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The Effects of Supercritical Fluids on Amorphous Polymers

by

Mark L. O'Neill

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfilment of the
requirements for the degree of

Doctor of Philosophy

Department of Chemistry

**Carleton University
Ottawa, Ontario
December, 1994**

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the Doctor of Philosophy degree

Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University,

December 1994

ABSTRACT

The changes in the glassy state of amorphous polymers due to the sorption of pressurized gases were studied, and used to delineate the dominant effects governing the extraction of monomers and low molecular weight oligomers from polystyrene.

A Tian-Calvet type heat flow calorimeter was modified to take measurements at high pressures. The apparatus was used to quantify the effects of carbon dioxide, ethylene, and methane on the glass transition temperature of polystyrene and poly(methyl methacrylate). Both carbon dioxide and ethylene were found to be strong plasticizers of polystyrene. Carbon dioxide proved to be an even better plasticizer of poly(methyl methacrylate), while ethylene was equally efficient for both. Both polymers were plasticized to a liquid state at ambient temperatures with pressures below 100 atm of carbon dioxide and ethylene. Methane was only a weak plasticizer for both polymers. It was shown that changes in the glass transition temperature of the polymer-gas mixture depends only on the concentration of the gas, and is not directly affected by polymer-gas interactions.

The solubilities of carbon dioxide, ethylene, and methane in both polystyrene and poly(methyl methacrylate) were determined from pressure decay measurements. The trends in solubility with pressure were identical to the

trends in the glass transition temperature with pressure. The changes in the glass transition temperature with pressure are thus a reflection of the relationship between the solubility of the gas in the polymer and pressure. The rate of sorption of these gases was found to be a strong function of temperature and gas concentration even in the glassy state of the polymer-gas mixture.

Extractions of styrene from polystyrene were performed using carbon dioxide and ethylene. The effects on the rate of extraction were tested using two separate sets of temperature and pressure conditions, and using static conditioning. Extractions using carbon dioxide were found to be limited by the thermodynamics of partitioning of styrene from polystyrene into supercritical carbon dioxide. This was a result of the strong interactions between styrene and polystyrene, and the weak interactions between carbon dioxide and styrene. Ethylene was found to be a better extractant than carbon dioxide due to its superior ability to plasticize the polymer matrix at these conditions, and due to a higher affinity of styrene for ethylene over that for carbon dioxide as reflected by the values of the partition coefficients for styrene. Extractions using ethylene were found to be limited mostly by kinetic factors, ie. the rate of desorption of styrene from the polymer surface, and the rate of styrene diffusion through the polymer matrix.

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Publications and Presentations

The publications that have resulted from this work to date are the following:

Y.P. Handa, M.L. O'Neill, "Plasticization of Polystyrene by High Pressure Gas: A Calorimetric Study", STP 1249, American Society for Testing Materials (ASTM) Symposium Series on Assignment of the Glass Transition, March 1993, Atlanta, Ga., pg 165

Y.P. Handa, S. Capowski, M. O'Neill, "Compressed Gas Induced Crystallization of Polymers", Thermochemica Acta, 226, 1993, pg 177

Y.P. Handa, S. Lampron, M.L. O'Neill, "On the Plasticization of Poly(2,6-dimethyl phenylene oxide) by CO₂", Journal of Polymer Science; Part B; Polymer Physics, 32, 1994, pg 2549

There were also several presentations given based on this work:

M. O'Neill, Y.P. Handa, "Gas Plasticization of Polymers", poster presentation at the 22nd annual North American Thermal Analysis Society Symposium, Sept. 19-22, 1993, Denver, Co.

P. Handa, M. O'Neill, "A High-Pressure Calorimetric Study of the Plasticization of Polymers by Supercritical Fluids", oral presentation at the Calorimetry Conference, July 1993, Durham, NC

M. O'Neill, Y.P. Handa, "An Examination of the Plasticization Effect of Gases on Polymers by High Pressure Calorimetry", oral presentation at the 76th Canadian Society for Chemistry Conference and Exhibition, May 30-June 3, 1993, Sherbrooke, Que.

M. O'Neill, Y.P. Handa, "High Pressure Calorimetry as a Tool for Measuring Gas Pressure Effects on the Glass Transition in Amorphous Polymers", oral presentation at the 4th annual Canadian Thermal Analysis Society Technical Meeting and Exhibition, May 18, 1993, Toronto, Ont.

M.L. O'Neill, Y.P. Handa, "Plasticization of Polystyrene by High Pressure Gas: A Calorimetric Study", oral presentation at the American Society for Testing Materials (ASTM) Symposium on Assignment of the Glass Transition, March 4-5, 1993, Atlanta, Ga.

P. Kruus, M.L. O'Neill, K. Pritchard, Y.P. Handa, "The Effects of High Pressure Gases on Amorphous Polymers", poster presentation at the Third International Symposium on Supercritical Fluids", Strasbourg, France, Oct. 1994

Some future papers to be submitted will likely be the following:

- The Quantitative Extraction of Styrene from Polystyrene using Supercritical CO₂ and C₂H₄.
- Gas Solubility and the Glass Transition Temperature.

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1.0 INTRODUCTION

1.1 Importance of this Work

Recently a number of applications have been developed in which polymers come in contact with high pressure gases or supercritical fluids (SFs). Polymers are now used as gas separation membranes; they can be modified through extraction or impregnation by SF solutions; and polymer morphology can sometimes be deliberately changed by high pressure gases.

There is in general a lack of information on, and understanding of the ways in which polymeric and gas phases interact, and the changes that occur in the polymer when it is exposed to high pressure gases. As a result, these newly developed techniques based on polymer-compressed gas combinations have not found widespread use. The purpose of the present study is to gain some insight into the effects that high pressure gases have on the polymer matrix, and the ramifications that this may have for various polymer-gas applications, especially in the area of supercritical fluid extractions.

1.2 Background on Polymers

Polymers can be characterized in a variety of ways. Polymers in the solid phase can be either amorphous or semi-crystalline. Amorphous polymers contain no long range order. For amorphous solids, the transition from a solid to

a liquid state occurs at the glass transition temperature (T_g). The physics of this transition will be expanded upon in Chapter 2. Polymers that can crystallize are termed semi-crystalline, since in general polymer's cannot achieve complete crystalline. Semi-crystalline polymers thus contain both a glass transition and a melting point (T_m). Frequently, semi-crystalline polymers are called rubbers at temperatures where $T_g < T < T_m$. In this temperature range, semi-crystalline polymers generally still maintain some structural integrity on a macroscopic scale. It is, however, the glass transition temperature that physically represents the upper temperature limitation to a polymer's mechanical integrity.

From a chemical point of view, polymers are split into two different groups: those which contain only carbon atoms along the polymer backbone, and those which contain non-carbon atoms along the backbone. Polymer's also contain functionalities attached to the backbone, frequently called "side-groups". The chemical structure of a polymer dramatically affects the polymer's physical character. Changes in the stereochemical structure of the monomeric units along a polymer chain (aka. tacticity), and the degree of polymer chain cross-linking, can also have a significant effect on a polymer's microscopic and macroscopic properties.

Polymers are also defined by their molecular weight.

Unlike most compounds, many polymers inherently possess a distribution of molecular weights defined by a polydispersity index. This parameter is a measure of the ratios of the weight average molecular weight (M_w) to the number average molecular weight (M_n). The mechanical properties of a polymer are molecular weight dependant and are usually governed by M_w . The physical character of a polymer is thus defined by its composition, molecular weight, molecular weight dispersity, tacticity, percent crystallinity, and thermal transition temperatures. Based on the aforementioned physical and chemical traits of a polymer, a specific polymer will be chosen for use in applications to which it is best suited. A number of different ways of blending various polymers to obtain specific polymer properties may also be used, but a discussion of this is well outside the scope of this thesis.

