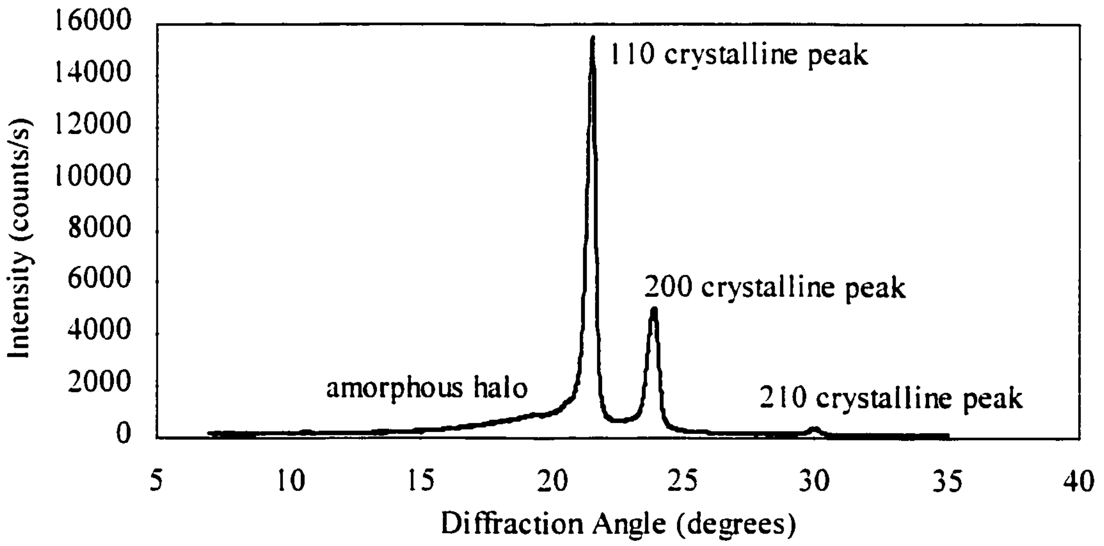


Figure 4.1.4.2 Intensity of Diffracted X-rays versus Diffraction Angle 2θ for Sample MM013

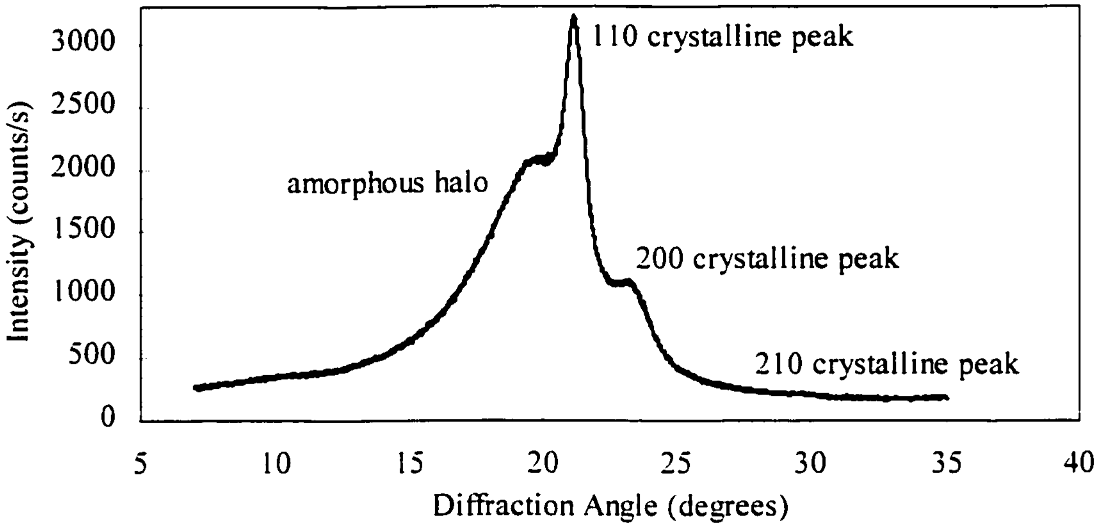


Figure 4.1.4.3 Intensity of Diffracted X-rays versus Diffraction Angle 2θ for Sample MM019

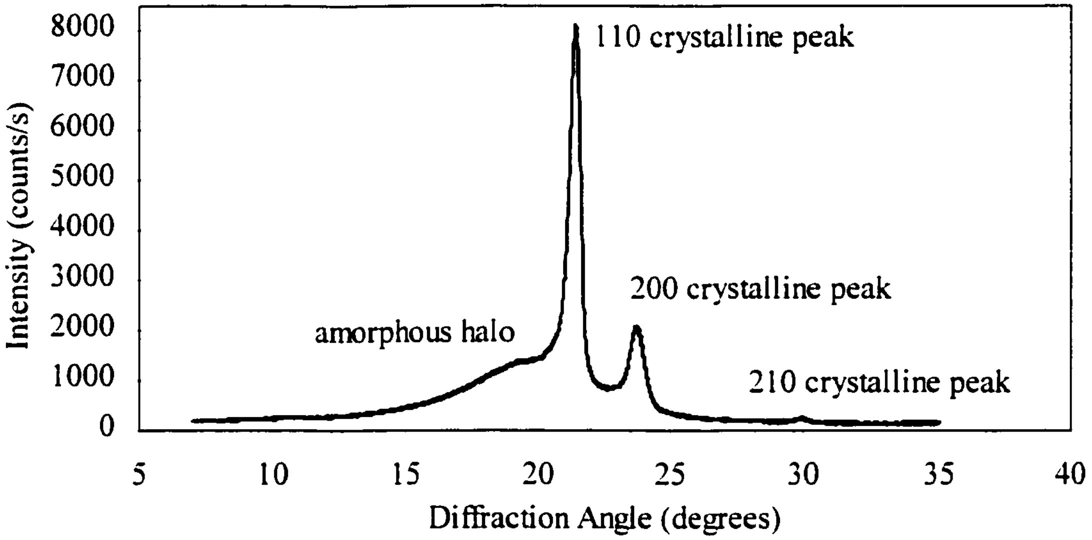


Figure 4.1.4.4 Intensity of Diffracted X-rays versus Diffraction Angle 2θ for Sample MM029

One note of interest was that a small peak centered at a diffraction angle of 11.3° was found on most of the x-ray patterns; however, no mention of this peak was found in the literature. This small peak may suggest some kind of purely amorphous part of the polyethylene. This explanation is suggested because it was found in this study that the center of the peaks always occurred at a smaller angle, as the samples became less crystalline. The samples that were highly crystalline had a 110 peak center of about 21.5° and an amorphous peak center at 19.6° while the low crystalline samples had a 110 peak center at 21.25° and an amorphous peak center at 18.9°. These angles are from the peak maxima of the fitted data, not the raw data. The presence of two amorphous peaks supports the idea that polyethylene consists of an amorphous phase and a transition phase as suggested as suggested by McFaddin et al. (1993).

Crystallinities for all the samples examined are listed in Appendix B. From all the samples tested, four samples with different crystallinities were chosen for solubility measurements. These samples were chosen so that a correlation between the solubility of gases in polyethylene and the crystallinity of the polyethylene could be determined. The samples chosen are shown in Table 4.1.4.

Table 4.1.4 Crystallinity of Polyethylene Samples Used in Subsequent Measurements

Sample	Crystallinity		Sample	Crystallinity	
	Uncorrected	Corrected		Uncorrected	Corrected
MM003	41.9%	50.4%	MM013	63.2%	70.2%
MM003p	42.1%	50.5%	MM013p	64.0%	71.5%
MM003e	44.8%	51.7%	MM013e	65.0%	70.9%
MM003b	46.0%	52.9%	MM013b	66.2%	71.8%
MM003h	48.6%	55.8%	MM013h	65.6%	71.3%
MM029	37.7%	47.0%	MM019	13.2%	18.5%
MM029e	40.9%	48.5%	MM019p	13.4%	18.8%
MM029b	42.2%	50.0%			
MM029h	41.2%	48.7%			

The samples that have a "p" at the end of their name are samples that were placed in the diffractometer perpendicular to the original direction of placement in the diffractometer. The fact that the crystallinity did not change by more then 0.8% when the samples were placed perpendicular shows that the crystals in the samples are randomly oriented, i.e., the samples are isotropic. This conclusion was also reached by Michaels and Bixler (1961). This is important because it allows the volume change of the polyethylene to be determined by measuring only one dimension.

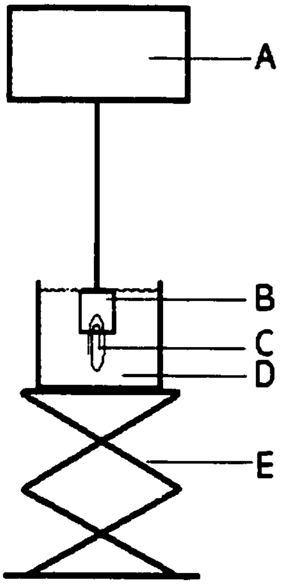
The samples with the "e", "b", or "h" at the end of their name are samples that have gone through the entire dilation measurement with gaseous ethylene, 1-butene or 1-hexene respectively. In all cases the crystallinity was higher than the original crystallinity, which is expected because in the dilation measurement the samples are cooled down at a slower rate than when the polyethylene sample was originally pressed. It is interesting to note that the crystallinity for the 1-butene and 1-hexene samples is always slightly higher than the ethylene suggesting that there are now more crystals in the samples after exposure to 1-butene and 1-hexene for prolonged periods. This is further supported by the dilation results discussed in Chapter 6, which found that the 1-butene and 1-hexene samples were slightly shorter after exposure to 1-butene and 1-hexene.

4.2 Density of Polyethylene

Since density is closely related to crystallinity, the density of each polyethylene sample was determined in order to support the accuracy of the crystallinity measurements. The density was calculated using Archimedes' principle, by which the density of a solid material, ρ_s, can be calculated by measuring the weight of the solid in air, W_a, and the weight of the substance when it is submerged, W_s, in a fluid of known density, ρ_f, i.e.

$$\rho_s = \rho_f \frac{W_a}{W_a - W_s} \tag{4.2.1}$$

A schematic of the apparatus used to measure the density of the polyethylene samples is shown below in Figure 4.2.1.



A) Ohaus TS120 electronic balance

B) Polyethylene sample

C) Paper clip

D) Oil with density 0.9612 g/cm^3 at 25°C

E) Laboratory jack

Figure 4.2.1 Density Measurement Apparatus

The procedure for determining the density was:

1) The Ohaus TS120 electronic balance was set up with a wire hanging from the weighing mechanism above a container of oil.
2) A square piece of polyethylene 35 mm by 35 mm was cut from the 0.5 mm thick sheet prepared in the hot press.
3) Two 1.6 mm holes were drilled in the square sample as shown in Figure 4.2.2.

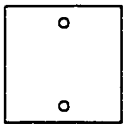


Figure 4.2.2 Drill holes for Density Measurement

4) The polyethylene sample was weighed on a Mettler AC100 electronic balance to obtain the weight of the sample in the air.
5) The paper clip was weighed on the Mettler balance. This paper clip was used as a weight to keep the polyethylene sample from floating on the oil.
6) The wire used to hang the sample from the Ohaus scale was weighed on the Mettler balance.
7) The combined weight of the sample. paper clip and wire was determined by the Mettler balance.
8) The sample was hung from the Ohaus balance by attaching the paper clip to the sample through one hole and the wire through the other hole. While the sample was still suspended above the oil the combined weight of the sample, paper clip and wire was determined by the Ohaus scale.

9) The oil container was raised with the laboratory jack until the polyethylene sample was entirely immersed in the oil. The weight of the paper clip and polyethylene sample immersed in oil was recorded.

10) The correction factor was calculated. The correction factor is the total weight of the sample, paper clip and wire in the air as recorded by the Mettler balance divided by the total weight in the air as recorded by the Ohaus balance.

11) The correction factor was applied to the weight of the sample and paper clip immersed in the oil.

12) The weight of the wire was subtracted from the corrected weight of the sample and paper clip immersed in the oil.

13) The density of the paper clip was calculated by repeating Steps 1 to 12 with only the paper clip hanging from the wire and using Equation 4.2.1. The density of the paper clip used in this study was measured to be 7.8362 g/cm^3. This value is in agreement with the density of stainless steel recorded by Perry (1973).

14) The weight of the paper clip in oil that was used to weigh down the polyethylene sample was calculated using Equation 4.2.1.

15) The weight of the paper clip in oil was subtracted from the total weight of the polyethylene sample and paper clip immersed in the oil.

16) The density of the polyethylene was calculated using Equation 4.2.1.

Detailed calculations to determine the density are included in Appendix C. The densities obtained for the four samples used in the solubility measurements are listed in Table 4.2.1.

Table 4.2.1 Density of Polyethylene Samples Used in the Measurements

Sample	Density (g/cm^3)	Manufacturer's Density(g/cm^3)
MM003	0.923	-
MM013	0.954	-
MM019	0.885	0.883
MM029	0.917	0.918

The fact that the values obtained from the manufacturers are so close to the measured density shows that the method used to measure the density was accurate.

Density can be used to calculate crystallinity in polyethylene using Equation 4.2.2.

$$X = \frac{d_c(d - d_a)}{d(d_c - d_a)} \tag{4.2.2}$$

Where d_c is the density of crystalline polyethylene, d_a is the density of a fully amorphous polyethylene and d is the measured density of the sample.

The crystallinity of the four samples used in this study was calculated using Equation 4.2.2 and compared with the crystallinity determined by the x-ray diffractometer. The value used for d_c was 1.00 g/cm^3 and for d_a was 0.853 g/cm^3 as reported by Vittoria (1995). The results of the comparison are shown in Table 4.2.2

Table 4.2.2 Comparison of Crystallinity from Density and X-ray Diffractometry

Sample	Crystallinity from X-ray	Crystallinity from Density
MM003	50.4%	51.6%
MM013	70.2%	72.0%
MM019	18.5%	24.6%
MM029	47.0%	47.5%

The values of crystallinity calculated from density are slightly different then those determined by x-ray diffractometry; however, this is expected since the density used for the amorphous phase of 0.853 g/cm^3 is most likely not 100% accurate, this is due to the difficulty of measuring the density of the 100% amorphous phase (Vittoria, 1995). The fact that the two methods yield similar crystallinity values increases the certainty of the measured crystallinity of the polyethylene samples.

5. SOLUBILITY MEASUREMENT

Many different methods to measure the solubility of gases in solid polyethylene were discussed in the literature review. Most of these methods fall into one of the following categories: (1) pressure decay methods (2) chromatography methods and (3) gravimetric methods (Miura et al. 1997). Method (1), the pressure decay method, determines the solubility by measuring the decay of pressure caused by sorption in a constant volume vessel containing the polymer. This method has the inherent weakness that the determination of the initial value of the pressure and the choice of an equilibrium pressure at will is not possible. Method (2), the chromatographic method, determines the solubility by first saturating the polymer with the desired gas for a set amount of time and then the excess gas not dissolved in the polymer is purged away with quick blast from another gas. The second gas is set to a low flowrate and from this point on a flame ionization detector continuously monitors the gas concentration in the gas stream. The solubility is obtained by measuring the total gas evolved over the entire time period that the gas concentration is measured. The greatest difficulty with this method is that it is necessary to remove all the excess gas from the space around the polymer without leaving any residual gas, while at the same time not removing any of the gas that is dissolved in the polymer. Methods (1) and (3) include some uncertainty arising from the volume change of the polymer caused by the sorption of gas, but this volume change can be determined by separate experiments and a volume change correction calculated. In the literature review three research groups measured the solubility of ethylene in polyethylene. The group that used the chromatography method produced values that were less then the other two groups, indicating that the chromatography method is not as accurate as the other methods. The one research group that measured the solubility of 1-butene and 1-hexene in polyethylene used a gravimetric method and one of the research groups that measured the solubility of ethylene in polyethylene up to 9635 kPa also used a gravimetric method. The method chosen to measure the solubilities of ethylene, 1-butene and 1-hexene in this present study was a gravimetric method using a Cahn microbalance and a procedure similar to the work of Kamiya and co-workers (1986a, 1986b, Hirose et al. (1986), 1988a, 1988b, 1989a, 1989b, Naito et al. (1991), 1992, 1995, Wang and Kamiya (1996)). This method was chosen because of the reliable results obtained by other researchers who used this method, the versatility of the gravimetric method and the excellent description of the procedure given by the many papers written by Kamiya and co workers (1986a, 1986b, Hirose et al (1986), 1988a, 1988b, 1989a, 1989b, Naito et al (1991) 1992, 1995, Wang et al (1996)).

5.1 The Gravimetric Method of Measuring the Solubility of a Gas in Polyethylene

In the gravimetric method the solubility of a gas is determined from the weight change of the sample due to the sorption of gases. A piece of the solid polyethylene is attached to a weighing mechanism and then exposed to the desired gas. The change in weight is recorded by the weighing mechanism as gas is sorbed into the polyethylene. The weight is recorded until the weight change is negligible, which indicates that the solid polyethylene and gas are in equilibrium. The total weight of the polyethylene and gas absorbed is used to determine the solubility of the gas in the polyethylene.

The weight recorded on the weighing mechanism must be corrected because of the buoyancy effect of the gas in the balance. The weight measurement begins when the balance is evacuated. As the desired gas is introduced into the measuring chamber the gas pushes up on the balance beams and other parts of the weighing mechanism. This buoyancy effect can be determined by performing the measurement without a polyethylene sample in the weighing chamber up to the desired gas pressure and using the results as a background buoyancy correction weight.

In this study a second buoyancy correction is also necessary. This is because the ethylene, 1-butene and 1-hexene cause the polyethylene to expand as the gases are absorbed and the volume of the polyethylene increases, which increases the buoyancy effect of the gases. In order to accurately determine the buoyancy affect of these gases the volume change of the polyethylene caused by the gases must be determined. This was carried out by a separate experiment in which the length of the polyethylene was measured as it was exposed to the gases at the pressures of interest.

In this study the solubility is also measured at different temperatures. It is necessary to correct for the buoyancy caused by the volume change of the polyethylene due to thermal expansion. This volume change was determined by the length measurement experiment where the change in length of the polyethylene was measured as it was exposed to the temperatures used in this study.

In order to accurately measure the solubility of 1-butene, 1-hexene and ethylene in polyethylene it is necessary to determine the length and weight change of the polyethylene as the gases are sorbed. The next two sections will describe the procedure and equipment used to determine the length and weight measurement.

5.2 Length Measurement

To accurately measure the solubility of gases in polyethylene at different pressures and temperatures the volume change of the polyethylene caused by the sorption of gases and the increase in temperature above some base temperature must be calculated. This volume change can be calculated by measuring two expansion coefficients.