In almost every cases, polymers require some type of alteration, either chemical (eg. additives) and/or physical (eg. foaming), to optimize their properties for a specific task. This includes adding chemicals to prevent thermal or light induced degradation of the matrix, anti-oxidants to inhibit degradation by oxidizing agents, lubricating or plasticizing agents to make the polymer more flexible, colourants, etc... In most cases, there are also chemicals left in the matrix after processing, including solvents, unreacted monomers, and the like. Clearly then it is of

foremost importance to understand how polymers interact with other chemicals.

1.3 Background on Supercritical Fluids

Compounds become supercritical fluids (SFs) when they are at a temperature and pressure exceeding their critical values (Figure 1.1). SFs have physical and chemical character which varies with temperature and pressure, ranging from those of liquids to those of gases. The solvating power of the fluid increases with an increase in its density (ρ). Therefore, changes in the system temperature and pressure allow for easy modification of the solvent strength. As is seen in Table 1.1, some of the more common SF solvents are gases at ambient temperature and pressure.

In the supercritical state, a compound is neither a liquid, though it has a density approaching that of its liquid state, nor a gas, though the transport properties are similar to its gaseous state. Because SFs have density and transport coefficients intermediate between those of liquids and gases, they can easily diffuse into the surfaces of solid matrices, and even penetrate into polymer matrices, while maintaining solvent powers close to those of liquid solvents. As well, since the fluid has only a single phase, there are no surface tension effects, and complete "wetting" of solid surfaces is possible¹.

Figure 1.1 Typical pressure-temperature phase diagram for a pure component where TP is the triple point, CP is the critical point, T_c and p_c are the critical temperature and pressure.

Table 1.1 Critical parameters for some common compounds.

Formula	Name	T_c (°C)	p_c (atm)	ρ_c (g/mL)
CO ₂	carbon dioxide	31.0	74.7	0.47
N ₂ O	nitrous oxide	36.5	73.5	0.46
CHClF ₂	Freon 22	96.1	50.4	0.24
SF ₆	sulphur hexa -fluoride	45.6	38.7	0.69
N ₂	nitrogen	-146.9	34.9	0.30
CH ₄	methane	-82.3	47.7	0.16
C ₂ H ₆	ethane	32.2	49.5	0.19
C ₂ H ₄	ethylene	9.9	51.2	0.22
C ₃ H ₈	propane	96.8	43.3	0.20
C ₃ H ₆	propylene	91.9	46.0	0.24
H ₂ O	water	374.2	223.9	0.24
CH ₃ OH	methanol	239.4	81.2	0.20
C ₆ H ₁₄	hexane	234.5	30.7	0.20

1.4 Supercritical Fluids in Polymer Processing

The field of polymer processing promises to hold some of the more important applications of SFs^{2,3}, and is subject to a great deal of current research⁴. Exploitation of the variable solvent power of SFs can allow for the replacement of organic solvents in polymerizations, polymer fractionation, modification of polymer morphology, and extraction/impregnation of polymer matrices to purify/modify the sample⁵.

There are also a number of deleterious effects that a SF may have on a polymer's physical character. Crazing, hazing, and crystallization represent a few of the physical changes that may be induced in a polymer due to interactions with SFs. As well, foaming, blistering, and fracturing of the polymer may be seen upon depressurization due to gas nucleation within the polymer matrix.

The production of microcellular foams is one of many ways in which a polymer's physical character may be tailored for a specific use. It was found in the initial stages of this study that SFs can be very efficient foaming agents. A review of a qualitative study performed on the foaming of polymers by SFs is given in Appendix I.

1.5 Extractions from Polymers using Supercritical Fluids

New plastics have been developed for packaging of foods and containment/transportation of materials for human

consumption (eg. pipe material for water). These plastics represent a potential new source of contamination due to the migration of chemical residues and additives into food and water^{6,7}. The increased awareness of our natural environment also dictates that attempts should be made to recycle plastics. There is an obvious need then to be able to quantify the residual chemicals present in polymers.

The extraction of polymers with SFs is undergoing intense research⁸⁻¹⁵. Residues (reaction solvents, monomers, low molecular weight oligomer, reaction side products, catalysts, initiators, inhibitors), additives (UV stabilizers, heat stabilizers, anti-oxidants, lubricants, colourants, surfactants) and chemicals that may have migrated from the contained substance, represent the gamut of compounds that may be present in a polymer. Their presence can also affect the nature and feasibility of reusing, recycling and reprocessing of plastics¹⁶.

1.6 Scope of this Study

Unlike most solids, polymers have a large amount of unoccupied volume in their bulk matrix. Exposure of polymers to high pressures can result in a compression or densification of the polymer matrix, known as the hydrostatic pressure effect. Gases under pressure can have significant solubility in the polymer, and can swell the matrix. The magnitude of the effects on the polymer matrix

when in contact with a pressurized gas will depend on the relative roles each of these competing processes plays. For most polymers, the hydrostatic pressure effect on the matrix is relatively small. Only at high pressures will its effect on the matrix be significant (ie. $p > 50$ atm).

The sorption of gases at high pressures leads to swelling of the polymer matrix and a reduction in the intermolecular interactions between polymer chains. The result is an increase in the enthalpy of the mixture, and a concomitant decrease in the glass transition temperature from that of the pure polymer. Gases which are significantly soluble in the polymer may reduce the T_g by 60°C or more at relatively moderate pressures (eg. < 100 atm for CO_2 ¹⁷⁻²⁰). Such a reduction in the T_g is referred to as plasticization of the polymer. A detailed review of the change in the glass transition temperature induced by sorbed chemicals and some of the theories used to describe it will be presented in Chapter 2. Thus, one of the goals of this thesis will be to quantify the effects of gas pressure on the glass transition temperature.

Solubility isotherms of gases in glassy polymers show a concave curvature over extended pressure ranges. Linearity of sorption isotherms at high pressures is frequently seen. If the gas solubility is sufficient to plasticize the polymer to a liquid state, the isotherm will then show a convex curvature as pressure increases. The inflection

point of this profile reflects the onset of the transition from a glass to a liquid state, and may be referred to as a transition pressure or concentration. It is another goal of this thesis to study the effects of temperature and pressure on the solubility of gases in glassy polymers.

Upon plasticization of a polymer, the diffusion rates for species dissolved in the matrix rise dramatically²¹. Quantification of the diffusion rates of these gases within the matrix as a function of solubility will be another goal of this thesis.

In general, the efficiency of an extraction, including SF extractions, is governed by the partition coefficient of the solute between solvent and the solid matrix¹. For extractions from polymers, the compounds of interest are contained within the matrix. Thus the rate of diffusion of these chemicals through the polymer will affect, and possibly even limit, the rate of extraction^{8,10,13}. The final goal of this thesis will be to study the limiting factors affecting the physical process of extractions from polymers using SFs.

1.7 Purpose and Plan of Research

The possible applications involving high pressure gases in polymer science and technology are numerous. As stated above, there appears to be a deficiency in the information on and understanding of the ways in which these two vastly

different phases interact. The impetus for this study was to gain some insight into the processes at work when gases come into contact with polymers so that a clearer picture might be obtained.

There is a plethora of theories for the analysis of the effects of penetrants on the physical properties of the polymer. Those chosen from the literature represent some of the more popular and novel theories available for this propose. The idea was to assess suitability of these models in describing the experimental data. For the most part, in each of the following chapters, the basic physics of the processes in question are described in detail. In all cases the simplest models that could realistically describe or emulate the experimental data were chosen over more complex ones, provided there was no significant benefit in using the latter.

The first two sections of this thesis deal with the effects of high pressure gases on amorphous polymers. This information will then be used in the last chapter to develop an understanding of the thermodynamic and kinetic factors governing the extraction of residual monomer and low molecular weight oligomer from polymers using supercritical fluids.

The polymer-gas systems studied in this work are polystyrene (PS) and poly(methyl methacrylate) (PMMA), with carbon dioxide (CO_2), ethylene (C_2H_4), and methane (CH_4).

The structures of these compounds may be seen in Figure 1.2. The glass transition temperatures of the polymer-gas systems were obtained using a Tian-Calvet type heat flow calorimeter. This calorimeter was modified for use at pressures up to 400 atm.

For each polymer-gas system, solubility isotherms at 35.0, 52.5, and 70.0°C were determined using the method of pressure decay over a pressure range spanning the glassy phase region of the mixture. This allowed the determination of the solubilities of gases at the glass transition point of the mixture. Diffusion coefficients for the gas in the polymer-gas mixture were obtained from the kinetics of gas sorption.

The extraction of chemicals from PS was performed using both C_2H_4 and CO_2 at specific sets of conditions. The purpose was to quantify the amount of monomer in the polymer, and use the knowledge acquired from the first sections of this study to determine the factors affecting the rate and the efficiency of monomer extraction.

polystyrene

poly(methyl methacrylate)

carbon dioxide

methane

ethylene

Figure 1.2 Structures of polymers and supercritical fluids used in this study.

2.0 THE EFFECT OF GAS PRESSURE ON THE GLASS TRANSITION

2.1 Introduction

The effect that a high pressure gas may have on a polymer's glass transition temperature (T_g) was realized at least as early as 1974 by Assink²². Using NMR, he was able to show that the relaxation time of polymers changed when contacted with high pressure gases. The realization that the solubilities of gases in polymers may be significant led to the idea of gas plasticization of polymer matrices.

Gases dissolved in polymers can swell the polymer matrix, resulting in changes in the glass transition temperature. The physical effects on polymer matrices due to sorbed gases have been studied in a variety of ways (eg. creep compliance^{17,20,23,24}, calorimetry^{18,25,26,27}, dielectric relaxations²⁸). The plasticization effect of gases is comparable to the effect of absorbed organic vapours or liquids. Experimental evidence indicates that in some cases sorbed gases have proven to be more effective plasticizers on a mass fraction basis than compounds that are liquids at ambient conditions²⁹. The ability of high pressure gases and SFs to plasticize polymers leads to implications for their use in polymer science and engineering.

2.2 The glass transition phenomenon

2.2.1 The Physics of the Glass Transition

The physics of the transition from the glassy to liquid state of an amorphous polymer has been the subject of much study. It is the non-equilibrium nature of the glassy state which inherently prohibits thermodynamics from yielding an accurate model of this phenomenon. Because the nature of this transition has some dependence upon the kinetics of cooling from the liquid to the glassy state, kinetics has been suggested as a means of describing this phenomenon. For the most part however, thermodynamics is used in preference to kinetics.

A comparison of first and second order thermodynamic transitions to the glass transition may be seen in Figure 2.1. Part (a) of this figure demonstrates the typical features of a first order transition. In this case, the profile of free energy (G) versus temperature (T) shows how a sample maintains a minimum free energy state, such that a crystalline state exists below the transition temperature and a liquid state exists above this temperature. The term "first order" transition arose from the discontinuity observed in the first derivative of g with respect to T or p at the transition temperature (ie. discontinuities in the volume (V), enthalpy (H), and entropy (S) of the system). Examples of first order transitions include melting and vapourization.

Figure 2.1 Comparison of (a) first order and (b) second order thermodynamic transitions to (c) the glass transition³⁰.

Part (b) of this same figure is an example of a second order transition. In this case, while the path of lowest free energy is still kept by the system both before and after the transition, the first derivative values are not discontinuous at the transition temperature. These transitions then are not associated with a phase change in the normal sense. Examples of this are the phase transition of He at 3K, and the Curie point³⁰. The second derivatives of g with respect to T and p (ie. the thermal expansion coefficient (α), the isothermal compressibility (κ), and the heat capacity (C_p)) are however discontinuous, and thus the term "second order" transition.

The glass transition phenomenon (part c) shows some of the same behaviour associated with a second order transition when the first and second derivatives of g with respect to T and p are compared. However, the system does not follow the path of lowest free energy upon cooling below the transition temperature. Both above and below the transition temperature the state of lowest free energy corresponds to the liquid or melt state. For these reasons the glass transition is commonly referred to as a pseudo-second order transition.

A manifestation of the non-equilibrium nature of the glassy state is a transition temperature dependant upon the rate of cooling from the liquid to the glassy state. The state of the polymer is essentially "frozen" once it

solidifies. While the transition may be described by thermodynamics, the temperature at which this transition occurs, and thus the thermodynamic state of the glassy polymer, is somewhat defined by the kinetics of cooling of the sample from its equilibrium liquid state to the glassy state. Thus, the concept of thermal history. As a result, the thermodynamic state of a glassy polymer is difficult to quantify.

The glass transition temperature will increase or decrease depending on the rate at which the polymer is cooled from the liquid or melt to the glassy state. If the cooling rate of a liquid polymer is fast, the polymer will not be able to obtain a physical state as close to the true equilibrium state as a slowly cooled polymer will. A slower cooling rate allows the polymer to more closely approach the true equilibrium state by allowing the polymer to densify or contract. By cooling the polymer quickly, the enthalpic state of the glassy polymer will be higher than at a slower cooling rates.

2.2.2 Hydrostatic Pressure Effects on the Glass Transition Temperature

Polymers have substantially larger compressibilities relative to other types of solids. The large amount of unoccupied volume present in the polymeric matrix is a result of the non-equilibrium nature of the polymer.

Hydrostatic pressure applied to a liquid polymer will cause it to densify further upon cooling to the glassy state. The polymer becomes constricted under the applied pressure, and attains a thermodynamically more favourable, smaller volume configuration. Unlike the densification achieved upon slow cooling of the liquid polymer, hydrostatic pressure decreases the enthalpy of the polymer, leading to a concomitant increase in the T_g . This may be seen in Figure 2.2, where an increase in pressure from p to $p+dp$ decreases the volume of the polymer by dv_{tr} , increasing the transition temperature from T_{tr} to $T_{tr}+dT$.

The glass transition temperature has been determined to be directly proportional to pressure up to at least 200 atm. In this region, the value of dT_g/dp_{hyd} is approximately 0.03°C/atm for atactic PS, and about 0.02°C/atm in PMMA³¹⁻³⁴.

2.2.3 Changes in the Glass Transition due to Dissolved Compounds

The effects of compounds dissolved in the polymer matrix on the glass transition temperature are well known. Dissolved gases and liquids can depress the temperature of the glass-liquid transition significantly^{17,29,35,36}. The change in the T_g due to dissolved penetrant is a result of the disruption of polymer interchain interactions, allowing for faster relaxation times for the mixture at a given T compared to the pure polymer. With increasing penetrant

Figure 2.2 The effect of hydrostatic pressure on the glass transition temperature³⁰.

Figure 2.3 The effect of a second component on the glass transition temperature³⁰.

concentration (eg. $w_2 > 0$), the mixture is able to maintain an equilibrium state to lower temperatures, thus reducing the transition temperature as seen in Figure 2.3.

In considering gaseous penetrants, the effects of pressure will be twofold. First, the dissolved gas will plasticize the matrix and reduce its T_g , while the hydrostatic pressure effect will try to compress the matrix and increase the T_g . Since the hydrostatic effect is constant to relatively high pressures (ie. up to 300 atm), the magnitude of changes in T_g depend mostly on the plasticizing effect of the gas on the polymer matrix.