(1) The thermal expansion coefficient, α_T^{Po}, which is the expansion of the polyethylene caused by an increase in temperature above some base temperature. It is measured when the pressure cell is evacuated. It can be represented by:

$$\alpha_T^{Po} = \frac{\left(\dfrac{L_T^{Po} - L_{Tb}^{Po}}{L_{T_b}^{Po}}\right)}{T} \tag{5.2.0.1}$$

where L_T^{Po} is the length of the polyethylene at temperature, T and $L_{T_b}^{Po}$ is the length of the polyethylene at some base temperature.

(2) The pressure expansion coefficient, β_P^{Po}, which is the expansion of the polyethylene caused by the sorption of the gas. It is measured at a constant temperature and at various pressures. It is represented by:

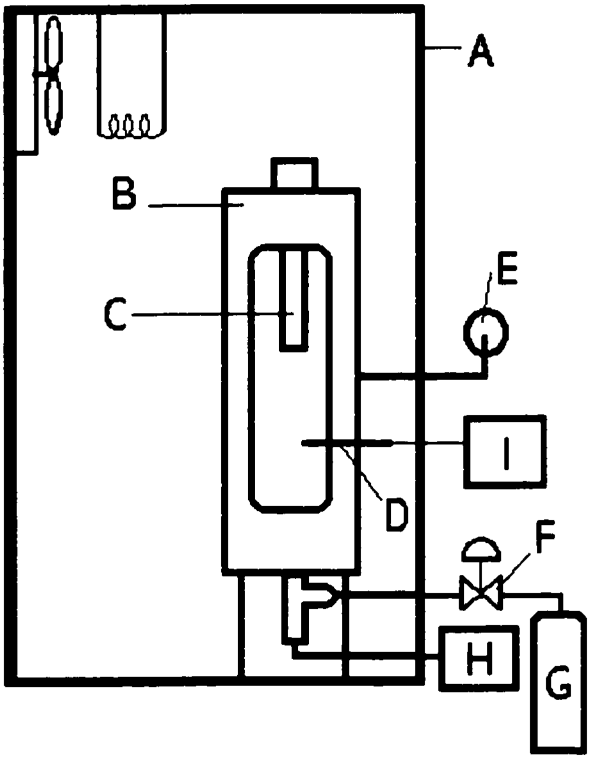
$$\beta_P^{Po} = \frac{L_P^{Po} - L_0^{Po}}{L_0^{Po}} \tag{5.2.0.2}$$

where L_P^{Po} is the length of the polyethylene at pressure, P and L_0^{Po} is the length of the polyethylene when the pressure cell is evacuated.

These equations both assume that polyethylene is macroscopically isotropic in the volume change caused by the sorption of gases or an increase in temperature. The isotropic nature of volume change can be assumed because of the random orientation of the crystalline regions in the polyethylene as determined by x-ray diffraction. Michaels and Bixler (1961) also concluded that polyethylene is macroscopically homogeneous and isotropic with respect to gas sorption. Since polyethylene is macroscopically isotropic only one dimension needs to be measured to determine the thermal and pressure expansion coefficients.

5.2.1 Length Measurement Procedure

A schematic of the apparatus used to measure the length of the polyethylene is shown in Figure 5.2.1.



A) Constant temperature bath

B) Jerguson pressure cell

C) Polyethylene sample

D) Thermocouple

E) Heise pressure gauge

F) Matheson gas pressure regulator

G) Sample gas cylinder

H) Edwards RV5 vacuum pump

I) Voltmeter

J) Gaertner cathetometer (not shown)

Figure 5.2.1 Length Measurement Setup

The procedure for measuring the length was:

1) A piece of polyethylene approximately 0.5 mm by 5 mm by 60 mm was cut from the 100 mm by 100 mm by 0.5 mm pressed sample. This was accomplished by placing a piece of stainless steel that had been machined to these dimensions on the polyethylene sheets and cutting around it with a utility knife.
2) The polyethylene sample was attached to a holder and then the holder was screwed into the top of the Jerguson pressure cell.
3) The Jerguson pressure cell was filled with a gas to a gauge pressure of about 4000 kPa and then checked for gas leaks.
4) The constant temperature bath was started and the control was set to 30°C.
5) The vacuum pump was started and the pressure cell was evacuated for 24 hours.
6) The distance from the top to the bottom of the polyethylene sample was measured with a cathetometer. The measurement was repeated two more times to improve reliability.
7) Ethylene gas was introduced into the pressure cell up to a gauge pressure of 690 kPa and the atmospheric pressure was recorded.
8) The length of the sample was measured when the sample had stopped elongating. The measurement was repeated to improve reliability.
9) Ethylene gas was introduced into the pressure cell up to a gauge pressure of 2070 kPa and the atmospheric pressure was recorded.
10) The length of the sample was measured when the sample had stopped elongating. The measurement was repeated to improve reliability.

11) Ethylene gas was admitted into the pressure cell up to a gauge pressure of 3450 kPa and the atmospheric pressure was recorded.

12) The length of the sample was measured when the sample had stopped elongating. The measurement was repeated to improve reliability.

13) The vacuum pump was started and the pressure cell was evacuated for 24 hours.

14) The distance from the top to the bottom of the polyethylene sample was measured with the cathetometer. The measurement was repeated two more times to ensure reliability.

15) Steps 4 to 14 were repeated three more times. Each time the controller on the constant temperature bath with increased by 20°C to 50, 70 and then 90°C.

16) Steps 1 to 15 were repeated until all four samples had been tested.

Steps 1 to 16 were repeated using 1-butene and then 1-hexene. In order to increase the vapor pressure of 1-butene and 1-hexene the gas cylinders were placed inside the constant temperature bath. The exact pressures and temperatures used were different then those used for the ethylene gas because of the lower vapor pressure of the gases (see Table 5.2.1 for details).

Table 5.2.1 Temperatures and Pressures Used in This Study

Temperature (°C)	Pressure (kPa absolute)		
	ethylene	1-butene	1-hexene
30	784	160	no measurement
	2164	260	because vapor
	3544	360	pressure = 30.5 kPa
50	784	250	no measurement
	2164	440	because vapor
	3544	590	pressure = 64.7 kPa
70	784	300	80
	2164	640	
	3544	950	130
90	784	500	90
	2164	990	160
	3544	1450	225

The length measurement could not be carried out for 1-hexene at temperatures of 30°C and 50°C because the vapor pressure at these temperatures is below atmospheric pressure. The pressures and temperatures chosen are the pressures and temperatures used to produce polyethylene in gas phase reactors. The length measurement could not be performed for Sample MM019 at 90°C for any gas and it was not measured at all for 1-hexene because the sample melted at 85°C and any measurements above 70°C were questionable because of the amount of deformation that took place.

5.2.2 Calibrations and Precision

The precision of the cathetometer used for the majority of the measurements was ± 0.01 mm.

The Heise pressure gauge and the thermocouple were calibrated to ensure accurate measurement. The Heise pressure gauge was found to be accurate to ±0.1% when tested in the range from 0 to 6890 kPa with the Ruska 2400 HL pressure calibration instrument. The type J thermocouple was calibrated using a platinum resistance calibration device with a water bath from 22.3 to 70°C and a dry well calibrator from 80 to 100°C. The results of the calibration are shown in Table 5.2.2.

Table 5.2.2 Calibration of Thermocouple Used in the Length Measurement

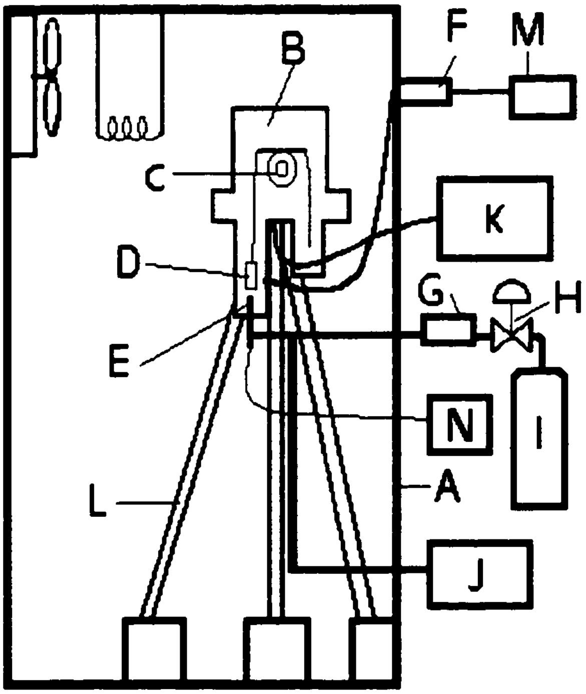
Actual Temperature (°C)	Thermocouple (mV)	Thermocouple (°C)	Error (°C)
22.27	1.142	22.38	+0.11
29.96	1.535	29.98	-0.02
39.97	2.052	39.88	-0.09
49.95	2.571	49.74	-0.21
59.98	3.096	59.64	-0.34
69.97	3.627	69.59	-0.38
80.03	4.157	79.46	-0.57
90.08	4.695	89.44	-0.64
100.00	5.230	99.31	-0.69

5.3 Weight Measurement

The gravimetric method of measuring the solubility of gases in polyethylene requires that the weight of the polyethylene be measured as the polyethylene sorbs the gas. In this study these measurements were only completed for one sample, Sample MM029 and with one gas, ethylene. The equipment to carry out the measurement was assembled and calibrated and a weight measurement procedure was developed.

5.3.1 Weight Measurement Equipment

The apparatus used to weigh the polyethylene was a Cahn D-110 electromicrobalance placed inside a constant temperature bath as shown in Figure 5.3.1.



A) Constant temperature air bath
B) Pressure chamber
C) Cahn D-110 electromicrobalance
D) Polyethylene sample
E) Thermocouple
F) Pressure transducer
G) Flow controller
H) Pressure regulator
I) Gas cylinder (inside chamber for 1-butene and 1-hexene)
J) Vacuum pump
K)Computer
L) Pressure chamber stand
M)Voltmeter
N) Fluke 52 thermometer

Figure 5.3.1 Weight Measurement Setup

The pressure was measured with an Omega PX425–600GV pressure transducer and the weight measurement was recorded by a computer set to record the weight every 20 seconds.

The weight measurement required the use of a mass flow controller to ensure a proper rate of gas entering the pressure chamber was maintained while the pressure was increased. Kamiya et al. (1986a) found that about 15 minutes was needed to change the pressure of the gas to avoid shifting the zero position of the electrobalance. The mass flow controller used in this study was a Matheson Model 8250 Series Modular Dyna Blender. It had a flow transducer that measured the flow and produced a 0 to 5 volt dc output signal, which was directed to a readout box. A digital potentiometer on the readout box was fed an internal 5.00 volt dc, which was reduced to a level selected by the operator. If the input and output signals did not match the control valve responded to modify the flow until the two signals matched.

5.3.2 Weight Measurement Procedure

The procedure for measuring the weight was:

1) The atmospheric pressure was recorded. This was necessary to determine the absolute pressure of the measurements since the pressures measured during the experiment were gauge pressures.
2) The wires to hang the sample and tare were placed onto the balance beam. Any bits of wire used to hang the sample were placed on the hang down wires; however, the polyethylene sample was not attached.
3) The pressure cell was attached and tightened. Gas was introduced into the pressure cell over a time period of one hour to a pressure of 4000 kPa to check for leaks.

4) The constant temperature bath was started and the controller was set to 30°C.

5) The vacuum pump was started and the pressure cell was evacuated for 24 hours.

6) The computer was turned on and the balance was tared.

7) A new file was created on the computer to record the output of the balance. The computer was set to record the output of the balance as the flow procedure for admitting gas into the cell as set out in Table 5.3.2 was followed.

8) Steps 4 to 7 were repeated three more times, increasing the temperature of the constant temperature bath by 20 °C each time, to temperatures of 50, 70 and 90°C. This was done to obtain a background, buoyancy reading for the ethylene gas at the different temperatures used in this study.

9) The constant temperature bath was shut off and the pressure cell was opened.

10) A piece of polyethylene that weighed about 0.5 g was cut from the 100 mm by 100 mm by 0.5 mm pressed sample.

11) The piece of polyethylene was weighed in air at atmospheric pressure on three balances to obtain an accurate measurement of the initial weight. The temperature at which these measurements took placed was recorded.

12) The polyethylene sample was attached to the wire that hangs down from the balance beam.

13) The pressure cell was tightened and gas was introduced to the cell over a one-hour period to a pressure of 4000 kPa to check for leaks.

14) The constant temperature bath was started and set to control to 30°C.

15) The vacuum pump was started and the pressure cell was evacuated for 24 hours.

16) The computer was turned on and the balance was tared.

17) A new file was created on the computer to store the output of the balance. The computer was set to record the output of the balance as the flow procedure for admitting gas into the cell as set out in Table 5.3.2 was followed.

18) Steps 14 to 17 were repeated three more times, increasing the temperature of the constant temperature bath by 20 °C each time, to temperatures of 50, 70 and 90°C.

Table 5.3.2 Flow Rates to Introduce Ethylene into the Cahn Microbalance Cell

Time h:mm:ss	Flow Meter (volts)	Flow (slpm)	Comments
0:05:00	0.0	0.0000	Close valve to vac pump and shut off vac pump
0:06:00	0.1	0.0134	Increase regulator to 690 kPa & flow meter to 0.1 v
0:07:00	0.5	0.0672	Increase flow meter to 0.5 v
0:08:00	1.0	0.1344	Increase flow meter to 1.0 v
0:13:00	1.5	0.2016	Increase flow meter to 1.5 v
0:16:00	3.5	0.4704	Atmospheric Pressure & flow meter to 3.5 v
0:36:00	0.0	0.0000	Pressure up to 690 kPa
2:36:00	5.0	0.6720	Inc. Regulator to 2070 kPa & flow meter to 5.0 v
3:10:00	0.0	0.0000	Pressure up to 2070 kPa
5:10:00	5.0	0.6720	Increase regulator to 3450 kPa
5:50:00	0.0	0.0000	Pressure up to 3450 kPa
7:50:00	0.35	0.0470	Decrease regulator to 0 kPa & start to evacuate
8:20:00	0.35	0.0470	At atmospheric Pressure
8:30:00	0.0	0.0000	At <0.1 Pa
10:00:0	0.0	0.0000	End of run

5.3.3 Solubility Calculation Procedure

Once the length measurement and weight measurement are completed the solubility of the gas in polyethylene can be calculated. The procedure for carrying out this calculation is presented here.

1) The volume of the polyethylene sample used in the weight measurement experiment was determined by dividing the average weight of the polyethylene sample measured on three balances by the density of the polyethylene.
2) The expanded volume of the polyethylene at the pressures and temperature of the weight measurement experiment was determined by using Equation 5.3.3 and the thermal and pressure expansion coefficients determined in the length measurement experiment.

$$V_{T,P}^{Po} = V_{T_b}^{Po}\left(1 + 3\alpha_T^{Po}(T - T_b)\right)\left(1 + 3\beta_P^{Po}\right) \tag{5.3.3}$$

Where $V_{T,P}^{Po}$ is the volume of the polyethylene at the temperature and pressure of the weight measurement experiment, T_b is the base temperature at which is the polyethylene was weighed in order to determine the initial volume. α_T^{Po} is the thermal expansion coefficient of the polyethylene sample and β_P^{Po} is the pressure expansion coefficient at the temperature and pressure of the weight measurement experiment as determined from the length measurement experiment. A sample calculation showing how to use Equation 5.3.3 is included in Appendix D.

3) The density of the gas at the pressure and temperature of the weight measurement was calculated using the Peng-Robinson (1976) equation of state. This was accomplished by using an Microsoft Excel spreadsheet as explained in Appendix D.
4) The buoyancy force exerted on the expanded polyethylene volume during the weight measurement was calculated by multiplying the density of the gas determined in Step 3 by the volume of the expanded polyethylene determined in Step 2.
5) The weight of the gas sorbed into the polyethylene sample at equilibrium was determined from the computer file recorded by the Cahn microbalance. Equilibrium was assumed when the weight recorded by the microbalance was increasing at less than 1 μg per minute.
6) The weight of the sorbed gas corrected for buoyancy was calculated by subtracting the background buoyancy weight and adding the expanded polyethylene volume buoyancy weight to the equilibrium weight recorded by the Cahn microbalance.
7) The solubility of the ethylene gas in the polyethylene sample was calculated by dividing the corrected sorbed gas weight by the initial weight of the polyethylene sample before exposure to the ethylene as recorded by the three balances.

6. RESULTS AND DISCUSSION

6.1 Length Measurement Results

All of the length measurement results are presented in appendix E.

6.1.1 Repeatability of Length Measurement

The length measurement was repeated for Sample MM029. The results are shown in Table 6.1.1.

Table 6.1.1 Repeatability of Length Measurement

Run #1			Run #2			Average	Cathetometer Precision (mm)
Temp (°C)	Press (kPa)	$L-L_0$ (mm)	Temp (°C)	Press (kPa)	$L-L_0$ (mm)	$L-L_0$ (mm)	
32.64	796	0.08	32.39	796	0.13	0.11	±0.04
32.64	2186	0.32	32.39	2170	0.38	0.35	±0.04
32.64	3568	0.59	32.39	3540	0.69	0.64	±0.04
49.84	789	0.11	50.74	797	0.12	0.12	±0.04
49.84	2187	0.36	50.74	2183	0.41	0.39	±0.04
49.84	3563	0.62	50.74	3562	0.67	0.65	±0.04
70.19	781	0.08	70.96	787	0.09	0.09	±0.04
70.19	2169	0.31	70.96	2178	0.36	0.34	±0.04
70.19	3540	0.55	70.96	3547	0.63	0.59	±0.04
89.59	803	0.08	90.01	796	0.05	0.07	±0.04
89.59	2182	0.32	90.01	2170	0.34	0.33	±0.04
89.59	3562	0.55	90.01	3540	0.57	0.56	±0.04

The "L_0" in Table 6.1.1 is the length of Sample MM029 after the pressure cell had been evacuated for 24 hours at the given temperature and "L" is the measured length of Sample MM029 at the temperature and pressure indicated. Table 6.1.1 shows that the difference in $L-L_0$ between Run #1 and Run #2 is within the precision of the cathetometer in every instance except one. This proves the repeatability of the length measurements.

6.1.2 Challenges to Obtaining Reliable Results

There were a number of instruments used in obtaining measurements of the length of the polyethylene that provided a challenge to acquiring accurate results.

1) Cathetometer

This instrument was the most important instrument in obtaining accurate results when measuring the elongation of the polyethylene. Four different cathetometers were used in this study before finding one that was able to consistently give reproducible results. The problem with the first three cathetometers is that they all had too many movable parts. For instance one of these cathetometers developed a lag in the screw gauge so that the screw gauge would not move the cross hairs of the eyepiece for the first few turns. Another cathetometer frequently stuck causing the lens to push over to one side resulting in inaccurate readings. At first it was thought that the solution would be to clean and lubricate the movable parts of these cathetometers; however, even after cleaning and lubricating the problems persisted. Another solution to compensate for the inaccuracy of the measurement of the length was to repeat the measurement several times and use the average length as the correct length; however, this was very time consuming. The ultimate solution was to obtain a cathetometer with few movable parts that consistently gave accurate results. The cathetometer that produced accurate, consistent results was a Gaertner model 0.01 mm by 100 cm, which had been purchased in 1971 for $2500.00.