2.2.4 Theoretical Interpretations of Changes in the Glass Transition Temperature with Gases

2.2.4.1 Free Volume Theories

Iso-free volume theories are based on the requirement of a specific amount of free volume being present in any amorphous system, pure or mixed with other components, for the transition to the liquid state to occur. According to some free volume theories^{37,38}, the free volume fraction of the polymer specific volume is ideally .025. Calculations of the amount of free volume available in a polymer matrix from group contribution methods yields a free volume fraction of .10 to .12 of the polymer specific volume. The discrepancy in the amounts of free volume arise from the different ways in which the free volume is defined.

While thermodynamics are frequently used to quantify the state of the polymer-penetrant system, the basis of free volume theories is kinetic in nature. Free volume theories rationalize reductions in the glass transition temperature on additivity effects of the free volumes of the polymer and penetrant phases upon homogeneous mixing.

In most cases, the penetrant (eg. a liquid or gas) will have a larger amount of free volume than the polymer. Thus free volume models predict a T_g that is strongly dependent upon penetrant concentration, and thus on pressure in the case of gaseous penetrants. The relations used to predict changes in T_g by this argument make use of physical parameters which are frequently not available, such as the T_g of the penetrant, and the penetrant's thermal expansion coefficient in its amorphous state. Calculation of free volumes of mixtures thus often requires rough estimates of these parameters.

Some of the main criticisms of the free volume theory include the fact that the iso-free volume state for the glass transition has been disproven experimentally, and that it cannot describe adequately the effects of hydrostatic pressure on the thermodynamic state of the system at high pressures³⁹. Despite this, free volume theories are widely used to predict the properties of polymer-penetrant systems, such as sorption and diffusion.

To relate the glass transition temperature of the pure

polymer (T_g) to that of the polymer-penetrant mixture ($T_{g,m}$), it is frequently assumed that the change in T_g is directly proportional to the mass fraction of penetrant (ω)

$$T_{g,m} = T_g - A\omega \quad [2.1]$$

where the parameter A is a measure of the plasticizing strength of the penetrant. Strictly speaking this may not be considered as a free volume relationship, however its use in free volume theories and other theories is widespread.^{20,38}

2.2.4.2 Chow's Model

Theories to describe the glass transition phenomenon are frequently thermodynamically based. One of the most widely accepted school's of thought assumes an isentropic state for the transition. Chow's model³⁶ is an example of such a thermodynamic model.

The theory of Chow is based on the assumption that the effects of penetrants on the measured glass transition temperature be a direct reflection of their effect on the true thermodynamic glass transition temperature (T_g^0). The assumption of an isentropic transition state thus allows the use of thermodynamics to characterize the effects on the polymer T_g .

The model relates the change in the glass transition temperature to the amount of penetrant in the mixture by

$$\ln\left(\frac{T_{g,m}}{T_g}\right) = \beta [(1-\theta)\ln(1-\theta) + \theta\ln\theta] \quad [2.2]$$

$$\beta = \frac{z R}{M_p \Delta C_p} \quad [2.3]$$

$$\theta = \frac{M_p}{zM_d} \frac{w_1}{1-w_1} = \frac{M_p}{zM_d} w \quad [2.4]$$

where M_p is the mass of the polymer repeat unit, M_d is the molar mass of the penetrant, R is the gas constant, ΔC_p is the heat capacity change associated with the glass transition of the pure polymer, w is the mass in grams of penetrant sorbed per gram of polymer, and z is a lattice coordination number. The parameter β is a polymer specific constant, and θ is dependant upon the penetrant concentration in the polymer. Both β and θ are dimensionless.

The equations 2.2 to 2.4 above predict that changes in the glass transition temperature of a given polymer are independent of the penetrant type. An equal concentration of penetrant in the matrix, in moles of penetrant per gram of polymer, will reduce the glass transition temperature by the same amount. The fit of $T_{g,m}$ -solubility data using this model has been shown to be reasonably quantitative for liquid penetrants^{29,36}.

2.3 Experimental

2.3.1 Chemicals and apparatus

Three different gases were chosen to test the effect of gas pressure on the glass transition temperature of amorphous polystyrene (PS) and poly[methyl methacrylate] (PMMA). Methane (CH_4), ethylene (C_2H_4), and carbon dioxide (CO_2) were 99.9% minimum purity as supplied by Matheson. The PS used was a clean commercial sample (ie. containing no additives) of Styron 680 pellets (ca. 2 mm diameter by 3 mm length cylindrical pellets) with a $M_w = 193700$, $M_w/M_n = 2.45$. The PMMA samples were pellets of virtually identical size and purity, with a M_w of about 200000, and M_w/M_n of about 2.0. The PS and PMMA samples were generously donated by Dow Chemicals Canada and Rohm and Haas USA, respectively.

A Tian-Calvet heat flow calorimeter (Setaram, model BT) was modified to allow for in-situ measurements of the glass transition in the polymers at various gas pressures. The system was designed and commissioned at the National Research Council of Canada. A schematic representation of the apparatus used can be seen in Figure 2.4.

The heart of the calorimeter is a massive aluminium block with two identical cavities located symmetrically about the centre, designated sample [S] and reference [R]. The thermopiles which surround each cavity are identical, and are connected in opposition to give the differential output. The apparatus contains two platinum sensors, each

Figure 2.4 Apparatus schematic of the calorimeter used for high pressure glass transition temperature measurements. The meanings of the captions are given in the text.

with four leads, enabling four-wire resistance measurements. The first sensor is used to control the temperature of the block, while the second is used as the sensor for either cavity.

The calorimeter accommodates matched stainless steel cells which are lowered into the two cavities. The cells used here were designed for pressures up to ca. 400 atm, with an internal volume of each high pressure cell being approximately 8 mL. The sample cell was frequently removed to replace the polymer contents; the reference cell was permanently installed in the calorimeter. The operating range of the calorimeter is -200 to +200°C. Dry helium was used as the heat exchanger fluid during annealing and cooling sequences, while dry nitrogen was used during measurements.

The major alteration to the apparatus was in developing new cells and a high pressure system. Both cells were modified to be connected to a high pressure manifold. A high pressure transducer was connected to the manifold to monitor the pressure in the system. As well, a thermostatted high pressure gas reservoir [GR] of approximately 500 mL internal volume was connected to the manifold to buffer changes in the system pressure throughout temperature scans. The reservoir was kept at 40.0°C for all measurements. The temperature of the GR was monitored with a platinum resistance thermometer [PRT]. With the pressure

ballast on-line, the system pressure still frequently rose 2-5% during a scan due the rising temperature in the calorimeter cells. This translates however to only a small pressure rise during the actual transition, and its effect was assumed to be negligible.

The manifold accommodates a connection for a gas cylinder. It was designed with several high pressure valves (NUPRO, model SS-DSVCO4) such that any desired condition could be applied to either cell alone if required. In all cases, the entire system external to the calorimeter was thermostatted at a temperature such that the gas phase could not condense in any section of the apparatus.

2.3.2 Procedure

The sample cell was charged with about 2.5 g of polymer. All samples were evacuated for a minimum of 30 minutes. Measurements were usually done in order of increasing pressure. For each new gas used, the entire system was evacuated. The high pressure reservoir was then filled with an appropriate amount of gas to generate the required pressure inside the cells. When pressures higher than that available from the gas cylinder [G] were desired, the gas reservoir was cooled with liquid nitrogen to condense the required amount of gas into it to generate the desired pressure.

Once the whole system was pressurized, the sample was

annealed at about 5°C above the estimated $T_{g,m}$ for a least 2 hours, and let cool to room temperature overnight. By annealing the polymer sample in this manner, the polymer-gas mixture was able to achieve its equilibrium solubility state with the gas much more quickly. This also allowed for the destruction of any conformational stains due to previous thermal history, and pressure testing of the system. A pressure loss greater than 2% per day was deemed unacceptable. Pressure transducers (Setra, model 204) [T] were used to monitor the gas pressures during scans.

The rate at which the system was allowed to cool was monitored to ensure that its magnitude was approximately the same as the rate of heating to be used in the subsequent scan. The cooling rate was allowed to increase once the calorimeter temperature was sufficiently below the transition temperature of the mixture. This annealing sequence provided for precise measurements of T_g .

Once the sample had been properly prepared for measurement, the calorimeter was then scanned from a minimum temperature of 2°C above the critical temperature of the gas to about 20°C above T_g , at a scan rate of 7 or 10°C per hour. The scanning procedure was frequently repeated after proper cooling to check for reproducibility in the data.

2.3.3 Data Acquisition and Analysis

The control and operation of the calorimeter was automated by interfacing the calorimeter with an IBM compatible PC. The differential thermopile output was measured with a 6 1/2 digit Keithley 181 nanovoltmeter [NV]. Resistance measurements were made with a 6 digit Hewlett-Packard HP 3456A digital voltmeter [DVM]. A Hewlett-Packard HP 6012A programmable d.c. power supply [PS] was used for heating the block. The digital voltmeter and the power supply received instruction from the computer via a Hewlett-Packard HP3497A data acquisition and control unit [DA/C]. This unit was equipped with a relay multiplexer which connects the digital voltmeter to the sensors and pressure transducers, a constant-potential source for driving the power supply for resistive heating, and a built-in clock for making measurements as a function of time and for generating interrupts.

The software was developed at the National Research Council of Canada. An interrupt of 15 seconds was used; on each interrupt, the data acquisition and controller transmitted the time to the computer, the digital voltmeter measured the resistance of the first sensor and transmitted the value, the nanovoltmeter measured output from the thermopile and transmitted the value, the output from the pressure transducer is transmitted to the computer, and the digital voltmeter measured the resistance of the second

sensor and transmitted the value. The sequence took approximately 1.5 seconds. The values received by the computer are then stored. The computer used the incoming value from the second sensor to calculate the required amount of power output to the block heater.

The temperature control algorithm consisted of a linear proportional band, and ramps were achieved by moving the proportional band at each interrupt by the appropriate increment. In the isothermal mode, the temperature of the block could be controlled to $\pm 0.001^{\circ}\text{C}$. In the ramp mode where the temperature of the block was varied linearly with time, ramp rates of 0.5°C/h to 20°C/h could be easily obtained. The precision of all electrical sensitivities were better than 0.5%.

The accuracy of the calorimeter was determined using indium calibration standards to be within 1°C of the accepted value. The accuracy of the calorimeter, however, was not of great concern since the information sought in this study was the difference between the transition temperature of the pure polymer and the impregnated sample.

The resulting data was plotted as the heat flow, temperature scan rate, and pressure versus temperature. The plot of pressure versus temperature was used to ensure that isobaric conditions were held during the scan. The plot of temperature scan rate versus temperature was used to ensure that the heat flux had reached its equilibrium value before

any changes occurred in the thermal curve which might be mistaken for transition in the sample.

Because of the non-equilibrium nature of the glassy state, the correct method of determining the T_g of a polymer requires that the measurement of heat flow be made at a constant cooling rate⁴⁰. In this manner, the polymer is in equilibrium with its surroundings, and the transition from the liquid to the glassy state is defined by the thermodynamic state of the system and not by the thermal history of the polymer.

Frequently only heat flow measurements at constant heating rate are possible. It has been suggested that the transition temperature obtained from a heating scan will be close to the value obtained from a cooling scan if a polymer is properly prepared by initially heating it to its liquid state, destroying any prior thermal history⁴⁰. The cooling rate during this "annealing" sequence must be similar to the subsequent heating rate for the scan for this approximation to hold.

The actual transition temperature is taken as the mid-point of the step change in the sample heat capacity (Figure 2.5). This represents the point where half of the polymer has participated in the transition. This can be determined by one of two methods. The first method uses the inflection point of the step change in heat flow. The second designates the mid-point of the transition as the mid-point

of the step change in the heat capacities of the liquid and glassy states. Frequently these two methods yield the same result.

According to Wunderlich⁴⁰, a proper characterization of the transition requires determination of several designated temperatures. The beginning and end points of the step change in the heat capacity on going from the glassy to rubbery states (T_b and T_e respectively) and the determination of the intercepts of the tangent line to the heat flow curve (T_1 and T_2) at T_g with the extrapolated heat flow profiles of the liquid and glassy state are useful for fully characterizing the transition.

Figure 2.5 Characterization of the glass transition⁴⁰.

2.4 Results and Discussion

2.4.1 Methods of Determining the Glass Transition

There has been a wide variety of methods used to assess effects on the glass transition temperature of polymer-penetrant systems. Methods which measure the mechanical behaviour and those which measure thermal behaviour of polymers are the most common. Creep compliance of a polymer film sample is one of the more common mechanical methods^{19,24,29}. A constant stress is applied to the polymer at a given temperature and pressure. The strain, or elongation, of the polymer is then measured as a function of time. The glass transition is taken as the point at which the modulus of the polymer sample significantly decreases.

There are only a few other instances of the use of calorimetry for the determination of changes in the T_g with gas pressure. Chiou et al¹⁸ used differential scanning calorimetry on preconditioned polymer samples. Although they used aluminium sample pans to seal the samples gas-tight almost immediately after removal from their conditioning chambers, the losses that would be expected to occur would likely be significant. Although these were accounted for to some extent by an empirical estimation of losses, the contribution to errors in the final result for the T_g of the system cannot be assumed to be negligible.

As well, because of the nature of the polymer samples, a minimum of two thermal scans are generally required to

eliminate any thermal history effects as previously discussed. With increases in temperature, a decrease in penetrant solubility is observed. If such annealing scans are carried out at pressures significantly lower than that at which the samples were equilibrated, there is a distinct possibility of gaseous nucleation (eg. foaming) and loss in penetrant solubility. Thus any void spaces in the sealed pans, or improper sealing of the pans, would negate any use of a second scan of the sample. Since a second scan is usually required for reliable data (at least in our experience), this severely limits the use of this type of sample preparation technique for measuring $T_{g,m}$.

A similar methodology to that mentioned above used known amounts of solid CO_2 and poly(phenylene oxide), once again sealed in a DSC pressure-tight pan²⁶. The authors indicated that the change in the T_g from that of the pure polymer was greater than 200°C due to only moderate pressures of CO_2 . Subsequently published data using a high pressure DSC apparatus provided more accurate data for this polymer-gas system²⁷, showing that the previous methodology may not be reliable. The point is that experimental methods are quite important when such measurements are to be made accurately.

The advantage of the method used in this study for measuring changes in the glass transition temperature of polymer-gas mixtures is that the thermodynamic state of the

system at the transition point is accurately known. In this manner, the relationship between T_g and the composition of the polymer-gas system may be obtained.

2.4.2 Limitations of the Data

The high pressure modifications to the DTA apparatus allowed for quantitative, in-situ measurements of the changes in T_g due to high pressure gases. However, the apparatus was not without limitations. At high pressures, the heat flow signal contained a significantly larger amount of noise. A small aliquot of helium (ca. 50 Torr) was frequently added to the cells before pressurizing with the desired gas. This was to ensure significant heat flow into both cells.

The restriction to temperatures above the critical temperature of the gas did not inhibit the measurement of glass transitions using CH_4 because of its relatively mild effect on the T_g and extremely low T_c . The T_c of both CO_2 (31°C) and C_2H_4 (10°C) are in the vicinity of ambient temperature. Because of the strong plasticization effects that CO_2 and C_2H_4 showed for both polymers, at high pressures they were both able to depress the glass transition temperature of the mixture below the T_c of the gases. The highest pressure for which the T_g could be unambiguously established was about 87 atm for C_2H_4 in both PS and PMMA, but only about 60 atm for CO_2 in PS and even lower in PMMA.