2) Gas Leaks

Since the elongation measurements were performed with the sample in a Jerguson pressure cell that was held at pressures above atmospheric pressure for extended periods of time it was essential that the cell did not leak. When a leak did occur the entire range of measurements for that sample was repeated. The best way to avoid this repetition was to ensure that the cell was properly sealed at the beginning of the run when the sample was first placed into the cell. It was found that this was best accomplished by using a proper gas leak detection solution formulated for detecting leaks. e.g. SNOOP®, and not a solution of soap and water. The gas leak detection solution repeatedly found leaks that went undetected with a solution of soap and water and saved repeating runs.

3) Light Bulb Heat

In order to measure the sample accurately it was necessary to illuminate the inside of the constant temperature bath with a light bulb. A problem arose when the constant temperature bath was trying to keep the temperature at 30°C, as the light bulb itself gave off heat and caused the temperature to rise to about 35°C. A number of different bulbs were tried to keep the temperature as close to 30°C as possible. It was found that 15 and 25 W bulbs did not give off enough light to obtain accurate measurements, so the lowest wattage bulb that could be used was a 40 W bulb. The light bulb heat also caused temperature fluctuations at higher temperatures unless the light was left on at all times.

4) Constant Temperature Bath Temperature Offsets

The constant temperature bath would sometimes control the temperature to a much lower temperature than the selected temperature. This was because of a bad connection between the controller and the temperature measuring device inside the constant temperature bath. The solution was to ensure that a proper connection was maintained. By maintaining a proper connection it was found that on average the temperature would not fluctuate more than ±0.3°C. The greatest fluctuations in temperature occurred at a temperature of 30°C and lowest fluctuations in temperature occurred at temperatures of 70 and 90°C.

6.1.3 Thermal Expansion Coefficients

The measured thermal expansion coefficients are presented in Table 6.1.3. They were determined by plotting the expansion of each sample versus the temperature at a pressure of 0.1 Pa and performing a linear regression analysis on the plot.

Table 6.1.3 Thermal Expansion Coefficients

Sample	Type	Crystallinity (%)	Thermal Expansion Coefficient (1/°C)
MM019	LLDPE	18.5	2.63×10^{-4}
MM029	LLDPE	47.0	2.01×10^{-4}
MM003	LDPE	50.4	1.95×10^{-4}
MM013	HDPE	70.2	0.94×10^{-4}

These measured thermal expansion coefficients are within the values expected for each of the particular types of polyethylene measured. Kaplan (1997) reports that for low and medium density branched polyethylene the thermal expansion coefficient is 1.00 to 2.20×10^{-4} and for high density polyethylene the value is 0.59 to 1.10×10^{-4}. The measured values fall within these ranges for all the samples except MM019, which is an extremely low-density polyethylene.

6.1.4 Pressure Expansion Coefficients

The pressure expansion coefficients were calculated by plotting the expansion of the polyethylene versus the pressure at a constant temperature. The resulting curves were fitted with an equation and this equation was used to determine the pressure expansion coefficient at a certain pressure. For ethylene gas, the equation to fit the expansion versus pressure curves in the range of pressures measured was a linear equation as shown in Figure 6.1.4.1.

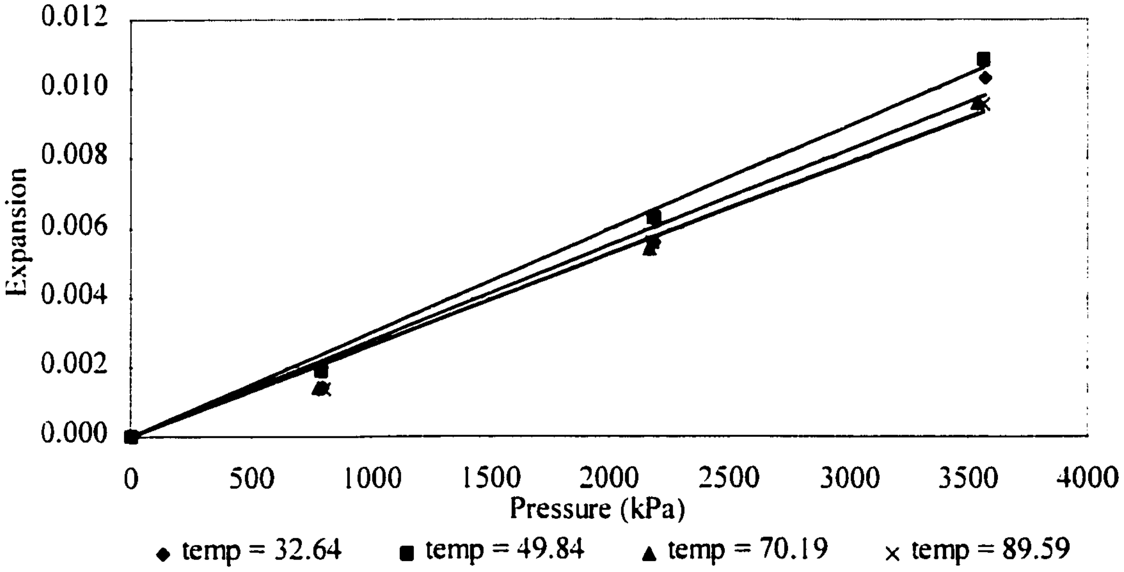


Figure 6.1.4.1 Expansion versus Pressure for Ethylene Gas - Sample MM029

Examples of the pressure expansion coefficients for ethylene at a pressure of 100 kPa are shown in Table 6.1.4.1. The values of the pressure expansion coefficients can be calculated from the equations shown in the tables for any pressure within the ranges used to measure the expansion of the polyethylene sample. The appropriate pressure ranges were presented in Table 5.2.1.

Table 6.1.4.1 Pressure Expansion Coefficients for Ethylene

Sample	Temperature (^oC)	Pressure (P) (kPa)	Pressure Expansion Coefficient = b x P	b
MM003	30	100	0.00032	3.16 x10^{-6}
MM003	50	100	0.00036	3.59 x10^{-6}
MM003	70	100	0.00025	2.52 x10^{-6}
MM003	90	100	0.00036	3.64 x10^{-6}
MM003	avg.	100	0.00032	3.23 x10^{-6}
MM013	30	100	0.00013	1.26 x10^{-6}
MM013	50	100	0.00015	1.51 x10^{-6}
MM013	70	100	0.00013	1.28 x10^{-6}
MM013	90	100	0.00012	1.22 x10^{-6}
MM013	avg.	100	0.00013	1.32 x10^{-6}
MM019	30	100	0.00061	6.08 x10^{-6}
MM019	50	100	0.00057	5.71 x10^{-6}
MM019	70	100	0.00054	5.40 x10^{-6}
MM019	avg.	100	0.00057	5.73 x10^{-6}
MM029	30	100	0.00031	3.05 x10^{-6}
MM029	50	100	0.00031	3.14 x10^{-6}
MM029	70	100	0.00028	2.81 x10^{-6}
MM029	90	100	0.00027	2.68 x10^{-6}
MM029	avg.	100	0.00029	2.92 x10^{-6}

The expansion of Sample MM029 as a function of pressure and temperature when 1-butene and 1-hexene are sorbed are shown in Figures 6.1.4.2 and 6.1.4.3.

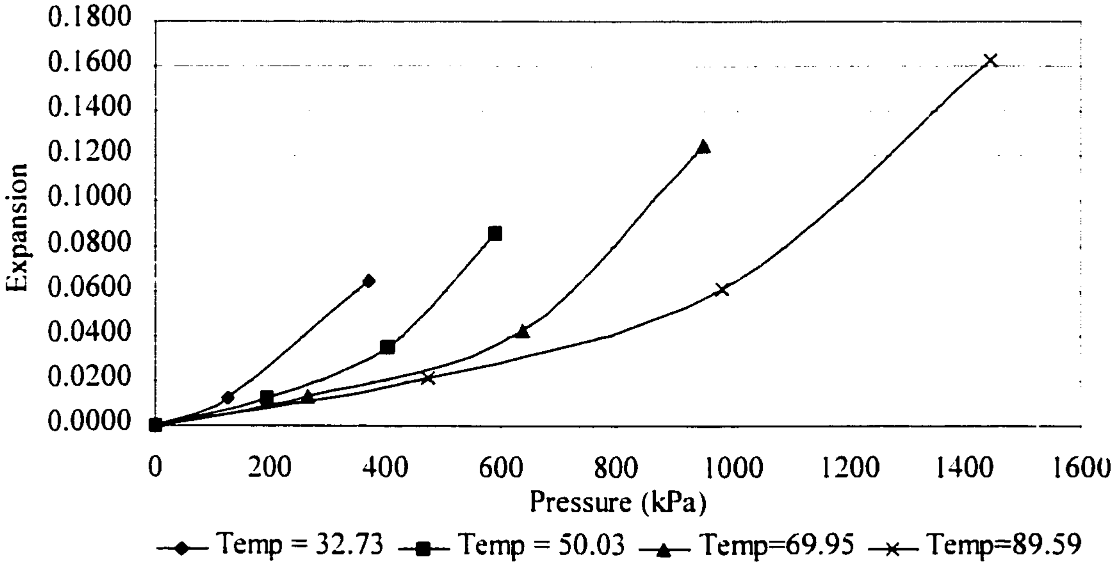


Figure 6.1.4.2 Expansion versus Pressure for 1-Butene Gas - Sample MM029

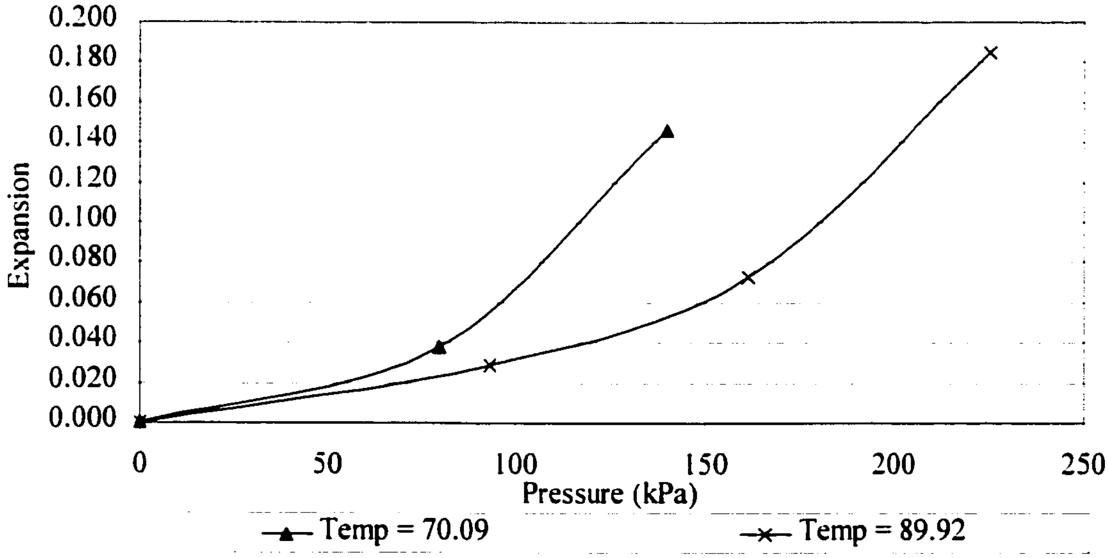


Figure 6.1.4.3 Expansion versus Pressure for 1-Hexene - Sample MM029

Examples of the pressure expansion coefficients for all the samples studied at a pressure of 100 kPa for 1-butene and 1-hexene are presented in Tables 6.1.4.2 and 6.1.4.3. The values of the pressure expansion coefficients can be calculated from the equations shown in the tables for any pressure within the ranges used to measure the expansions. The appropriate pressure ranges were presented in Table 5.2.1.

Table 6.1.4.2 Pressure Expansion Coefficients for 1-Butene

Sample	Temperature (°C)	Pressure (P) (kPa)	Pressure Expansion Coefficient = $bP + cP^2 + dP^3$	Coefficients of Equation		
				b	c	d
MM003	30	100	0.00696	$8.11\text{x}10^{-5}$	$-6.29\text{x}10^{-8}$	$3.42\text{x}10^{-10}$
MM003	50	100	0.00882	$1.20\text{x}10^{-4}$	$-3.85\text{x}10^{-7}$	$6.74\text{x}10^{-10}$
MM003	70	100	0.00597	$7.45\text{x}10^{-5}$	$-1.72\text{x}10^{-7}$	$2.39\text{x}10^{-10}$
MM003	90	100	0.01379	$1.74\text{x}10^{-4}$	$-3.88\text{x}10^{-7}$	$2.72\text{x}10^{-10}$
MM013	30	100	0.00269	$8.26\text{x}10^{-6}$	$2.19\text{x}10^{-7}$	$-3.26\text{x}10^{-10}$
MM013	50	100	0.00251	$2.66\text{x}10^{-5}$	$-2.32\text{x}10^{-8}$	$8.07\text{x}10^{-11}$
MM013	70	100	0.00139	$1.34\text{x}10^{-5}$	$4.01\text{x}10^{-9}$	$1.47\text{x}10^{-11}$
MM013	90	100	0.00078	$6.56\text{x}10^{-6}$	$1.26\text{x}10^{-8}$	$1.43\text{x}10^{-12}$
MM019	30	100	0.02205	$4.29\text{x}10^{-4}$	$-2.89\text{x}10^{-6}$	$8.05\text{x}10^{-9}$
MM019	50	100	0.04395	$8.07\text{x}10^{-4}$	$-4.34\text{x}10^{-6}$	$6.65\text{x}10^{-9}$
MM019	70	100	0.00388	$2.28\text{x}10^{-5}$	$1.60\text{x}10^{-7}$	-
MM029	30	100	0.00870	$5.49\text{x}10^{-5}$	$3.21\text{x}10^{-7}$	-
MM029	50	100	0.00687	$8.41\text{x}10^{-5}$	$-2.07\text{x}10^{-7}$	$5.29\text{x}10^{-10}$
MM029	70	100	0.00627	$7.70\text{x}10^{-5}$	$-1.67\text{x}10^{-7}$	$2.38\text{x}10^{-10}$
MM029	90	100	0.00575	$6.45\text{x}10^{-5}$	$-7.76\text{x}10^{-8}$	$7.68\text{x}10^{-11}$

Table 6.1.4.3 Pressure Expansion Coefficients for 1-Hexene

Sample	Temperature (°C)	Pressure (P) (kPa)	Pressure Expansion Coefficient = $bP + cP^2 + dP^3$	Coefficients of Equation		
				b	c	d
MM003	70	100	0.06600	$-4.50\text{x}10^{-4}$	$1.11\text{x}10^{-5}$	-
MM003	90	100	0.01800	$1.62\text{x}10^{-3}$	$-2.67\text{x}10^{-5}$	$1.23\text{x}10^{-7}$
MM013	70	100	0.03766	$4.53\text{x}10^{-4}$	$-7.64\text{x}10^{-7}$	-
MM013	90	100	0.01059	$3.73\text{x}10^{-5}$	$8.56\text{x}10^{-7}$	$-1.70\text{x}10^{-9}$
MM029	70	100	0.06710	$-2.61\text{x}10^{-4}$	$9.32\text{x}10^{-6}$	-
MM029	90	100	0.03090	$5.29\text{x}10^{-4}$	$-4.99\text{x}10^{-6}$	$2.79\text{x}10^{-8}$

6.1.5 Length Expansion versus Crystallinity

The expansion of the polyethylene caused by the sorption of ethylene, 1-butene or 1-hexene increased as the crystallinity of the polyethylene decreased. This is shown in Figure 6.1.5.1 and Figure 6.1.5.2 for ethylene and 1-butene. This is consistent with the findings of Michaels and Parker (1959), Rogers et al. (1960), Michaels and Bixler (1961), Eby (1964), Lowell and McCrum (1967), Deas et al. (1972), Takeuchi and Okamura (1975), Ghosal and Freeman (1993), Vittoria (1995) and Yoon et al. (1996) who measured the solubility of various gases in polyethylene.

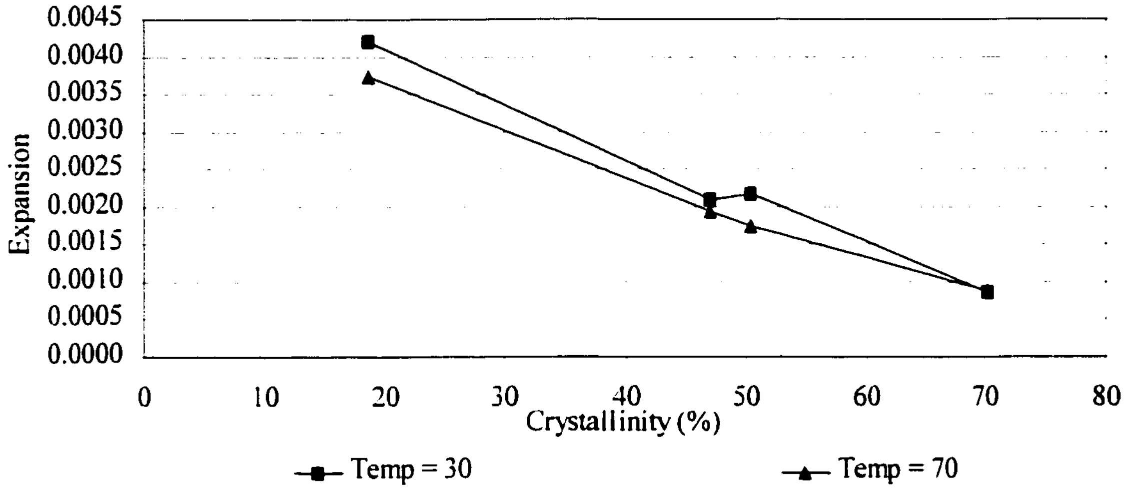


Figure 6.1.5.1 Expansion versus Crystallinity - Ethylene Gas at a Pressure of 690 kPa

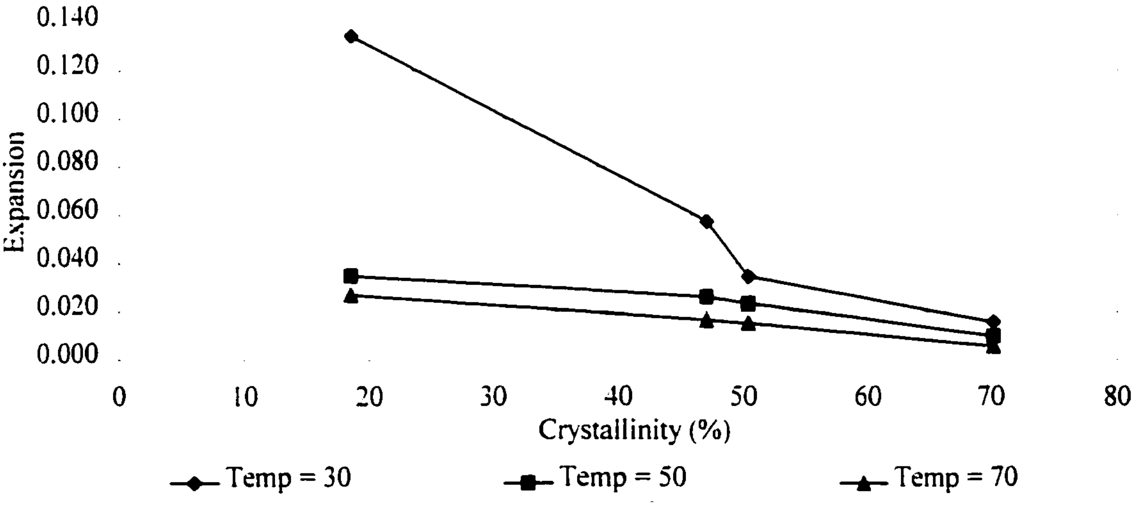


Figure 6.1.5.2 Expansion versus Crystallinity - 1-Butene Gas at a Pressure of 345 kPa

6.1.6 Length Expansion and Condensability of Gases

Gas critical temperature, molecular weight and the molar volume of the condensed vapor are all measures of condensability. Table 1.1 showed the critical temperature of ethylene, 1-butene and 1-hexene to be 282.3, 419.5 and 504.0 K the molecular weight to be 28.054, 56.107 and 84.161 kg/kmol and the liquid molar volume to be 0.0492, 0.0896 and 0.1261 m^3/kmol, respectively. Figures 6.1.4.1, 6.1.4.2 and 6.1.4.3 showed that the expansion of the polyethylene caused by the sorption of ethylene was the lowest and the expansion caused by the sorption of 1-hexene was the highest at similar pressures. These results reveal that the sorption of paraffin organic gases in polyethylene increases as the condensability of the gas increases. This conclusion is confirmed by Rogers et al. (1960), Michaels and Bixler (1961), Stern et al. (1969, 1972, 1983a, 1983b, 1986) and Ghosal and Freeman (1993).