A further restriction arises from the calorimeter itself. Because of the large size of the calorimeter inner aluminium core, an initiation time of about 1.5 hours was required to reach a steady scan rate in the present system. While this was not a problem for CH_4 , again due to its low value for T_c and smaller effect on T_g , it proved to be the major stumbling block in obtaining data for the polymer- CO_2 and C_2H_4 systems near the critical temperatures of the penetrants. Lower scan rates were tried in attempts to reduce the thermal lag effect on the lower temperature boundary, but scans which were too slow resulted in reduction in the measured heat flow changes, obscuring the transition. This was due to previously discussed problems with heat flow in these cells and the fact that the step change in the system heat capacity is not large for a glass transition. A scan rate of $7^\circ\text{C}/\text{h}$ was found to be optimal.

The proper annealing of the polymer samples was found to be of utmost importance. The annealing procedure used reduced any anomalies in the thermal curve by heating the sample to at least 20°C above the predicted $T_{g,m}$ for a few hours. Cooling was performed at a rate similar to that of the subsequent temperature scan. Complete equilibration time for the sample took at least 12 hours.

The gas pressure was monitored throughout all scans to ensure that there were no major pressure changes in the apparatus so that the polymer would be in an equilibrium

solubility state. The decrease in diffusion rates with decreasing penetrant concentration results in a self-retarding effect on the sample in reaching equilibrium solubility, and may result in gas nucleation within polymer particles. Small increases in pressure were tolerated since increases in solubility of the penetrant increase diffusion rates and result in a self-accelerated process in reaching equilibrium solubility.

As outlined in section 2.3.3, proper assessment of the transition requires measurements of the heat flow at a constant cooling rate. The cooling rates after annealing of the sample were carefully monitored throughout all measurements to ensure that this was indeed the case.

The results of thermal scans were plotted as heat flow versus temperature. The T_g was obtained by graphical analysis of the step change in the heat flow signal. Graphical interpretation proved to be sufficiently precise for the data obtained.

2.4.3 Thermal Curves

Thermal curves for the PS-C₂H₄ system can be seen in Figure 2.6. These represent typical thermal curves obtained from the high pressure DTA system. In spite of the high thermal mass of the sample cell and the slow scan rates, the step change in the heat flow profiles are quite obvious. The curves were analyzed according to the convention of

Figure 2.6 Thermal curves for PS- C_2H_6 at various pressures. The curve for the pure polymer is analyzed as indicated by Wunderlich⁴⁰.

Wunderlich⁴⁰. The mid-point of the extrapolated heat flow profile was designated as the T_g of the mixture. This analysis is seen in the thermal curve for the pure polymer in Figure 2.6.

There was a broadening or spreading out of the transition step with increasing pressure (and thus solubility) seen in these thermal curves of Figure 2.6. This same effect was seen during isothermal creep tests of polymer-gas systems¹⁷. The explanation for this is due to the changing relaxation rates for the mixture, producing a larger distribution of activation energies for the transition of the glass to the liquid state. The changing relaxation rates for the polymer-gas system are also the cause of the disappearance of the enthalpic overshoot seen in Figure 2.6 as pressure increases.

In Figure 2.7, thermal curves were obtained at moderate pressure (eg. 90 atm) which gave the appearance that the transition to the liquid state had started at a temperature lower than the starting temperature of the scan. In these cases only the end of the transition could be seen. It was inferred from the thermal curve at 300 atm that the sample was in a liquid state throughout the scan. The transition temperature had dropped below the measurement starting temperature for this system.

Figure 2.7 Thermal curves for the PS-C₂H₄ system at high pressures.

Annealing of the polymer sample was repeated at each new set of conditions. The effects of annealing may be seen in Figure 2.8. Thermal curves for the pure polymer (1) and the sample annealed at about 25 atm of C_2H_4 (2b) may be compared with the first scan of the polymer exposed to the gas at 25 atm (2a). For the unannealed sample it can be seen that the initial change in slope of the heat flow occurs at the same point as in the annealed sample, and the end of the transition occurs at the same point as the pure polymer. This indicates that while the outer portions of the polymer may be at or close to equilibrium solubility with the gas, the interior is still essentially pure polymer. Therefore proper annealing of the sample was of utmost importance. The glass transition was almost always obtained from the second scan of the sample. Reproducibility was found to be better than $\pm 0.5^\circ C$ between subsequent scans under isobaric conditions.

For every new set of conditions, the annealing sequence was repeated. Frequently polymer samples were reused, but only for higher pressure measurements. No scans were done on samples where the polymer had been previously exposed to a higher pressure (other than that used in the conditioning step) because of the requirement of excessive equilibrium times for re-equilibration, and because of unknown sample integrity after depressurization.

Figure 2.8 Thermal Curves for PS-C₂H₄, showing the effect of annealing; pure polymer (1); first scan of polymer-gas at 25 atm (2a); second scan at 25 atm (2b).

2.4.4 Trends in the dT_g/dp Data

The change in the glass transition of PS and PMMA with the C_2H_4 , CO_2 , and CH_4 are shown in Figures 2.9 and 2.10 respectively. According to the convention of Wunderlich⁴⁰, the values T_b , T_1 , T_g , T_2 , and T_e needed for complete characterization are tabulated in Appendix II.

The initial trends in the glass transition temperature with pressure for the PS- CO_2 and PS- C_2H_4 systems are essentially identical ($-.9^\circ C/atm$). The magnitude of the effect due to CO_2 agrees with what that quoted in the literature^{5,14}; both CO_2 and C_2H_4 are effective plasticizers for PS. The effect due to CH_4 is relatively mild ($-.2^\circ C/atm$). The non-polarizable nature of CH_4 may be assumed to play a role in producing this effect.

Based on a corresponding states argument, the effect on the T_g due to C_2H_4 may be expected to be slightly smaller than that seen for CO_2 , while that of CH_4 should be significantly less than both. The observed results suggest that the plasticizing strength of C_2H_4 , equivalent to that of CO_2 , may be due to some chemical similarity between PS and C_2H_4 .

In the case of PMMA, the magnitude of the depression of T_g due to C_2H_4 ($-.9^\circ C/atm$) and CH_4 ($-.2^\circ C/atm$) is essentially identical to that seen in PS. However CO_2 shows a much larger effect on the T_g for PMMA ($-1.2^\circ C/atm$). Chemical similarity between the PMMA and CO_2 may be responsible for

Figure 2.9 Glass transition temperature-pressure profiles for PS with CO_2 (dots), C_2H_4 (triangles), and CH_4 (filled triangles). The solid lines shown are lines of fit, and the dashed line is the correction for the hydrostatic pressure effect to CH_4 data.

Figure 2.10 Glass transition temperature-pressure profiles for PMMA with CO_2 (dots), C_2H_4 (triangles), and CH_4 (filled triangles). The solid lines shown are lines of fit, and the dashed line is the correction for the hydrostatic pressure effect to CH_4 data.

this.

In both Figures 2.9 and 2.10, the hydrostatic corrections are shown only for CH_4 since this effect is really of significance at pressures above about 100 atm. Below this pressure, and especially for cases where the magnitude of dT_g/dp is large, showing the hydrostatic correction only serves to clutter the data shown in the figures.

The hydrostatic correction was made by subtracting the increase in temperature that would occur in the pure polymer, at the given pressure, from the T_g data. The actual plasticizing effect of CH_4 on the matrix is thus defined by the dashed line shown in these figures. The curvature in the T_g - p trends at higher pressures are assumed to be at least partially the result of solubility limitations to the gas in the polymer. It may also be that hydrostatic pressure influences the state of the polymer-gas mixture over and above its effect on the pure polymer. The relative magnitudes of such effects could not be determined from this study.

Based on the curvature observed in dT_g/dp , it is expected that the $T_{g,m}$ for both PS and PMMA- CH_4 will "bottom-out" at high enough pressures, eventually causing them to return to higher temperatures. Pressures as high as 350 atm were used in the testing of most polymer-gas systems. For the PS- CO_2 system, the effect of hydrostatic pressure has

been proposed to cause a rebound in the measured T_g at pressures above about 200 atm^{19,28}. No such effects were seen on the dT_g/dp profiles measured here for either CO_2 or C_2H_4 . While the apparatus used was limited to temperatures slightly above T_c , the literature values quoted indicate transitions at temperatures sufficiently high enough (ca. 45°C) that they should have been seen to some degree in this study.

2.4.5 Analysis by Chow's Model

The equations of Chow (equations 2.2 to 2.4, pg 23) were utilized to relate $T_{g,m}$ to the concentration of gases in the polymers obtained from solubility measurements presented in Chapter 3. There was insufficient data for both $T_{g,m}$ and the solubility of CH_4 in either polymer to allow for a proper analysis of polymer- CH_4 systems by Chow's model.

Figures 2.11 and 2.12 compare the predicted values from Chow's equation (solid line) and equation 2.1 (dashed line) with those obtained here and from the limited data available in the literature for the PS- CO_2 and - C_2H_4 systems^{18,41}. Qualitative comparisons of the experimental data from this study and from the literature are in fairly good agreement considering the different methodologies used to obtain $T_{g,m}$.

For the PS- CO_2 system, the values used for Chow's equation were $M_p=104.2 \text{ g mol}^{-1}$, $\Delta C_p=0.259 \text{ JK}^{-1}\text{g}^{-1}$, and $z=2$. A value of $z=2$ was found to accurately fit the changes in T_g

Figure 2.11 The glass transition temperature of the mixture versus concentration for PS-CO₂. Values are compared with Chow's equation (solid line, $z=2$) and equation 2.1 (dashed line). Solid triangles are values from reference 41, hollow triangles from reference 18.

Figure 2.12 The glass transition temperature of the mixture versus concentration for PS- C_2H_4 . Values are compared with Chow's equation (solid line, $z=2$) and equation 2.1 (dashed line).

induced by liquids dissolved in the polymer as well³⁶. The equation of Chow fits the experimental data very well up to the highest gas concentrations measured. The fit of equation 2.1 is however limited to concentrations below about 0.03 mass fraction of gas. Similar agreement between the experimental results from this study and that predicted by Chow's equation and equation 2.1, was also seen for PS-C₂H₄ using $z=2$.

The results for the PMMA-CO₂ and -C₂H₄ systems are shown in Figures 2.13 and 2.14 compared to equation 2.1 (dashed line) Chow's equation (solid line) using $M_p=100.1$ g mol⁻¹ and $z=1$. The same value for ΔC_p was used for both PS and PMMA. Chow's equation again fits the data very well up to the highest concentrations shown. The differences seen in Figure 2.13 between the present data and the literature data is a result of the differing values of T_g for the pure polymer. This is likely a result of the different measurement methods and polymer samples used.

As in the PS-gas systems, equation 2.1 is limited in its application to PMMA-gas systems as indicated in Figures 2.13 and 2.14. It is worth noting that Chow's equation is shown to fit the polymer-gas data best using a value of $z=2$ for PS and $z=1$ for PMMA. The results here and from the literature^{29,36} suggest that z is polymer specific.

The results shown in Figures 2.11 to 2.14 indicate that the change in T_g is constant for a given molal concentration

Figure 2.13 The glass transition temperature of the mixture versus concentration for PMMA- CO_2 . Values are compared with Chow's equation (solid line, $z=1$) and equation 2.1 (dashed line). Solid triangles are values from reference 41, hollow triangles from reference 18.

Figure 2.14 The glass transition temperature of the mixture versus concentration for PMMA- C_2H_4 . Values are compared with Chow's equation (solid line, $z=1$) and equation 2.1 (dashed line).

of gas, regardless of the gas type. This implies that specific interactions between the gas and polymer do not directly affect the glass transition temperature of the mixture. At a constant molal concentration of gas in the polymer, the sensitivity of the polymer's T_g to a compound dissolved in the matrix depends on the monomeric mass and the value of z , and so can be considered a polymer property. Therefore, the parameter $T_{g,m}$ may be considered as a colligative property of the system.

Chow's model predicts that at significantly high concentrations of a component (ie. gas or liquid) added to the polymer, a minimum in the T_g -solubility profiles exists. Such minima have been seen in the literature¹⁹; it would seem that there is a minimum in the polymer- CH_4 T_g - p profiles obtained in this study as well. As mentioned, the appearance of minima in these profiles may be attributed to a solubility limitation for CH_4 , and a constant hydrostatic pressure effect.

One of the main downfalls of Chow's model in its application to gaseous penetrant-polymer systems is that the form of equation 2.2 is not pressure explicit, and as such it cannot relate the effects of gas pressures directly to $T_{g,m}$. However, it should be duly noted that based on the results of this study, Chow's equation is a major improvement over previous equations used in this same capacity, such as equation 2.1.

2.4.6 Johnston-Sanchez Equation of State for Gas-Polymer Mixtures

Equations of state (EOS) use the properties of the pure components to predict the properties of the mixture. They benefit over models, such as that of Chow, in that they do not require any experimental data to predict the composition of the mixture. The Johnston-Sanchez EOS is a modification of the well known Sanchez-Lacombe EOS designed to model small molecule-polymer systems^{20,42-44}.

The potential usefulness of the Johnston-Sanchez EOS comes in its prediction of "retrograde vitrification", a phenomenon whereby an increase in temperature produces a transition from the liquid to the glassy state. This phenomenon has a great deal of possible implications for the processing polymers with high pressure gases.

Figure 2.15 is an example of the retrograde vitrification process for a gas with high solubility in the polymer. There exists a pressure maximum above which the polymer-gas mixture exists in a liquid state, regardless of temperature. It is possible then, at lower pressures and temperatures, the polymer-gas mixture exists in a liquid state as well. Using Figure 2.15 to exemplify this, if the polymer-gas system was at a pressure p_1 and a temperature T_{in} , then an isobaric calorimetric scan should exhibit an exothermic transition first (at T_{exo}) as the system vitrifies, then at higher temperatures an endothermic

Figure 2.15 Schematic representation of the retrograde vitrification phenomenon produced by a highly soluble gas²⁰.

transition (at T_{endo}) at the glass-to-liquid transition.

In this study, thermal curves at higher pressures of CO_2 and C_2H_4 occasionally contained what appeared to be the superpositioning of two transitions. Unfortunately, transitions could not be unambiguously assigned for these thermal curves. Manipulation of both temperature and pressure were made in an attempt to properly anneal a polymer sample to a liquid state at a temperature below that

commonly seen (ie. shadow the T_g -p profile during annealing). In a few cases what appeared to be an initial low T exotherm was seen, but attempts to obtain a single thermal curve containing the double transition were unsuccessful.

The experimental methods used by Johnston et al²⁴ to prove this phenomenon used creep compliance measurements. By performing pressure scans isothermally, a more accurate determination of the retrograde region may be obtained.

The equations of state used to predict the retrograde phenomenon can only predict the concentrations of the components of the mixture, and are not able to alone produce $T_{g,m}$ data. For this, Johnston and Sanchez²⁰ assumed a linear relationship between the mass fraction of gas and the change in the glass transition temperature, as in equation 2.1. As has been demonstrated, this equation may be sufficient for values of ω_1 as $\omega_1 \rightarrow 0$, but it predicts a much stronger sensitivity of T_g on gas concentration, at high concentrations, than has been seen experimentally^{29,36}. Despite this possible weakness in the model, the retrograde vitrification phenomenon has been substantiated somewhat by literature data^{17,24,43,44}.