6.1.7 Length Expansion and Temperature

In general the expansion caused by the sorption of ethylene, 1-butene and 1-hexene appears to decrease with increasing temperature at a constant gas pressure. This is evident from Figures 6.1.4.2, 6.1.4.3, 6.1.5.1 and 6.1.5.2. This was the case for most researchers who determined the solubility of organic vapors in polyethylene. Beret and Hagar (1979) found that the solubility of ethylene in polyethylene decreased with an increase in temperature. Also Rogers et al. (1960) and Robeson and Smith (1967, 1968) and Takeuchi and Okamura (1975) and Castro et al. (1987) all studied the solubility of organic vapors in polyethylene and found that the solubility decreased as the temperature increased. Kulkarni and Stern (1983) were the only researchers that found that the solubility of ethylene in polyethylene increased with increasing temperatures. Therefore for ethylene solubility in polyethylene there are conflicting reports on the effect of temperature. This is also seen from the data collected here on the expansion of polyethylene caused by ethylene. Figure 6.1.4.1 shows that at a temperature of 50°C the expansion of the polyethylene is the greatest, then at 30°C the expansion is less, but at 70 and 90°C even less.

6.1.8 Before and After Length Differences

An unusual result observed in performing the length measurements was that the polyethylene samples were consistently shorter after exposure to 1-butene and 1-hexene. The length of the samples measured at a pressure of <0.1 Pa before and after exposure to ethylene, 1-butene and 1-hexene is presented in Table 6.1.8.

Table 6.1.8 Length Before and After Exposure to Gases at 70°C under vacuum

Sample	Crystalline (%)	Gas	Length Before (mm)	Length After (mm)	Cathetometer Precision (mm)	Difference Before-After (mm)
MM019	18.5	ethylene	57.51	57.55	±0.04	+0.04
MM029	47.0	ethylene	57.28	57.30	±0.04	+0.02
MM003	50.4	ethylene	57.40	57.44	±0.04	+0.04
MM013	70.2	ethylene	58.40	58.38	±0.04	-0.02
MM029	47.0	1-butene	57.90	57.68	±0.04	-0.22
MM003	50.4	1-butene	57.35	56.99	±0.04	-0.36
MM013	70.2	1-butene	59.09	58.99	±0.04	-0.20
MM029	47.0	1-hexene	59.09	58.78	±0.04	-0.31
MM003	50.4	1-hexene	57.28	56.89	±0.04	-0.39

Table 6.1.8 shows that the difference in the length before and after sorption of 1-butene and 1-hexene are outside the range of the precision of the cathetometer, i.e. ±0.04 mm. The crystallinity of these samples before and after exposure to the gases was presented in Table 4.1.3. These results showed that the crystallinity of the samples exposed to 1-butene and 1-hexene had increased more than the samples exposed to ethylene; this increase in crystallinity is in agreement with the observed decreases in length resulting from exposure to 1-butene and 1-hexene.

6.2 Weight Measurement Results

The scope of this study was not to complete the weight measurement of all four samples with all three gases, at all four temperatures, but to set up the equipment and procedure so that the measurement of the solubility of gases in polyethylene could be carried out. Therefore the results presented here include:

(1) The establishment of the optimum flow rates to admit ethylene gas into the microbalance.

(2) The repeatability of the microbalance in measuring weights with and without a polyethylene sample attached.

(3) The background buoyancy weight runs using ethylene gas at 30, 50, 70 and 90°C.

(4) The weight measurement, solubility and some diffusion rates for polyethylene Sample MM029 sorbing ethylene gas at 30, 50 and 70°C.

6.2.1 Establishing Optimum Flow Rates for Admitting Ethylene in Balance

A mass flow controller was installed and a number of runs were performed to determine the optimum flow rate of ethylene gas into the pressure cell. Details of the final run is shown in Table 6.2.1. In this run the ethylene gas was introduced into the cell to a gauge pressure of 690 kPa and then the cell was evacuated. The ethylene gas was again admitted into the cell to a gauge pressure of 690 kPa after which more gas was introduced to bring the gauge pressure up to 2070 kPa, Then more gas was admitted into the cell to bring the gauge pressure up to 3450 kPa. Finally the cell was evacuated.

Table 6.2.1 Ethylene Flow Rate Determination for Weight Measurement

Time (min)	Weight	Temp (°C)	Comments
0.0	0.00000	49.7	Balance was tared
2.1	0.00000	49.7	Vacuum off and valve to vacuum shut
3.0	0.00000	49.7	Start to bring in ethylene (flow meter to 0.1 v)
8.1	-0.00005	49.7	Flow meter increased to 0.2 v (pressure - 0.00353 v)
11.1	-0.00003	49.7	Flow meter increased to 0.3 v (pressure - 0.00344 v)
14.1	-0.00004	49.8	Flow meter increased to 0.4 v (pressure - 0.00327 v)
17.1	-0.00003	49.8	Flow meter increased to 0.5 v (pressure - 0.00301 v)
20.1	-0.00001	49.8	Flow meter increased to 0.6 v (pressure - 0.00268 v)
23.1	-0.00001	49.9	Flow meter increased to 0.7 v (pressure - 0.00230 v)
26.1	0.00000	49.8	Flow meter increased to 0.8 v (pressure - 0.00187 v)
29.1	0.00002	49.8	Flow meter increased to 1.0 v (pressure - 0.00135 v)
32.1	0.00003	49.9	Flow meter increased to 1.5 v (pressure - 0.00070 v)
35.1	0.00004	49.9	Flow meter increased to 2.0 v (pressure + 0.00030 v)
38.1	0.00007	50.0	Flow meter increased to 2.5 v (pressure + 0.00166 v)
41.1	0.00009	50.1	Flow meter increased to 3.0 v (pressure + 0.00336 v)
44.1	0.00011	50.1	Flow meter increased to 3.5 v (pressure + 0.00539 v)
47.1	0.00013	50.2	Flow meter increased to 4.0 v (pressure + 0.00766 v)
50.1	0.00015	50.2	Flow meter increased to 5.0 v (pressure + 0.01034 v)
53.1	0.00016	50.2	Pressure 0.01234 v = 720 kPa
65.1	0.00012	49.7	Start to evacuate
81.9	-0.00006	48.7	Down to atmospheric pressure
85.2	0.00012	48.8	Pressure down to <0.1 Pa and valve 0.5 turns open
83.1	0.00000	49.8	Vacuum off and valve to vacuum shut
114.9	0.00000	49.7	Start to bring the ethylene into the cell again
116.1	-0.00001	49.8	Increase flow meter to 1.0 v
125.1	0.00002	49.9	up to atmosphere pressure - increase flow meter 3.0 v
146.1	0.00015	50.1	Finished bringing in ethylene (pressure 683 kPa)
159.0	0.00012	49.8	Start to increase pressure - 2070 kPa (flow met 4.0 v)
198.3	0.00024	50.0	Pressure up to 2089 kPa
213.3	0.00027	49.7	Start to increase pressure to 3450 kPa (flow met 4.5 v)
255.3	0.00004	50.0	Pressure up to 3447 kPa
345.3	0.00013	49.8	Start to evacuate
375.3	0.00031	48.7	Pressure at atmospheric pressure
395.3	0.00008	49.0	Pressure at <0.1 Pa
449.8	0.00005	49.3	End of run

In Table 6.2.1 the flow meter and the pressure are reported in volts. A plot of weight versus time for this run is shown in Figure 6.2.1.

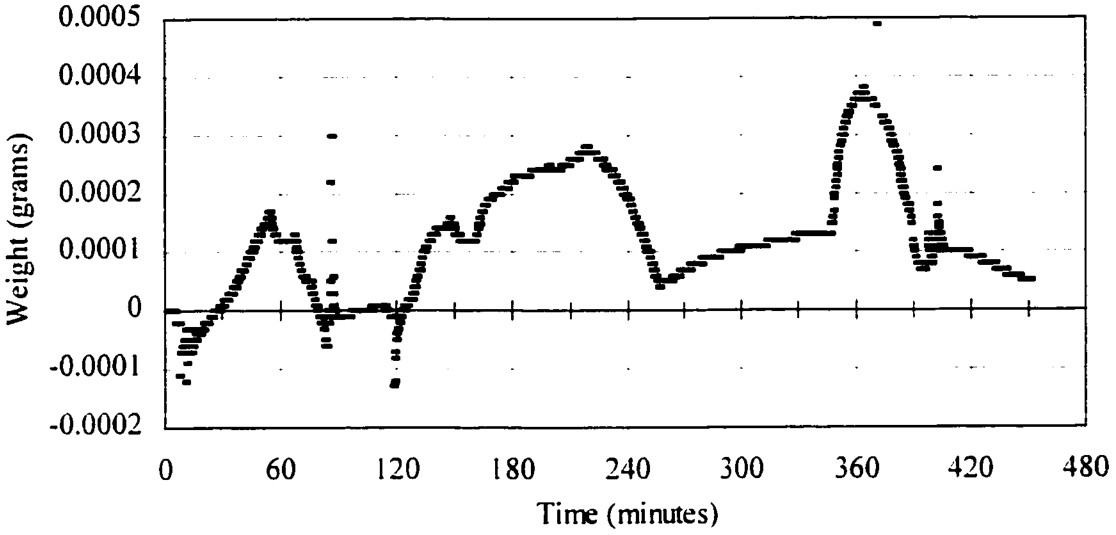


Figure 6.2.1 Weight versus Time-See Table 6.2.1 for Details

6.2.2 Weight Measurement Repeatability Without Sample - First Attempt

Weight measurements using ethylene gas without a polyethylene sample in the balance were performed. The weight measurement run began with the balance evacuated. Ethylene was then introduced into the cell up to a pressure of 690 kPa and then evacuated. This procedure of pressurization followed by evacuation was performed three times. The ethylene gas was introduced into the cell over a period of thirty minutes. Time was then given for the weight to come to a stable reading and finally the cell was evacuated, again over a thirty minute time period. Table 6.2.2 shows the details of this run and the weight versus time was plotted in Figure 6.2.2.

Table 6.2.2 First Repeatability Attempt - No Sample in the Balance

Time (min)	Weight	Temp (°C)	Comments
0.00	0.00000	49.6	Balance was tared (after it had been evacuated)
3.00	0.00009	49.6	Start to bring the ethylene into the cell
3.30	-0.00313	49.7	18 seconds later the weight is way down
33.00	-0.00178	49.7	Finished bringing in ethylene to a pressure of 690 kPa
93.00	-0.00231	49.5/6	Start to evacuate
93.30	-0.00241	49.5	18 seconds later there is little change in the weight
127.00	0.00751	49.0	Pressure down to <0.1 Pa
183.05	-0.00108	49.5/6	Start to bring the ethylene into the cell
183.35	-0.00107	49.5/6	18 seconds later there is little change
206.00	-0.00098	49.9	Finished bringing in ethylene to a pressure of 712 kPa
212.15	-0.00191	49.6	Temperature down to 49.6°C
263.17	-0.00190	49.6	Start to evacuate
263.47	-0.00226	49.5	18 seconds later there is little change
288.07	-0.0034	49.0	Opened valve to vacuum
289.27	0.00441	49.0	72 seconds after opening valve weight is way up
293.17	0.00508	49.0	Pressure down to <0.1 Pa
299.17	-0.00674	49.5	Temperature up to 49.5°C
385.90	-0.00264	49.6	Start to bring in ethylene
386.20	-0.00263	49.6	18 seconds later there is no change
405.1	-0.00267	49.9	Finished bringing in ethylene to a pressure of 693 kPa
454.92	-0.00292	49.6	Start to evacuate
455.27	-0.00372	49.6	18 seconds after evacuation there is little change
477.12	-0.00413	49.1	Opened valve to vacuum
479.52	0.00543	49.1	144 seconds later weight is way up
484.93	0.00656	49.3	Pressure down to <0.1 Pa
495.13	-0.00506	49.5/6	Temperature up 49.5/6°C
600.15	-0.00210	49.5/6	End of run with vacuum pump still running
3480.00	-0.00210	49.5/6	Valve shut off for 48 hours and weight did not change

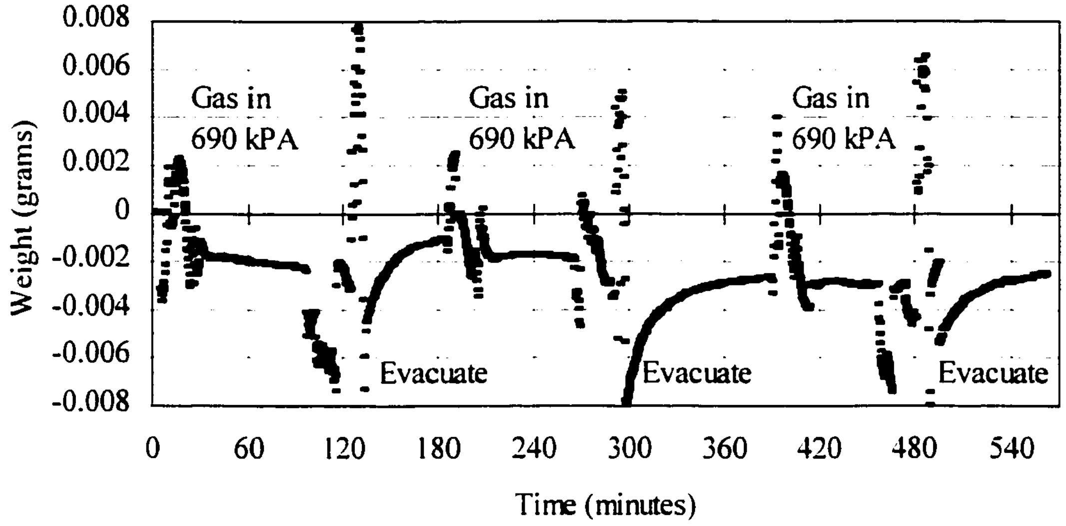


Figure 6.2.2 First Repeatability Attempt - No Sample - See Table 6.22 for Details

This run shows that after the ethylene gas was up to a pressure of 690 kPa and the weight stabilized, the weight for each of the three runs was -0.00178 g, -0.00190 g and -0.00292 g. The three weights show a fluctuation of 0.00114 g, which is not as consistent as the Cahn D-110 microbalance should be, according to the Cahn technicians.

6.2.2.1 Why The First Weight Measurement Attempts Were Not Repeatable

A number of possibilities as to why the results of this run were so inconsistent were considered. The possibility of temperature fluctuations were considered; however, from inspecting the data it was obvious that the inconsistencies were not caused by extreme temperature fluctuations since the temperature fluctuated by only 0.6°C.

It was also determined that the weight measurement was not affected by a sudden vibration such as the door to the laboratory slamming or bumping the table next to the constant temperature bath, turning on and off the computer or bumping the valves.

It was discovered, however, that turning the vacuum pump on and off did cause sharp fluctuations in the weight recorded on the computer. Reducing the vibrations that reach the microbalance from the vacuum pump eliminated this problem. This was accomplished by cutting the stainless steel line that runs from the vacuum pump to the pressure cell and inserting 50 cm of rubber vacuum hose. The vacuum pump was turned on and off a few times after this repair and there was no effect on the measured weight.

It was also determined from studying the plot, that bringing gas into the cell caused the weight to fluctuate considerably. The microbalance pressure cell was opened up and it was found that the hang down wire from the beam to where the sample would be attached was wrapped around the balance beam, which would make the weight fluctuate considerably. The pressure cell had been pressure tested before the ethylene was admitted to the cell. The pressure testing gas was admitted into the cell at a very fast rate, which must have blown the wire up around the beam. The wire was repaired and pieces of paper clips were installed on the hang down wires on the sample and tare side. These pieces of paper clips are very close to the same weight and volume. The cell was reassembled and gas was introduced into the cell at a slow rate, taking thirty minutes to go from a pressure of <0.1 Pa to a pressure of 690 kPa and thirty minutes to go from 690 kPa to 3450 kPa. The cell was then evacuated at a slow rate, going from a pressure of 3450 kPa down to a pressure of <0.1 Pa in 25 minutes. The cell was disassembled and the condition of the hang down wires were examined and found to be properly positioned. This showed that the wires were not affected by this rate of gas flow. The wires being wrapped around the balance beam had caused the large fluctuations in weight measurements.

6.2.3 Weight Measurement Repeatability Without Sample - Second Attempt

The ethylene gas was again introduced into the cell to a pressure of 690 kPa and evacuated three times, just as in the first repeatability attempt. The ethylene gas was introduced into the cell and evacuated from the cell over a 30 minute time period just as before. Before the third run was performed the balance was tared and a flow controller was introduced to the setup in order to determine flow rates. The results of this run can be seen in Table 6.2.3 and a plot of weight versus time is shown in Figure 6.2.3.

Table 6.2.3 Second Repeatability Attempt - No Sample in the Balance

Time (min)	Weight	Temp (°C)	Comments
0.0	0.00000	49.7	Balance was tared (after it had been evacuated)
11.1	-0.00004	49.7	Vacuum off and valve to vacuum shut
14.0	-0.00009	49.8	Started to bring the ethylene into the cell
45.0	0.00020	50.2	689 kPa and found and repaired leak
54.0	0.00017	49.8	Finished bringing in ethylene to a pressure 712 kPa
75.0	0.00018	49.7/8	Started to evacuate
105.0	0.00007	49.5	Pressure down to <0.1 Pa and valve 0.5 turns open
134.1	0.00008	49.7	Vacuum off and valve to vacuum shut
135.6	0.00006	49.7	Started to bring the ethylene into the cell
177.9	0.00020	49.9	Finished bringing in ethylene to a pressure of 692 kPa
208.5	0.00021	49.8	Started to evacuate
229.5	0.00012	49.4	Pressure down to <0.1 Pa and valve 0.5 turns open
270.3	0.00000	49.7	Microbalance tared to 0.00000 g
282.3	-0.00001	49.7	Vacuum off and valve to vacuum shut
286.2	-0.00020	49.8	Start to bring the ethylene into the cell (flow 0.1 slpm)
294.3	-0.00000	50.1	Pressure at atmospheric (flow = 2.15 slpm)
304.5	0.00009	50.2	Pressure at 238 kPa (flow = 2.90 slpm)
315.3	0.00014	50.1	Finished bringing in ethylene to a pressure of 684 kPa
325.2	0.00011	49.8	Start to evacuate
345.3	0.00000	49.4	Pressure down to <0.1 Pa
360.0	0.00000	49.7	End of run

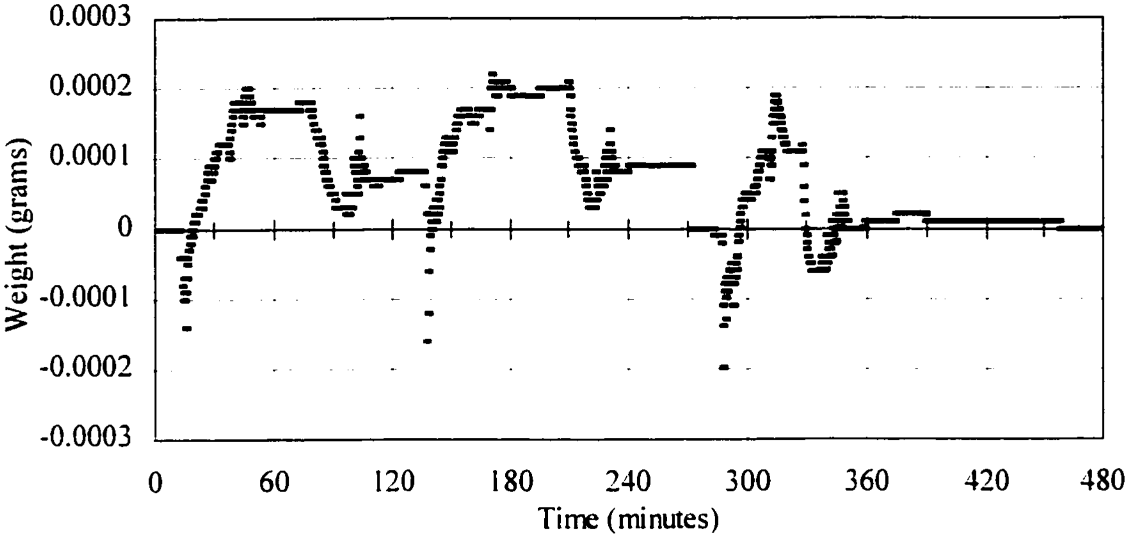


Figure 6.2.3 Second Repeatability Attempt - No Sample - See Table 6.2.3 for Details

Table 6.2.3 and Figure 6.2.3 shows that this Cahn D110 microbalance does give repeatable weight measurements with ethylene gas. The recorded weight after 690 kPa of pressure of ethylene was introduced is 0.00017 g after Run 1 and 0.00020 g after Run 2 and 0.00014 g after Run 3. The difference between the weights at a pressure of 690 kPa for these three runs is only ±0.00003 g, revealing very repeatable results without a polyethylene sample attached to the balance.

6.2.4 Weight Measurement Repeatability With Sample in Balance

The repeatability of the Cahn D-110 microbalance at measuring the weight of ethylene gas sorbing into a 47% crystalline polyethylene at a temperature of 30°C and up to a pressure of 3450 kPa was tested. The ethylene was admitted into the pressure chamber at three pressures, 690, 2070 and 3450 kPa. At each pressure the ethylene and polyethylene were allowed to reach equilibrium before more ethylene was admitted into the pressure cell. When the weight change was no more then 1 μg/minute it was assumed that equilibrium between the ethylene and polyethylene had occurred. After the ethylene had reached equilibrium with the polyethylene at 3450 kPa the pressure cell was evacuated.

Table 6.2.4.1 and Figures 6.2.4.1 and 6.2.4.2 show the repeatability of the Cahn D-110 microbalance at weighing the sorption of ethylene into polyethylene.

Table 6.2.4.1 Repeatability of Weighing Sorption of Ethylene in Polyethylene

Pressure (kPa absolute)	Run 1 Weight (g)	Run 2 Weight (g)	Difference in Weight Run 2 - Run 1
784	-0.00246	-0.00253	-0.00007
2164	-0.00731	-0.00730	+0.00001
3544	-0.01480	-0.01487	-0.00007

These results indicate that the reliability of the measured amounts of sorbed ethylene is better than 0.0001 g.

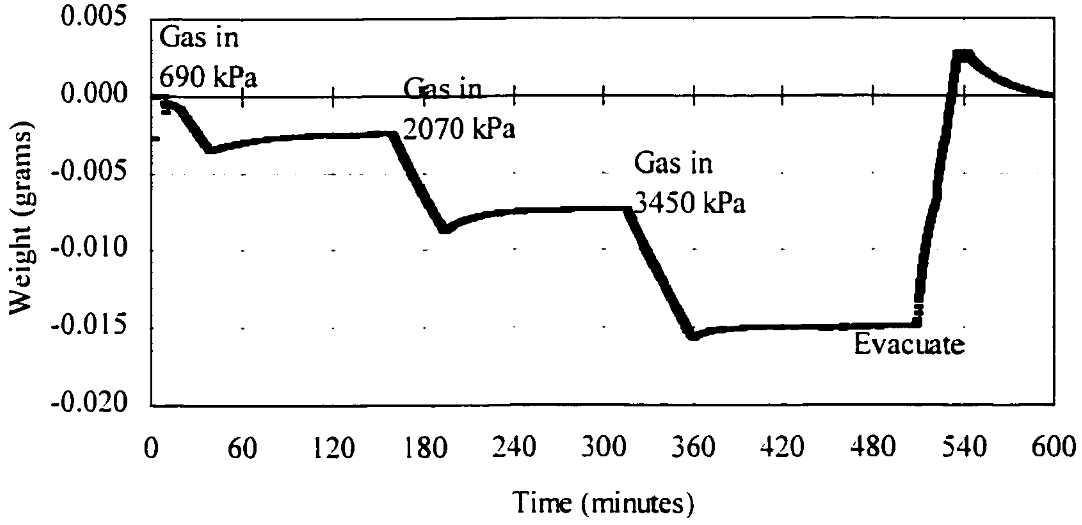


Figure 6.2.4.1 Repeatability # 1 - Ethylene gas to 3450 kPa Using Sample MM029 - 47% Crystalline - Temperature 30°C

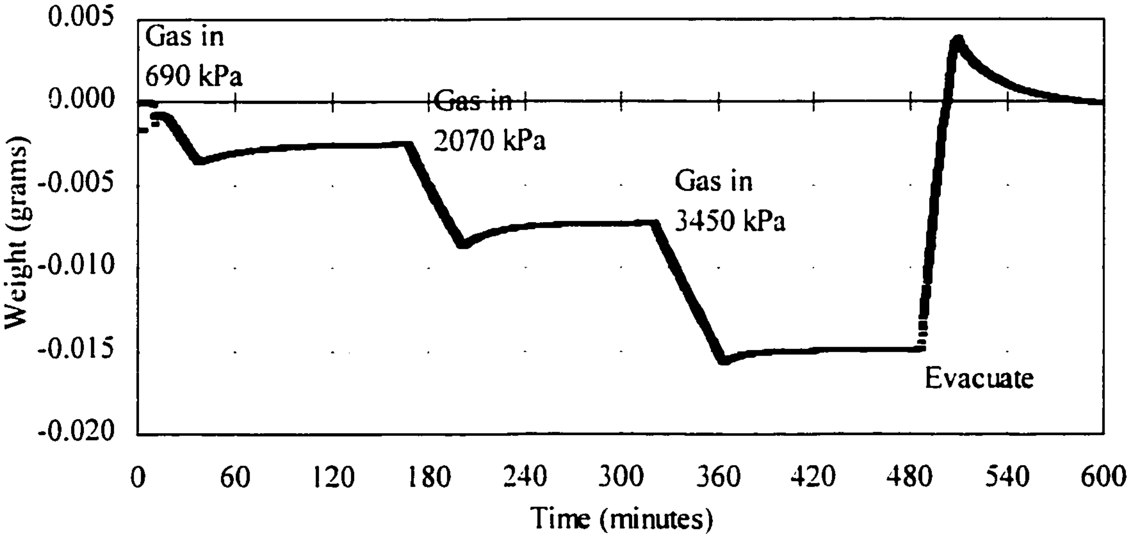


Figure 6.2.4.2 Repeatability # 2 - Ethylene gas to 3450 kPa Using Sample MM029 - 47% Crystalline - Temperature 30°C

6.2.5 Determination of the Background Weight for Ethylene

The background buoyancy weight recorded when ethylene was introduced into the pressure cell at 690, 2070 and 3450 kPa pressure without a polyethylene sample present at temperatures of 30, 50, 70 and 90°C are presented in Tables 6.2.5.1, 6.2.5.2, 6.2.5.3 and 6.2.5.4. Plots of the results are presented in Figures 6.2.5.1, 6.2.5.2, 6.2.5.3 and 6.2.5.4

Table 6.2.5.1 Background Weight Recorded By Cahn D110 Microbalance Using Ethylene Gas and No Polyethylene Sample at a Temperature of 30°C

Time (min)	Weight (g)	Flow (slpm)	Temp (°C)	Comments
5.1	0.00000	0.000	29.8	Close valve to vacuum and shut off vac pump
6.0	0.00000	0.0134	29.8	Increase regulator to 690 kPa & flow meter 0.1 v
7.2	-0.00011	0.0672	29.8	Increase flow meter to 0.5 v
8.4	-0.00012	0.134	29.8	Increase flow meter to 1.0 v
16.8	0.00001	0.403	29.9	Atmospheric press & increase flow meter 3.0 v
41.1	0.00015	0.000	30.2	Pressure up to 712 kPa gauge
101.1	0.00016	0.403	29.8	Increase regulator to 2070 kPa
102.9	0.00018	0.605	30.1	Increase flow to meter to 4.5 v
139.2	0.00027	0.000	30.2	Pressure up to 2075 kPa gauge
200.1	0.00032	0.605	29.8	Increase regulator to 3450 kPa
249.0	-0.00003	0.000	30.0	Pressure up to 3454 kPa gauge
322.5	0.00000	0.0336	29.8	Start to evacuate (max. flow 0.30 v)
362.7	0.00012	0.0336	28.2	At atmospheric pressure
370.5	0.00016	0.000	29.1	Pressure at <0.1 Pa
585.5	0.00004	0.000	29.8	End of run

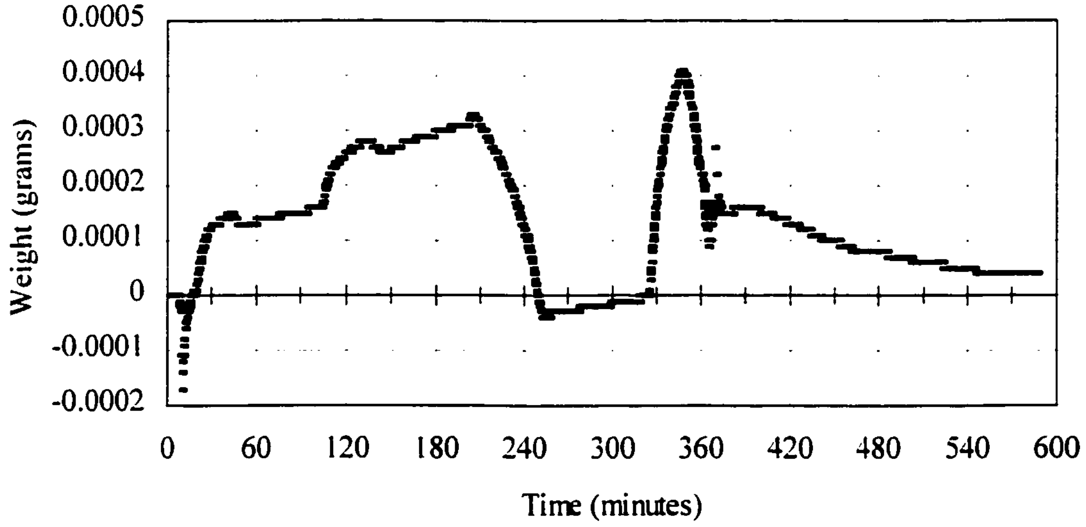


Figure 6.2.5.1 Background Weight Recorded By Cahn D110 Microbalance Using Ethylene Gas and No Polyethylene Sample at a Temperature of 30°C

Table 6.2.5.2 Background Weight Recorded By Cahn D110 Microbalance Using Ethylene Gas and No Polyethylene Sample at a Temperature of 50°C

Time (min)	Weight (g)	Flow (slpm)	Temp (°C)	Comments
5.0	0.00000	0.000	49.8	Close valve to vacuum and shut off vac pump
6.0	-0.00001	0.0134	49.8	Increase regulator 690 kPa & flow meter 0.1 v
7.0	-0.00003	0.0672	49.8	Increase flow meter to 0.5 v
8.0	-0.00012	0.134	49.8	Increase flow meter to 1.0 v
13.0	-0.00002	0.202	50.1	Increase flow meter to 1.5 v
15.0	-0.00001	0.403	50.1	Atmospheric press & increase flow meter 3.0 v
20.0	0.00007	0.470	50.2	Increase flow meter to 3.5 v
35.0	0.00015	0.000	50.2	Pressure up to 692 kPa
105.0	0.00016	0.605	49.8	Increase regulator to 2070 kPa & flow to 4.5 v
135.5	0.00030	0.672	50.1	Increase flow to meter to 5.0 v
140.0	0.00030	0.000	50.1	Pressure up to 2075 kPa
210.0	0.00039	0.672	49.8	Increase regulator to 3450 kPa
247.0	0.00018	0.000	50.2	Pressure up to 3447 kPa
317.0	0.00024	0.0403	49.8	Start to evacuate (max. flow 0.30 v)
364.0	0.00017	0.0403	49.0	At atmospheric pressure
376.0	0.00020	0.000	49.6	Pressure <0.1 Pa
588.0	0.00000	0.000	49.8	End of run

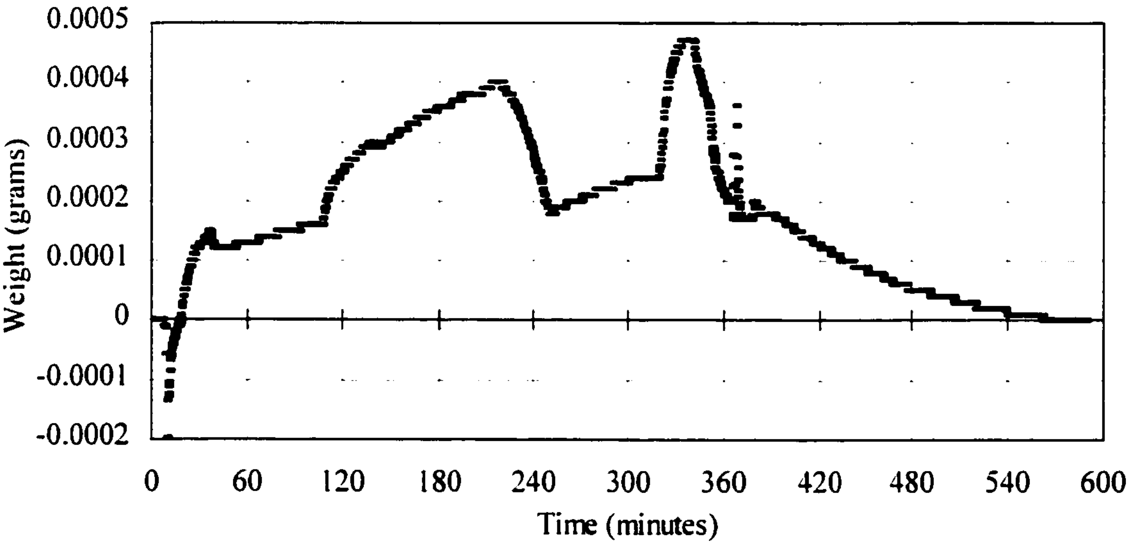


Figure 6.2.5.2 Background Weight Recorded By Cahn D110 Microbalance Using Ethylene Gas and No Polyethylene Sample at a Temperature of 50°C

Table 6.2.5.3 Background Weight Recorded By Cahn D110 Microbalance Using Ethylene Gas and No Polyethylene Sample at a Temperature of 70°C

Time (min)	Weight (g)	Flow (slpm)	Temp (°C)	Comments
5.0	0.00000	0.000	69.9	Close valve to vacuum and shut off vacuum pump
6.0	-0.00001	0.0134	69.9	Increase regulator to 690 kPa and flow meter 0.1 v
7.0	-0.00002	0.0672	69.9	Increase flow meter to 0.5 v
8.0	-0.00018	0.134	69.8	Increase flow meter to 1.0 v
13.0	0.00000	0.202	70.0	Increase flow meter to 1.5 v
16.0	0.00002	0.403	70.0	Atmospheric pressure & increase flow meter 3.0 v
20.0	0.00008	0.470	70.1	Increase flow meter to 3.5 v
36.0	0.00014	0.000	70.0	Pressure up to 700 kPa
106.0	0.00015	0.672	69.6	Increase regulator to 2070 kPa & flow meter 5.0 v
136.0	0.00024	0.000	70.0	Pressure up to 2130 kPa
200.0	0.00029	0.672	69.6	Increase regulator to 3450 kPa
238.0	0.00015	0.000	69.6	Pressure up to 3485 kPa
298.0	0.00023	0.0403	69.0	Start to evacuate (max. flow 0.30 v on flow meter)
339.0	0.00005	0.0403	68.0	At atmospheric pressure
342.0	0.00017	0.000	68.4	Pressure <0.1 Pa
480.0	0.00000	0.000	69.6	End of run

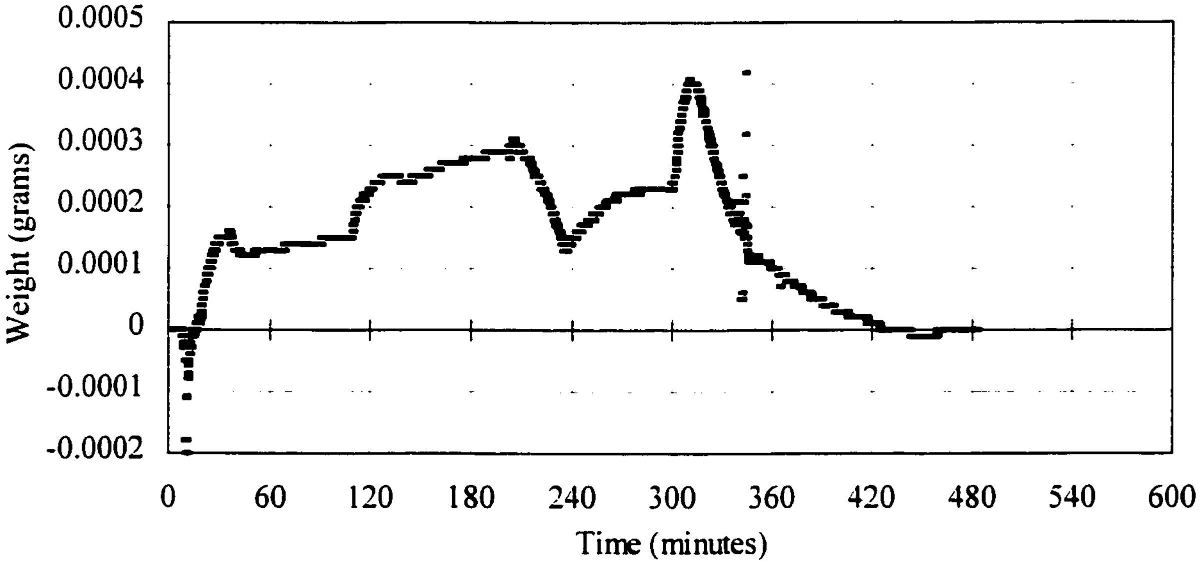


Figure 6.2.5.3 Background Weight Recorded By Cahn D110 Microbalance Using Ethylene Gas and No Polyethylene Sample at a Temperature of 70°C

Table 6.2.5.4 Background Weight Recorded By Cahn D110 Microbalance Using Ethylene Gas and No Polyethylene Sample at a Temperature of 90°C

Time (min)	Weight (g)	Flow (slpm)	Temp (°C)	Comments
5.0	0.00000	0.000	89.9	Close valve to vacuum and shut off vac pump
6.0	0.00000	0.0134	89.9	Increase regulator 690 kPa & flow meter 0.1 v
7.0	-0.00013	0.0672	89.9	Increase flow meter to 0.5 v
8.0	-0.00013	0.134	89.9	Increase flow meter to 1.0 v
13.0	0.00000	0.202	90.0	Increase flow meter to 1.5 v
15.0	0.00002	0.403	90.1	Atmospheric press & increase flow meter 3.0 v
19.0	0.00008	0.470	90.3	Increase flow meter to 3.5 v
33.0	0.00017	0.000	90.2	Pressure up to 720 kPa
188.0	0.00014	0.672	89.9	Increase regulator to 2070 kPa & flow to 5.0 v
215.0	0.00028	0.000	90.4	Pressure up to 2097 kPa
309.0	0.00026	0.672	89.8	Increase regulator to 3450 kPa
347.0	0.00021	0.000	90.4	Pressure up to 3421 kPa
450.0	0.00020	0.0403	89.7	Start to evacuate (max. flow 0.30 v)
471.0	-0.00020	0.0403	87.5	At atmospheric pressure
476.0	-0.00012	0.000	88.7	Pressure <0.1 Pa
885.0	-0.00008	0.000	89.9	End of run

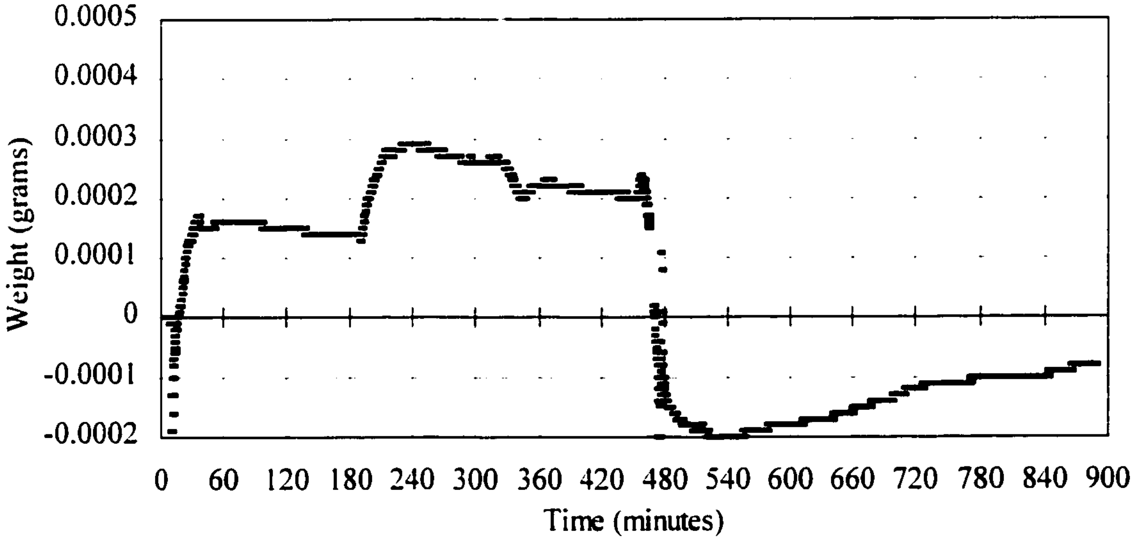


Figure 6.2.5.4 Background Weight Recorded By Cahn D110 Microbalance Using Ethylene Gas and No Polyethylene Sample at a Temperature of 90°C

Table 6.2.5.5 shows the background buoyancy weights of ethylene gas at pressures used in this study. This summary shows that all of the values are very similar regardless of the temperature except at 30°C and 3547 kPa where the weight is much less than all the others. The background buoyancy weight run was performed again at 30°C and the weights obtained were identical to the first run.

Table 6.2.5.5 Summary of Background Buoyancy Weights for Ethylene Gas

Temperature (°C)	Pressure (kPa absolute)	Weight (g)
30	805	0.00014
	2168	0.00026
	3547	-0.00002
50	785	0.00013
	2168	0.00030
	3540	0.00019
70	793	0.00013
	2223	0.00025
	3578	0.00019
90	813	0.00015
	2190	0.00028
	3514	0.00021

6.2.6 Solubility and Diffusion Rate of Ethylene Sorption Into Sample MM029

Solubility, diffusion rates and the time to reach equilibrium of ethylene gas sorbing into polyethylene Sample MM029 at 30, 50 and 70°C are presented in Table 6.2.6. Details of the calculations necessary to obtain the solubility are presented in Appendix D. The diffusion rates were determined by the output of the Cahn D110 microbalance, which recorded the weight change of the polyethylene every 20 seconds. Equilibrium was determined to be when the change in weight with time was less then 1 μg/minute, which was the weight drift of the microbalance without a sample.

Table 6.2.6 Solubility and Rate of Diffusion of Ethylene Sorption in Sample MM029

Temp (°C)	Absolute Pressure (kPa)	Rate of Diffusion in First Minute (μg/min)	Time to Reach Equilibrium (minutes)	Solubility (g of ethylene /g of polyethylene)	Solubility (g of ethylene /g of polyethylene /atmosphere)
29.7	776	40	112	0.003363	4.74×10^{-4}
	2148	80	117	0.011880	5.60×10^{-4}
	3527	80	93	0.019636	5.64×10^{-4}
49.9	799	50	56	0.004025	5.10×10^{-4}
	2147	60	69	0.011266	5.32×10^{-4}
	3563	60	58	0.018556	5.28×10^{-4}
69.6	802	50	20	0.004124	5.21×10^{-4}
	2160	60	25	0.010874	5.10×10^{-4}
	3560	60	20	0.017427	4.96×10^{-4}

The rate of diffusion mentioned here is only an estimate of the actual diffusion since this diffusion assumed the background and polyethylene expansion buoyancy force to be constant. The actual background and polyethylene expansion buoyancy force would be changing as the ethylene was sorbed.

6.2.6.1 Comparison of Measured Solubility with Other Researchers

A comparison of the solubility of ethylene in polyethylene to the results of Li and Long (1969), Beret and Hagar (1979) and Kulkarni and Stern (1983) is shown in Table 6.2.6.1.

Table 6.2.6.1 Comparison of the Solubility of Ethylene in Polyethylene Measured in This Study with the Solubility Measured in Other Studies

Research Group	Solubility (g of ethylene/ g of polyethylene /atmosphere)	Crystallinity of Polyethylene (%)	Temperature (°C)	Press (kPa)
Li and Long (1969)	5.88×10^{-4}	55	25	1379
Beret and Hagar (1979)	3.4×10^{-5}	48	23	101
Kulkarni and Stern (1983)	6.66×10^{-4}	45	20	4053
This study	5.59×10^{-4}	47	30	2148

Table 6.2.6.1 shows that the solubility of ethylene in polyethylene measured in this study is close to the values obtained by other researchers.

6.2.6.2 Solubility of Ethylene in Polyethylene and Henry's Law

Li and Long (1969) and Kulkarni and Stern (1983) both concluded that Henry's law was obeyed for the solubility of ethylene in polyethylene within the pressure range of this present study. Figure 6.2.6.2 shows that Henry's law is obeyed for the solubilities measured in this study at 30, 50 and 70°C.

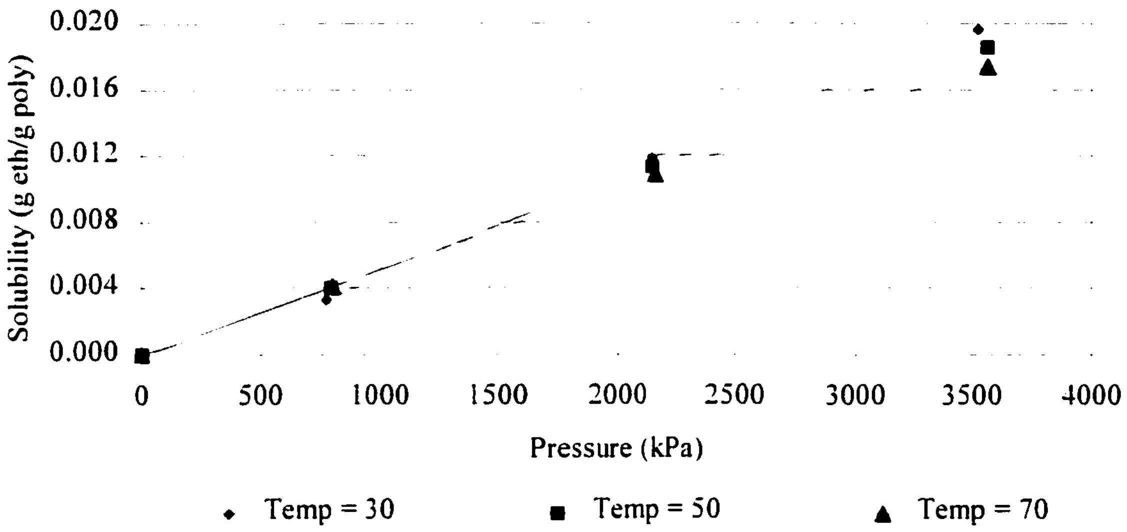


Figure 6.2.6.2 Solubility of Ethylene in Polyethylene Sample MM029 versus Pressure

6.2.6.3 Effect of Temperature on the Solubility of Ethylene in Polyethylene

Table 6.2.6.3 shows that the solubility of ethylene in polyethylene decreases with an increase in temperature. The decrease of the solubility of ethylene in polyethylene as the temperature increases was also observed by Beret and Hagar (1979). Furthermore, Rogers et al. (1960), Robeson and Smith (1967, 1968), Takeuchi and Okamura (1975), Castro et al. (1987) and Ghosal and Freeman (1993) all observed a decrease in the solubility of organic vapors in polyethylene with an increase in temperature.

Table 6.2.6.3 Effect of Temperature on the Solubility in Polyethylene

Temperature (°C)	Solubility (g of ethylene/g of polyethylene/atmosphere)
30	5.59×10^{-4}
50	5.28×10^{-4}
70	5.01×10^{-4}

7. CONCLUSIONS

The results of this work led to the following conclusions:

1. A cathetometer is a reliable instrument to measure the length expansion of polyethylene caused by the sorption of gases or temperature variations. This is shown by the good repeatability of the length measurement results for Sample MM029 and by the close agreement of the measured thermal expansion coefficients with the values reported in the literature.
2. The crystals in the polyethylene samples are randomly oriented as shown by the x-ray diffraction results. Thus the polyethylene samples are isotropic with respect to volume expansion caused by the sorption of gases or temperature changes.
3. The sorption and desorption of 1-butene and 1-hexene into polyethylene increases the crystallinity of polyethylene. This is shown by the x-ray diffraction results, as well as the length measurement results.
4. Expansion of the polyethylene caused by the sorption of ethylene, 1-butene or 1-hexene increased as the crystallinity of the polyethylene decreased.
5. The expansion of the polyethylene caused by the sorption of the paraffin organic gases increased as the condensability of the gases increased. For example the expansion of the polyethylene increased as the molar volume of the condensed vapor, the molecular weight or the critical temperature of the paraffin organic gas increased. This would suggest that the solubility of the paraffin organic gases in polyethylene would increase as the condensability of the gases increased. This conclusion is in agreement with the observations by Rogers et al. (1960), Michaels and Bixler (1961), Stern et al. (1969, 1972, 1983a, 1983b, 1986) and Ghosal and Freeman (1993).

6. It is necessary to admit gas into the Cahn D110 electromicrobalance at a very slow rate. About 30 minutes was needed to change the pressure of the gas at each step in order to avoid shifting the zero position of the electromicrobalance.
7. The Cahn D110 electromicrobalance is a reliable instrument to measure the weight change of polyethylene caused by the sorption of gases. This is shown by the good repeatability of the weight measurement results for Sample MM029 and by the close agreement of the measured solubility with the values reported in the literature by other researchers.
8. Henry's law is obeyed for the solubility of ethylene in a 47% crystalline polyethylene up to a pressure of 3500 kPa and in the temperature range of 30 to 70°C.
9. The solubility of ethylene in the linear low density polyethylene, having a crystallinity of 47%, decreased with increasing temperature.

8. RECOMMENDATIONS

The following recommendations and suggestions for further work are made to improve the data base and understanding of olefins in polyethylene:

1. Complete the weight measurements of 1-butene and 1-hexene sorbed by polyethylene Sample MM029 with the Cahn D110 electromicrobalance at the pressures and temperatures of this study.
2. Complete the weight measurements of ethylene, 1-butene and 1-hexene sorbed by polyethylene samples MM003, MM013 and MM019 with the Cahn D110 electromicrobalance at the pressures and temperatures of this study.
3. Calculate the solubilities of 1-butene and 1-hexene in Sample MM029.
4. Calculate the solubilities of ethylene, 1-butene and 1-hexene in samples MM003, Mm013 and MM019.
5. Calculate diffusion rates for ethylene, 1-butene and 1-hexene diffusing into samples MM003, MM013, MM019 and MM029 from the weight measurement runs performed with the Cahn D110 microbalance.
6. A cathetometer with few movable parts should be used to measure length changes in polyethylene in order to determine the volume expansion caused by the sorption of gases in polyethylene.
7. The light bulb in the constant temperature bath should be left on at all times when measuring the length changes caused by the sorption of gases in polyethylene in order to maintain a constant temperature.

8. A Jerguson Pressure Cell with sight glass should be modified to fit onto the Cahn D110 electromicrobalance so that the weight and length measurements can be performed at the same time.

9. REFERENCES

Aggarwal, S. L. and Tilley, G. P., "Determination of Crystallinity in Polyethylene by X-ray Diffractometer", *Journal of Polymer Science*, **18**, 17-26 (1955).

Beret, S. E., Muhle, M. E. and Villamil, I. A., "Purging Criteria for LDPE Make Bins", *Chemical Engineering Progress*, **73(12)**, 44-49, (1977).

Beret, S. and Hager, S. L., "Ethylene Solubility and Diffusion in Low-Density Polyethylene and Ethylene Copolymers", *Journal of Applied Polymer Science*, **24**, 1787-1796 (1979).

Bu, N., Lynch, D. T. and Wanke, S. E., "Kinetics of Catalytic Gas-Phase Homopolymerization of Ethylene over $SiO_2/MgCl_2$ - Supported $TiCl_4$ Catalysts", *Polymer Reaction Engineering*, **3**, 1-22, (1995).

Bunn, C.W., "The Crystal Structure of Long-chain Normal Paraffin Hydrocarbons", *Transaction of the Faraday Society*, **35**, 482-491 (1939).

Butts, R. A., "Crystallinity of Polyethylene: Fitting X-Ray Diffraction Profiles", CH E 458 Project Report, Department of Chemical Engineering, University of Alberta, April 1994.

Castro, E. F., Gonzo, E. E. and Gottifredi, J. C., "Thermodynamics of the Absorption of Hydrocarbon Vapors in Polyethylene Films", *Journal of Membrane Science*, **31**, 235-248 (1987).

Castro, E. F., Gonzo, E. E. and Gottifredi, J. C., "The Analysis of Sorption Data of Organic Vapors in Polymeric Membranes Through Novel Theories", *Journal of Membrane Science*, **113**, 57-64 (1996).

Cullity, B. P., *Elements of X-ray Diffraction*, Second Edition, Addison-Wesley Publishing Company, Reading, Massachusetts, USA, 1978.

Daubert, T. E. and R. P. Danner, *Physical and Thermodynamic Properties of Pure Chemicals Data Compilation*, Hemisphere Publishing Corporation, New York, 1989.

Deas, T. M. Jr., Hofer, H. H. and Dole, M., "Solubility of Hydrogen in Polyethylene by a Semimicro Method", Macromolecules, 5, 223-226 (1972).

Doong, S.J. and Ho, W. S., "Sorption of Organic Vapors in Polyethylene", *Industrial and Engineering Chemistry Research*, **30**, 1351-1361 (1991).

Eby, R.K., "Diffusion in Polymer With Lamellar Morphology, Polyethylene", *Journal of Applied Physics*, **35** n9, 2720-2724 (1964).

Ghosal, K. and Freeman, B. D., "Gas Separation Using Polymer Membranes: An Overview", *Polymers for Advanced Technologies*, **5**, 673-697 (1993).

Hirose, T., Mizoguchi, K. and Kamiya, Y., " Dilation of Polyethylene by Sorption of Carbon Dioxide", *Journal of Polymer Science: Part B: Polymer Physics*, **24**, 2107-2115 (1986).

Kamiya, Y., Mizoguchi, K., Naito, Y. and Hirose, T., " Gas Sorption in Poly(vinyl benzoate)", *Journal of Polymer Science: Part B: Polymer Physics*, **24**, 535-547 (1986a).

Kamiya, Y., Hirose, T., Mizoguchi, K. and Naito, Y., " Gravimetric Study of High-Pressure Sorption of Gases in Polymers", *Journal of Polymer Science: Part B: Polymer Physics*, **24**, 1525-1539 (1986b).

Kamiya, Y., Hirose, T., Naito, Y. and Mizoguchi, K., " Sorptive Dilation of Polysulfone and Poly(ethylene terephthalate) Films by High-pressure Carbon Dioxide", *Journal of Polymer Science: Part B: Polymer Physics*, **26**, 159-177 (1988a).

Kamiya, Y., Hirose, T., Mizoguchi, K. and Terada, K., " Sorptive Dilation of Poly(vinyl benzoate) and Poly(vinyl butyral) by Carbon Dioxide", *Journal of Polymer Science: Part B: Polymer Physics*, **26**, 1409-1424 (1988b).

Kamiya, Y., Mizoguchi, K., Hirose, T. and Naito, Y., " Sorption and Dilation of Poly(ethyl methacrylate) - Carbon Dioxide System", *Journal of Polymer Science: Part B: Polymer Physics*, **27**, 879-892 (1989a).

Kamiya, Y., Naito, Y. and Mizoguchi, K., " Sorption and Partial Molar Volume of Gases in Polybutadiene", *Journal of Polymer Science: Part B: Polymer Physics*, **27**, 2243-2250 (1989b).

Kamiya, Y., Terada, K., Mizoguchi, K. and Naito, Y., " Sorption and Partial Molar Volume of Gases in Rubbery Polymers", *Macromolecules*, **25**, 4321-4324 (1992).

Kamiya, Y., Terada, K., Naito, Y. and Wang, J., " Sorption, Diffusion and Partial Molar Volume of C_4 Hydrocarbons in Rubbery Polymers", *Journal of Polymer Science: Part B: Polymer Physics*, **33**, 1663-1671 (1995).

Kaplan, W. A., *Modern Plastics Encyclopedia*, McGraw-Hill Companies Inc., Hightstown, New Jersey, Volume 73, Number 12, 1997.

Kubo, S. and Dole, M., "The solubility of Small Permanent Gases in Polyethylene as Related to Its Morphological Structure", *Macromolecules*, **7**,190-199 (1974).

Kulkarni, S. S. and Stern, S. A., "The Diffusion of CO_2, CH_4, C_2H_4 and C_3H_8 in Polyethylene at Elevated Pressures", *Journal of Polymer Science: Polymer Physics Edition*, **21**, 441-465 (1983).

Lee, J. G. and Flumerfelt, R. W., "Nitrogen Solubilities in Low Density Polyethylene at High Temperatures and High Pressures", *Journal of Applied Polymer Science*, **58**, 2213-2219 (1995).

Li, N. N. and Long, R. B., "Permeation through Plastic Films", *AIChE Journal*, **15** n1, 73-80 (1969).

Liu, C. P. A. and Neogi, P., "Sorption of Benzene and n-Hexane in Polyethylene", *Journal of Membrane Science*, **35**, 207-215 (1988).

Lowell, P. N. and McCrum, N. G., "The Solubility of Cyclopropane in Single Crystal Mats of Linear Polyethylene", *Journal of Polymer Science B Polymer Letters*, **5**, 1145-1151 (1967).

McFaddin, D.C., Russel, K.E., Wu, G. and Heyding, R. D., "Characterization of Polyethylene by X-ray Diffraction and ^{13}C-NMR: Temperature Studies and the Nature of the Amorphous Halo", *Journal of Polymer Science: Part B: Polymer Physics*, **31**, 175-183, (1993).

Michaels, A. S. and Parker Jr, R. B., "The Determination of Solubility Constants for Gases in Polymers", *Journal of Physical Chemistry*, **62**, 1604 (1958).

Michaels, A. S. and Parker Jr. R. B., *Journal of Polymer Science*, **41**, 53 (1959).

Michaels, A. S. and Bixler, H. J., "Solubility of Gases in Polyethylene", *Journal of Polymer Science*, **50**, 393-412 (1961).

Miura, K., Otake, K., Kurosawa, S., Sako, T., Sugeta, T., Nakane, T., Sato, M., Tsuji, T., Hiaki, T., Hongo, M., "Solubility and Adsorption of High Pressure Carbon Dioxide to Poly(Styrene)", *International Symposium on Molecular Thermodynamics and Molecular Simulation*, January, 371-377, (1997).

Naito, Y., Mizoguchi, K., Terada, K. and Kamiya, Y., "The Effect of Pressure on Gas Permeation through Semicrystalline Polymers above the Glass Transition Temperature", *Journal of Polymer Science: Part B: Polymer Physics*, **29**, 457-462, (1991).

Narh, K. A. and Keller, A., "Phase Transition in High Molecular Weight Polyethylene During Capillary Extrusion: The Reversibility of the Temperature Window", *Polymer*, **32**(14), 2512-2518 (1991).

Peng, D.-Y. and Robinson, D. B., " A New Two-Constant Equation of State", *Industrial and Engineering Chemistry Fundamentals*, **15**, 59-65, (1976).

Perry, R. H. and Chilton, C. H., *Chemical Engineers' Handbook Fifth Edition*, McGraw-Hill Book Company, New York, 1973, pp23-40.

Robeson, L. M. and Smith, T. G., "The Desorption of Ethane-Butane Mixtures from Polyethylene", *Journal of Applied Polymer Science*, **11**, 2007-2019 (1967).

Robeson, L. M. and Smith, T. G., "Permeation of Ethane-Butane Mixtures through Polyethylene", *Journal of Applied Polymer Science*, **12**, 2083-2095 (1968).

Rogers, C., Stannett, V. and Szwarc, M., "The Sorption, Diffusion and Permeation of Organic Vapors in Polyethylene", *Journal of Polymer Science*, **45**, 61-82 (1960).

Stern, S. A., Mullhaupt, J. T. and Gareis, P. J., "The Effect of Pressure on the Permeation of Gases and Vapors through Polyethylene. Usefulness of the Corresponding States", *AIChE Journal*, **15**(1), 64-73 (1969).

Stern, S. A., Fang, S. M. and Frisch, H. L., "Effect of Pressure on Gas Permeability Coefficients. A New Application of "Free Volume" Theory", *Journal of Polymer Science Part A-2*, **10**, 201-219 (1972).

Stern, S. A., Kulkarni, S. S. and Frisch, H. L., "Test of a "Free Volume" Model of Gas Permeation through Polymer Membranes. I. Pure CO_2, CH_4, C_2H_4 and C_3H_8 in Polyethylene", *Journal of Polymer Science Polymer Physics Edition*, **21**, 467-481 (1983a).

Stern, S. A., Mauze, G. R. and Frisch, H. L., "Test of a Free-Volume Model for the Permeation of Gas Mixtures through Polymer Membranes. CO_2-C_2H_4 CO_2-C_3H_8 and C_2H_4-C_3H_8 Mixtures in Polyethylene", *Journal of Polymer Science Polymer Physics Edition*, **21**, 1275-1298 (1983b).

Stern, S. A., Sampat, S. R. and Kulkarni, S. S., "Test of a "Free Volume" Model of Gas Permeation through Polymer Membranes. II. Pure Ar, SF_6, CF_4 and $C_2H_2F_2$ in Polyethylene", *Journal of Polymer Science: Part B: Polymer Physics*, **24**, 2149-2166 (1986).

Takeuchi, Y. and Okamura, H., "Permeation of Hydrocarbon Vapors through Polyethylene Films", *Journal of Chemical Engineering in Japan*, **9**, 136-139 (1976).

Vittoria, V., "Influence of the Crystallinity on the Transport Properties of Polyethylene", *Journal of Materials Science*, **30**, n15, 3954-3958, (1995).

Wang, J. S. and Kamiya, Y., "Concurrent Measurements of Sorption and Dilation Isotherms and Diffusivity for Polysulfone Membrane/Carbon Dioxide System", *Journal of Membrane Science*, **98**, 69-76 (1996).

Yoon, J. S., Yoo, H. S. and Kang, K. S., "Solubility α-Olefins in Linear Low Density Polyethylenes", *European Polymer Journal*, **32**, n11, 1333-1336 (1996).

APPENDIX A

LIST OF ALL POLYETHYLENE SAMPLES PRESSED

Table A.1 Listing of All Polyethylene Samples Pressed

Sample	Producer	Producer #	Type	Comonomer
MM001	AT Plastics	191	LDPE	-
MM002	AT Plastics	191	LDPE	-
MM003	AT Plastics	502	LDPE	-
MM003	AT Plastics	502	LDPE	-
MM004	AT Plastics	502	LDPE	-
MM005	-	GRSN 7047	-	-
MM006	-	GRSN 7047	-	-
MM007	AT Plastics	234R	LDPE	-
MM008	AT Plastics	234R	LDPE	-
MM009	AT Plastics	472	LDPE	-
MM010	AT Plastics	472	LDPE	-
MM011	AT Plastics	175	LDPE	-
MM012	AT Plastics	175	LDPE	-
MM013	Nova	HB-L357-A	HDPE	-
MM013	Nova	HB-L357-A	HDPE	-
MM014	Nova	HB-L357-A	HDPE	-
MM015	AT Plastics	209	LDPE	-
MM016	AT Plastics	209	LDPE	-
MM017	Nova	GF 0118A	LLDPE	-
MM018	Nova	GF 0118A	LLDPE	-
MM019	Exxon	SLP 9095	LLDPE	1-hexene
MM019	Exxon	SLP 9095	LLDPE	1-hexene
MM020	Exxon	SLP 9095	LLDPE	1-hexene
MM021	Exxon	SLP 9095	LLDPE	1-hexene
MM022	Nova	-	HDPE	-
MM023	U of A	SLY 8927	HDPE	-
MM024	U of A	SLY 8920	HDPE	-
MM025	U of A	SLY 8939B	HDPE	-
MM026	U of A	SLY 8938	HDPE	-
MM027	Nova	SCLAIR 13J7	LLDPE	1-octene
MM028	Nova	TF 0119	LLDPE	1-hexene
MM029	Nova	PF 0218	LLDPE	1-butene
MM030	Nova	PF 0118	LLDPE	1-butene
MM031	Nova	TD-9035-E	LLDPE	1-hexene
MM032	Nova	HB-W952-A	HDPE	-
MM033	Nova	-	HDPE	-

The Samples used in this study were samples MM003, MM013, MM019 and MM029.

APPENDIX B

CRYSTALLINITY CALCULATIONS AND SAMPLES

Crystallinity Calculation Details

1) The uncorrected areas under the intensity versus diffraction angle plot for each of the peaks was determined using the computer program Peak-fit.
   For example for Sample MM003:
   First amorphous peak area = 4754
   Second amorphous peak area = 3715
   110 crystallinity peak area = 4791
   200 crystallinity peak area = 1244
   210 crystallinity peak area = 60
   NOTE: the units of the area are not important as the crystallinity is calculated as a ratio of the areas.

2) The uncorrected crystallinity is calculated by Equation 4.1.3.1.

$$X_{uc} = \frac{A_{110} + A_{200} + A_{210}}{A_{110} + A_{200} + A_{210} + A_{A1} + A_{A2}} \tag{4.1.3.1}$$

   Where A_{110}, A_{200}, and A_{210}, is the area under the 110, 200 and 210 crystalline peaks, A_{A1}, and A_{A2} is the area under the first and second amorphous peaks and X_{uc} is the uncorrected crystallinity.
   Therefore Uncorrected Mass % crystallinity
   = (4791 + 1244 + 60)/(4791 +1244 + 60 + 4754 +3715) x 100 %
   = 6095/14564 x 100 %
   = 41.9 %

3) The center diffraction angle of each peak was found from the functions by Peak-fit.
   For Example for Sample MM003:
   First amorphous peak is centered at = 19.42°
   Second amorphous peak is centered at = 20.32°
   110 crystalline peak is centered at = 21.40°
   200 crystalline peak is centered = 23.69°
   210 crystalline peak is centered at = 29.82°

4) The intensity correction factors for each peak was calculated.

4.1 The Lorentz-Polarization intensity correction factor is calculated from Equation 4.1.2.1.

$$Lp = \frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta} \tag{4.1.2.1}$$

For example for Sample MM003 the center of the first amorphous peak is at 2θ = 19.42°.

$$\begin{aligned} Lp &= \{[1+\cos^2(19.42)]/[\sin^2(19.42/2)\cos(19.42/2)]\} \\ &= \{[1+0.88945]/[(0.02845)(0.98567)]\} \\ &= 67.38 \end{aligned}$$

4.2 The temperature intensity correction factor is calculated from Equation 4.1.2.2.

$$f_t = e^{-2B} \tag{4.1.2.2}$$

Where f_t is the temperature factor and Bunn (1939) calculated the B factor to be

$$B = \frac{5\sin^2\theta}{\lambda^2} \tag{4.1.2.2.1}$$

For example for Sample MM003 the center of the first amorphous peak is at 2θ = 19.42°

The wavelength of the x-ray used in this study was 1.54178 Å

$$\begin{aligned} B &= \{5\sin^2(0.19.42/2)/(1.54178^2)\} \\ &= 0.14223/2.3771 \\ &= 0.05983 \end{aligned}$$

$$\begin{aligned} f_t &= e^{-2 \times 0.05983} \\ &= 0.887 \end{aligned}$$

4.3 The atomic scattering intensity correction factor is a function of sinθ/λ, where λ is the wavelength of the x-ray in units of angstroms and θ is the diffraction angle divided by two. Values for this factor for polyethylene are obtained from the atomic scattering factor of Carbon in tables such as Appendix 12 of Cullity (1978)

For example for Sample MM003 the center of the first amorphous peak is at 2θ = 19.42°.

Therefore sinθ/λ = sin(9.71)/1.54178 = 0.1094

The atomic scattering from the chart in Appendix 12 of Cullity (1978) for Carbon (C) is 4.45. This value must be squared to obtain the atomic scattering correction factor as mentioned by Aggarwal and Tilley (1955).

Therefore, the atomic scattering correction factor is 19.80

5) The overall correction factor for each peak area was calculated using the overall 110-peak correction as a correction of 1.

The overall correction factor for the first amorphous peak is shown by Equation 4.1.3.2.

$$C_{A1} = \frac{Lp_{110}as_{110}f_{t110}}{Lp_{A1}as_{A1}f_{tA1}} \qquad (4.1.3.2)$$

Where C_{A1} is the overall correction factor for the first amorphous area. Lp_{110} is the Lorentz-Polarization correction factor for the 110 peak, as_{110} is the atomic scattering correction factor for the 110 peak, f_{t110} is the temperature correction factor for the 110 peak, Lp_{A1} is the Lorentz-Polarization correction factor for the first amorphous peak, as_{A1} is the atomic scattering correction factor for the first amorphous peak and f_{tA1} is the temperature correction factor for the first amorphous peak.

For example for Sample MM003
Lp_{110} =55.11, as_{110} = 18.26, f_{t110} = 0.865
Lp_{A1} = 67.39, as_{A1} = 19.80, f_{tA1} = 0.887
C_{A1} = (55.11 x 18.26 x 0.865)/(67.39 x 19.80 x 0.887)
= 0.74

6) The corrected crystallinity of the polyethylene was calculated by Equation 4.1.3.3.

$$X_c = \frac{A_{110}C_{110} + A_{200}C_{200} + A_{210}C_{210}}{A_{110}C_{110} + A_{200}C_{200} + A_{210}C_{210} + A_{A1}C_{A1} + A_{A2}C_{A2}} \qquad (4.1.3.3)$$

Where A_{110}, A_{200}, and A_{210}, is the uncorrected area under the 110, 200 and 210 crystalline peaks, respectively and A_{A1} and A_{A2} is the uncorrected area under the first and second amorphous peaks, respectively. C_{110}, C_{200}, and C_{210} are the overall correction factors to correct the 110, 200 and 210 crystalline areas and C_{A1}, and C_{A2} are the overall correction factors for the first and second amorphous areas

For example for Sample MM003
A_{110} = 4791; A_{200} = 1245; A_{210} = 60; A_{A1} = 4754; A_{A2} = 3715
C_{110} = 1.00; C_{200} = 1.41; C_{210} = 3.37; C_{A1} = 0.74; C_{A2} = 0.85
X_c = (4791x1.00 + 1245x1.41 + 60x3.37)/ (4791x1.00 + 1245x1.41 + 60x3.37 + 4754x0.74 + 3715x0.85) x 100 %
= 50.3%

Table B.1 Crystallinity of All Polyethylene Samples Pressed

Sample	No correction	Corrected	Sample	No correction	Corrected
MM001	34.2%	42.6%	MM016	36.1%	45.1%
MM002	34.2%	42.7%	MM017	40.0%	48.7%
MM003*	41.9%	50.4%	MM018	40.0%	48.7%
MM003**	42.1%	50.5%	MM019*	13.2%	18.5%
MM003e	44.8%	51.7%	MM019**	13.4%	18.8%
MM003b	46.0%	52.9%	MM020	12.9%	18.3%
MM003h	48.6%	55.8%	MM021	12.8%	17.9%
MM004	41.5%	50.1%	MM022	63.7%	70.6%
MM005	38.6%	47.5%	MM023	47.9%	56.9%
MM006	38.7%	47.6%	MM024	40.8%	49.5%
MM007	40.5%	49.0%	MM025	37.9%	46.5%
MM008	40.4%	48.7%	MM026	51.4%	60.1%
MM009	35.4%	44.2%	MM027	47.3%	55.4%
MM010	34.9%	43.8%	MM028	39.3%	48.6%
MM011	43.4%	51.6%	MM029*	37.7%	47.0%
MM012	42.7%	51.2%	MM029e	40.9%	48.5%
MM013*	63.2%	70.2%	MM029b	42.2%	50.0%
MM013**	64.0%	71.5%	MM029h	41.2%	48.7%
MM013e	65.0%	70.9%	MM030	37.9%	47.2%
MM013b	66.2%	71.8%	MM031	38.7%	48.4%
MM013h	65.6%	71.3%	MM032	62.9%	70.2%
MM014	62.9%	70.2%	MM033***	70.8%	75.9%
MM015	35.5%	44.5%			

* sample used in the solubility study

** x - ray diffraction performed perpendicular to the normal

*** This is the same as Sample MM022 except it was held at 140°C for 10 hours and then cooled at a rate of 1.5°C per hour from 140°C to 22°C

MM003e, MM013e and MM029e are samples, which have gone through the entire dilation measurement with ethylene

MM003b, MM013b and MM029b are samples, which have gone through the entire dilation measurement with gaseous 1-butene

MM003h, MM029h and MM029h are samples, which have gone through the entire dilation measurement with gaseous 1-hexene

APPENDIX C

DENSITY SAMPLE CALCULATIONS

Density Calculation Details

The density of the polyethylene was calculated using Equation 4.2.1.

$$\rho_s = \rho_f \frac{W_a}{W_a - W_s} \qquad (4.2.1)$$

Where ρ_s is the density of the polyethylene. W_a, is the weight of the polyethylene in air and W_s is the weight of the polyethylene when it was submerged in an oil with a density, ρ_f, of 0.9612 g/cm^3 at 25°C.

For example for Sample MM029.

W_a, = 0.5000 g.
Weight of paper clip in air = 0.2000 g.
Weight of wire in air = 0.0200 g.
Combined weight of sample + paper clip + wire on Mettler scale = 0.7209 g.
Combined weight on Ohaus scale in air (scale used to weigh in oil) = 0.732 g.
The correction factor was determined by 0.7209/0.732 = 0.9848.

Combined weight in oil = 0.174 g.

The corrected combined weight in oil was calculated by 0.174x0.9848 = 0.1714 g.

The weight of the paper clip immersed in the oil was determined as follows:

Density of paper clip = 7.8362 g/cm^3.
Weight of paper clip in air = 0.2000 g.
Therefore from Equation 4.2.1,
$7.8362 = 0.9612[0.2/(0.2000-W_s)]$
$8.1525 = [0.2/(0.2000-W_s)]$
$1.6305 - 8.1525\ W_s = 0.2$
$8.1525\ W_s = 1.4305$
weight of paper clip in oil = W_s = 0.17547 g.

The weight of the wire in the air and weight of paper clip immersed in oil was subtracted from the corrected combined weight in oil.
= 0.17137 – 0.0200 – 0.17547 = -0.0241 g.
This is the weight of the polyethylene sample in oil.

The density of polyethylene was then calculated from Equation 4.2.1.

$$\begin{aligned}\rho_s &= 0.9612[0.5000/(0.5000-(-0.0241))] \\ &= 0.9612[0.5000/0.5241] \\ &= 0.917\ \text{g/cm}^3\end{aligned}$$

APPENDIX D

SOLUBILITY SAMPLE CALCULATIONS

Solubility Calculation Details

1) The initial volume of the polyethylene sample was calculated.

   The Sample used here is MM029.
   The density of MM029 is 0.917 g/cm^3.
   The weight of the sample used in the weight measurement experiment at 25°C is 0.40741 g.
   Therefore the initial volume of the sample used in the weight measurement experiment is:

   $$0.40741/0.917 = 0.444 \text{ cm}^3.$$

2) The expanded volume of the polyethylene at the temperature and pressure of the weight measurement was calculated.

   The temperature of the weight measurement was 30°C.
   The base temperature, t_b was 25°C (this is the temperature at the initial weight).
   The pressure of the weight measurement was 776 kPa absolute.
   The thermal expansion coefficient, $\alpha_{t,0}^{Po}$ for the polyethylene sample was obtained as described in Section 6.1.3 and was 2.01×10^{-4}.
   The pressure expansion coefficient, $\beta_{t,p}^{Po}$ for the Sample MM029 at 30°C was determined from the equation to calculate the pressure expansion coefficient as described in Section 6.1.4:

   $$\begin{aligned}\beta_P^{Po} &= 3.05 \times 10^{-6} \times \text{pressure of weight measurement}\\ &= 3.05 \times 10^{-6} \times 776\\ &= 2.37 \times 10^{-3}.\end{aligned}$$

   The equation to calculate the expanded volume of the polyethylene is Equation 5.3.3.

   $$V_{T.P}^{Po} = V_{T_b}^{Po}\left(1 + 3\alpha_T^{Po}(T - T_b)\right)\left(1 + 3\beta_P^{Po}\right) \qquad (5.3.3)$$

   Substituting in the values given above gives:

   $$\begin{aligned}\text{Volume Polyethylene}_{30.776} &= 0.444\{[1+3(2.01 \times 10^{-4})(30-25)](1+3(2.37 \times 10^{-3})\}\\ &= 0.444\{[1 + 0.00302](1+0.00711)\}\\ &= 0.4485 \text{ cm}^3.\end{aligned}$$

3) The density of the gas at the pressure and temperature of the experiment was calculated.

This was accomplished using the Peng-Robinson (1976) equation of state and an Excel spreadsheet. The Peng-Robinson (1976) equation of state is

$$P = \frac{RT}{v_S - b} - \frac{a(T)}{v_S(v_S + b) + b(v_S - b)}$$

where $a(T) = 0.45724[(R^2T_c^2)/P_c]\alpha(T)$

$b = 0.07780(RT_c/P_c)$

$\sqrt{\alpha} = 1 + k[1-\sqrt{(T/T_c)}]$

$k = 0.37464 + 1.54226\omega - 0.26992\omega^2$

R = universal gas constant (kPa*m^3/kmol*K)

P = pressure of the weight measurement (kPa)

T = temperature of the weight measurement (K)

v_s = specific volume of the gas used in the weight measurement (m^3/kmol)

Note that $1/v_s$ gives the density of the gas (kmol/m^3)

T_c = critical temperature of the gas used in the weight measurement (K)

P_c = critical pressure of the gas used in the weight measurement (kPa)

ω = acentric factor of the gas used in the weight measurement

The values of T_c, P_c, ω for the gases used in this experiment were obtained from the Physical and Thermodynamic Properties of Pure Chemicals edited by Daubert et al. (1989).

For ethylene the constants used in "a" and "b" were changed from 0.45724 and 0.7780 to 0.408 and 0.070 as reported by Bu et al. (1995). The specific volumes of ethylene predicted with the modified constants were within 0.1% of the tabulated values in the IUPAC ethylene tables for all the experimental temperatures and pressures.

The solver function in Microsoft Excel was used to iteratively solve for the specific volume in the Peng-Robinson (1976) equation. The specific volume was estimated and then the pressure was calculated. This pressure was compared with the actual pressure of the weight measurement entered into the spreadsheet. The iterative process was continued until the actual pressure of the measurement minus the calculated pressure squared was close to zero.

The density calculated by the Peng-Robinson (1976) equation is in units of kmol/m^3 this is converted to kg/ m^3 by using the molecular weight of the gas.

For example at a temperature of 30°C and a pressure of 776 kPa absolute the density of ethylene is calculated to be 0.009028 g/cm^3

4) The buoyancy force exerted on the expanded polyethylene was calculated.

The buoyancy force exerted on the polyethylene is equal to the density of the gas times the expanded volume of the polyethylene.
In this example:
buoyancy force = 0.009028 x 0.4485 = 0.004051 g.

4) The weight of the gas sorbed into the polyethylene sample at equilibrium was determined from the computer file recorded by the Cahn microbalance.

5) The corrected weight of the ethylene gas sorbed in the polyethylene sample at equilibrium was calculated.

Corrected polyethylene plus sorbed gas weight = weight recorded with the microbalance – the background buoyancy weight + the expanded polyethylene buoyancy weight. The background buoyancy weights were determined by performing weight measurement runs without a polyethylene sample in the microbalance. These are recorded in Section 6.2.5
In this example:
Corrected polyethylene plus sorbed gas weight = - 0.00254 – 0.00014 + 0.004051
= 0.00137 g.

6) The solubility of the ethylene in the polyethylene sample was calculated.

Solubility = weight of ethylene sorbed / initial weight of the polyethylene.
In this example the solubility = 0.00137/0.40741
= 0.003363 g of ethylene/g of polyethylene at a temperature of 30°C and a pressure of 776 kPa.

APPENDIX E

COMPLETE LENGTH MEASUREMENT RESULTS

The following tables show the results of the length measurement. The increase was calculated according to equation E.1

$$In = \frac{L - L_0}{L_0} \tag{E.1}$$

Where In is the length increase of the polyethylene sample, L is the length of the polyethylene at pressure, P and L_0 is the initial length of the polyethylene after the pressure cell had been evacuated.

Table E.1 Length Measurement Results for Sample MM003

Gas	Temperature (°C)	Absolute Pressure(kPa)	Length (mm)	Standard Deviation	Increase
ethylene	30.40	0	57.01	0.12	0.0000
ethylene	30.40	796	57.16	0.12	0.0027
ethylene	30.40	2141	57.42	0.13	0.0073
ethylene	30.40	3520	57.63	0.10	0.0108
ethylene	49.94	0	57.02	0.06	0.0000
ethylene	49.94	790	57.26	0.07	0.0042
ethylene	49.94	2172	57.49	0.08	0.0082
ethylene	49.94	3540	57.72	0.02	0.0122
ethylene	69.62	0	57.42	0.04	0.0000
ethylene	69.62	789	57.48	0.06	0.0010
ethylene	69.62	2175	57.73	0.08	0.0053
ethylene	69.62	3537	57.95	0.07	0.0092
ethylene	89.95	0	57.61	0.11	0.0000
ethylene	89.95	789	57.78	0.08	0.0030
ethylene	89.95	2151	58.04	0.09	0.0074
ethylene	89.95	3523	58.36	0.06	0.0130
1-butene	33.10	0	57.18	0.02	0.0000
1-butene	33.10	160	57.91	0.02	0.0128
1-butene	33.10	262	58.50	0.02	0.0231
1-butene	33.10	367	60.12	0.02	0.0382
1-butene	49.94	0	57.23	0.02	0.0000
1-butene	49.94	256	58.19	0.02	0.0168
1-butene	49.94	449	59.36	0.02	0.0372
1-butene	49.94	585	61.42	0.02	0.0732
1-butene	70.02	0	57.35	0.02	0.0000
1-butene	70.02	263	58.04	0.02	0.0120
1-butene	70.02	668	59.88	0.02	0.0441
1-butene	70.02	946	64.15	0.02	0.1186
1-butene	90.00	0	57.19	0.02	0.0000
1-butene	90.00	524	58.55	0.02	0.0238
1-butene	90.00	976	60.21	0.02	0.0528
1-butene	90.00	1441	71.95	0.02	0.2581
1-hexene	70.00	0	57.28	0.02	0.0000
1-hexene	70.00	79	59.25	0.02	0.0344
1-hexene	70.00	131	64.86	0.02	0.1323
1-hexene	89.96	0	57.30	0.02	0.0000
1-hexene	89.96	78	58.58	0.02	0.0223
1-hexene	89.96	161	61.90	0.02	0.0803
1-hexene	89.96	216	78.80	0.02	0.3452

Table E.2 Length Measurement Results for Sample MM013

Gas	Temperature (^oC)	Absolute Pressure(kPa)	Length (mm)	Standard Deviation	Increase
ethylene	32.33	0	58.35	0.02	0.0000
ethylene	32.33	786	58.35	0.02	0.0001
ethylene	32.33	2182	58.50	0.02	0.0026
ethylene	32.33	3551	58.62	0.04	0.0047
ethylene	50.00	0	58.30	0.10	0.0000
ethylene	50.00	796	58.40	0.10	0.0017
ethylene	50.00	2172	58.50	0.10	0.0034
ethylene	50.00	3530	58.60	0.10	0.0051
ethylene	70.06	0	58.39	0.10	0.0000
ethylene	70.06	794	58.45	0.10	0.0011
ethylene	70.06	2167	58.55	0.10	0.0028
ethylene	70.06	3532	58.65	0.10	0.0045
ethylene	88.62	0	58.35	0.10	0.0000
ethylene	88.62	803	58.43	0.10	0.0013
ethylene	88.62	2182	58.53	0.10	0.0030
ethylene	88.62	3560	58.59	0.10	0.0041
1-butene	31.47	0	58.99	0.02	0.0000
1-butene	31.47	127	59.22	0.02	0.0039
1-butene	31.47	251	59.62	0.02	0.0107
1-butene	31.47	368	60.19	0.02	0.0164
1-butene	49.96	0	59.03	0.02	0.0000
1-butene	49.96	249	59.41	0.02	0.0064
1-butene	49.96	439	59.86	0.02	0.0141
1-butene	49.96	586	60.44	0.02	0.0239
1-butene	69.95	0	59.09	0.02	0.0000
1-butene	69.95	332	59.41	0.02	0.0054
1-butene	69.95	635	59.91	0.02	0.0139
1-butene	69.95	945	60.78	0.02	0.0286
1-butene	89.90	0	59.06	0.02	0.0000
1-butene	89.90	541	59.50	0.02	0.0075
1-butene	89.90	988	60.25	0.02	0.0201
1-butene	89.90	1436	61.40	0.02	0.0396
1-hexene	70.01	0	58.89	0.02	0.0000
1-hexene	70.01	72	60.57	0.02	0.0285
1-hexene	70.01	132	61.63	0.02	0.0465
1-hexene	89.98	0	59.92	0.02	0.0000
1-hexene	89.98	93	60.49	0.02	0.0095
1-hexene	89.98	155	61.12	0.02	0.0200
1-hexene	89.98	225	62.45	0.02	0.0324

Table E.3 Length Measurement Results for Sample MM019

Gas	Temperature (°C)	Absolute Pressure(kPa)	Length (mm)	Standard Deviation	Increase
ethylene	31.84	0	56.96	0.02	0.0000
ethylene	31.84	800	57.24	0.02	0.0049
ethylene	31.84	2162	57.68	0.02	0.0126
ethylene	31.84	3535	58.20	0.04	0.0218
ethylene	49.99	0	57.18	0.10	0.0000
ethylene	49.99	811	57.47	0.10	0.0051
ethylene	49.99	2190	57.84	0.10	0.0115
ethylene	49.99	3556	58.37	0.10	0.0208
ethylene	69.95	0	57.53	0.10	0.0000
ethylene	69.95	790	57.73	0.10	0.0035
ethylene	69.95	2186	58.18	0.10	0.0113
ethylene	69.95	3551	58.66	0.10	0.0196
1-butene	32.15	0	57.49	0.02	0.0000
1-butene	32.15	178	59.22	0.02	0.0301
1-butene	32.15	259	60.77	0.02	0.0571
1-butene	32.15	357	68.16	0.02	0.1510
1-butene	50.08	0	57.64	0.02	0.0000
1-butene	50.08	252	59.60	0.02	0.0340
1-butene	50.08	452	62.95	0.02	0.0921
1-butene	50.08	586	76.11	0.02	0.3204
1-butene	70.05	0	57.83	0.02	0.0000
1-butene	70.05	384	59.70	0.02	0.0323
1-butene	70.05	715	63.50	0.02	0.0980

There are no results for the sorption of 1-hexene in Sample MM019 because the vapor pressure of 1-hexene is below atmospheric pressure below 70°C and Sample MM019 was close to its melt temperature above 70°C.

Table E.4 Length Measurement Results for Sample MM029

Gas	Temperature (°C)	Absolute Pressure(kPa)	Length (mm)	Standard Deviation	Increase
ethylene	32.64	0	57.30	0.02	0.0000
ethylene	32.64	796	57.38	0.02	0.0014
ethylene	32.64	2186	57.62	0.02	0.0056
ethylene	32.64	3568	57.89	0.04	0.0103
ethylene	49.84	0	57.15	0.02	0.0000
ethylene	49.84	789	57.26	0.02	0.0019
ethylene	49.84	2187	57.51	0.02	0.0063
ethylene	49.84	3563	57.77	0.02	0.0108
ethylene	70.19	0	57.29	0.02	0.0000
ethylene	70.19	781	57.37	0.02	0.0014
ethylene	70.19	2169	57.60	0.02	0.0054
ethylene	70.19	3540	57.84	0.02	0.0096
ethylene	89.59	0	57.46	0.02	0.0000
ethylene	89.59	803	57.54	0.02	0.0014
ethylene	89.59	2182	57.78	0.02	0.0056
ethylene	89.59	3562	58.01	0.02	0.0096
1-butene	32.73	0	57.34	0.02	0.0000
1-butene	32.73	126	58.03	0.02	0.0120
1-butene	32.73	371	61.04	0.02	0.0645
1-butene	50.03	0	57.59	0.02	0.0000
1-butene	50.03	196	58.31	0.02	0.0125
1-butene	50.03	402	59.59	0.02	0.0347
1-butene	50.03	589	62.53	0.02	0.0858
1-butene	69.95	0	57.90	0.02	0.0000
1-butene	69.95	266	58.66	0.02	0.0131
1-butene	69.95	638	60.38	0.02	0.0428
1-butene	69.95	948	65.15	0.02	0.1252
1-butene	89.59	0	57.92	0.02	0.0000
1-butene	89.59	472	59.15	0.02	0.0212
1-butene	89.59	983	61.47	0.02	0.0613
1-butene	89.59	1446	67.37	0.02	0.1632
1-hexene	70.09	0	59.09	0.02	0.0000
1-hexene	70.09	79	61.33	0.02	0.0379
1-hexene	70.09	140	67.72	0.02	0.1460
1-hexene	89.92	0	59.07	0.02	0.0000
1-hexene	89.92	93	60.75	0.02	0.0284
1-hexene	89.92	161	63.35	0.02	0.0725
1-hexene	89.92	225	71.99	0.02	0.1850

Table E.5 Second Length Measurement Results for Sample MM029

Gas	Temperature (°C)	Absolute Pressure(kPa)	Length (mm)	Standard Deviation	Increase
ethylene	32.39	0	56.42	0.02	0.0000
ethylene	32.39	796	56.55	0.02	0.0024
ethylene	32.39	2170	56.80	0.02	0.0068
ethylene	32.39	3540	57.10	0.04	0.0121
ethylene	50.74	0	56.63	0.02	0.0000
ethylene	50.74	797	56.75	0.02	0.0021
ethylene	50.74	2183	57.04	0.02	0.0072
ethylene	50.74	3562	57.30	0.02	0.0118
ethylene	70.96	0	56.96	0.02	0.0000
ethylene	70.96	787	57.04	0.02	0.0015
ethylene	70.96	2178	57.31	0.02	0.0062
ethylene	70.96	3547	57.58	0.02	0.0110
ethylene	90.01	0	57.34	0.02	0.0000
ethylene	90.01	796	57.38	0.02	0.0008
ethylene	90.01	2170	57.67	0.02	0.0058
ethylene	90.01	3540	57.91	0.02	0.0100

This measurement was performed to determine the repeatability of the length measurement.