3.0 GAS SORPTION IN AMORPHOUS POLYMERS

3.1 Introduction

The solubility and rates of diffusion of chemicals in glassy polymers has been studied for a variety of reasons. These stem from environmental and industrial impetus, ranging from the degassing of chemical species in manufactured plastics and foams, to the characterization of polymer membranes for gas separations or gas barrier properties for packaging materials⁴⁵.

The most widely accepted description of a glassy amorphous polymer at the microscopic level seems to be a non-homogeneous mixture of polymer molecules and free space. The mobility of these voids in the polymer matrix is arrested when the polymer vitrifies. This description of the polymer matrix arises from the changes observed in the volumetric behaviour of the polymer as it is cooled from an equilibrium liquid state to a glassy state. From Figure 3.1 it may be seen that the onset of the glassy state is reflected by the "freezing-in" of excess volume (ΔV_e); the difference in volume from the equilibrium liquid to the glassy state contributes to the free volume in a polymer matrix.

In the description of the solubility and diffusion of gases in polymers, general experimental trends in the volumetric and thermal behaviour of the mixture will

Figure 3.1 Schematic representation of the temperature dependence of an amorphous polymer's volume, both above and below the glass transition temperature³⁰; ΔV_e reflects the excess volume frozen into the matrix.

Figure 3.2 Schematic representation of sorption isotherms for an amorphous polymer both below (1) and above (2) the glass transition³⁸; c is the concentration of penetrant, p is pressure.

be referred to as they pertain to the theories used in the present work. There was, however, no experimental work done in this study on the partial molar volumes of dissolved gases or on the permeation of gases through polymers. Most of the experimental work stressed the effects of gases on the glassy state of the polymer since much less work has been done in this area relative to the equilibrium state of the polymer.

3.2 Solubility in Amorphous Polymers

3.2.1 Introduction to Solubility in Polymers

It has been observed that the sorption isotherms of gases and vapours in polymers can follow one of several trends. The trends exhibited depend mainly on the state of the polymer, and on the gas type^{46,47}.

Non-linearity of some form is commonly observed in the solubility isotherms plotted as concentration (c , in mL of gas at standard temperature and pressure per g of polymer) or mass fraction (ω) of gas against pressure (p) as seen in Figure 3.2. For gases and vapours in liquid polymers (curve 2), the curvature observed in the solubility isotherms follows the relationship $(\partial^2 c_1 / \partial p_1^2)_T > 0$, so that the isotherm is convex to the pressure axis. For glassy polymers, where T is less than the glass transition temperature of the mixture ($T_{g,m}$), a trend opposite to this is most frequently observed (ie. $(\partial^2 c_1 / \partial p_1^2)_T < 0$) . Such

isotherm profiles are concave to the pressure axis.

Isolated cases where sorption isotherms in glassy polymers have followed the former trend associated with sorption in rubbery polymers have been observed. This has been seen with some noble gases in PS, and water vapour in PMMA⁴⁶.

Linear trends in the c-p profiles at high pressures have been attributed to the onset of the glass-to-liquid transition (ie. region around the intercept of curves 1 and 3 in Figure 3.2). Here, the concentration of the gas is sufficient to depress the $T_{g,m}$ to below the measurement T. This assumption is based on the fact that "inverse" sigmoidal shaped isotherms have been observed in the sorption profiles of highly soluble gases in glassy polymers (ie. combination of curves 1 and 3 in Figure 3.2), but such profiles have not been observed for sorption in rubbery polymers.

The classical theory of Flory-Huggins is generally used to describe polymer-penetrant thermodynamics. Since this theory is based on equilibrium thermodynamics, it is in general only applicable to polymers in a liquid state. As this work is concerned with the non-equilibrium glassy state, other more recent and applicable theories need be considered.

The sorption of gases in the glassy state of polymers is frequently described using the "Dual-Mode" model. While

free volume theories are generally not useful for predicting the changes in glass transition temperatures, they are relatively successful in their applications to sorption data. The remainder of the introduction to this chapter will be used to describe the dual-mode sorption model and the Vrentas free volume model.

3.2.2 The Dual-Mode Sorption Model

A dual-site sorption model for glassy polymers was first proposed by Barrer in 1958^{48,49}. The model describes the dissolved gas existing in two distinct populations; the first being gases dissolved in the matrix, governed by Henry's law; the second of gases adsorbed into the holes or free volume in the matrix, governed by Langmuir adsorption. Although the dual-mode model is phenomenologically based, its ability to fit experimental data has resulted in it being one of the more accepted models for gas solubility in glassy polymers.

The total concentration of gas molecules in the polymer (c) is thus the sum of the concentrations in the dissolved state (c_D) and of that adsorbed into the holes in the polymer matrix (c_H)⁴⁹⁻⁵¹

$$c = c_D + c_H = k_D p + \frac{c_H' b p}{1 + b p} \quad [3.1]$$

where k_D is the Henry's law constant for the polymer-gas system, and c_H' and b are the Langmuir parameters denoted as

the hole saturation and hole affinity constants, respectively. Physically, b represents a partitioning of gas between the adsorbed and non-adsorbed states, while c_H' is related to the amount of void space in the matrix.

At low pressures, the second term of equation 3.1 may be estimated as the numerator, so that the total penetrant concentration may be defined as

$$c = k_D p + c_H' b p \quad [3.2]$$

In general $c_H' b p > k_D p$ at low pressures, so the adsorption or hole-filling process of the polymer free volume dominates at low pressures. Similarly, at high pressures equation 3.1 reduces to

$$c = k_D p + c_H' \quad [3.3]$$

Since c_H' is a constant at a given temperature, the dissolution of gases into the polymer matrix dominates at higher pressures.

Graphical procedures may be used to obtain values for the dual-mode parameters^{50,52}. From the slope of solubility data at high pressures, k_D may be found. Then, by subtracting $k_D p$ from c , c_H' may be found. A plot of $1/c_H'$ versus $1/p$ will yield a slope of $1/bc_H'$ and an intercept of $1/c_H'$. Because of the insensitivity of the c_H' and b

parameters to the fit of the data, computer programs using non-linear regressions should be used to obtain accurate values for these parameters. A routine to accurately determine dual mode parameters from experimental sorption data is given by Koros⁴⁵.

Heats of sorption for gases in glassy polymers have been shown to be somewhat more exothermic than in liquid polymers by some 10-15 kJ mol⁻¹ ^{30,51}. The rationalization of this experimental observation is that molecules being sorbed into the glassy polymer can occupy pre-existing void space. Molecules sorbed in liquid polymers on the other hand must overcome the cohesive forces between polymer segments to exist in the bulk matrix. The existence of void volume in glassy polymers is also substantiated by negative excess volumes of mixing for polymer-gas mixtures^{38,53}.

Enthalpies for gases held in each population can be obtained from van't Hoff plots of k_D vs $1/T$ and b vs $1/T$. The values of b have been shown to have a higher dependence on T than does k_D ^{51,54}. In general, more negative enthalpies are seen for adsorbed gases as already discussed.

The value of c_H' has also been seen to be dependant on temperature^{51,54,55}. Koros⁵¹ has shown that the value of c_H' follows a linear relationship with $(T_g - T)$, and goes through the origin. Thus increases in temperature will reduce the concave curvature of the sorption isotherms³⁸ through both decreases in $(T_g - T)$ and in the density of the adsorbed gas

species. Since the density of adsorbed gas species are only mildly dependent upon T , this parameter is a reflection of the difference in the volumetric properties of the glass and true equilibrium liquid state at the given T .

The values of both c_{∞}' and b approach 0 as T approaches T_g , while the value of k_D approaches the value of the Henry's law constant for the gas in the liquid polymer⁵¹. Once the polymer-gas system has surpassed its glass transition point, all gas molecules in the polymer are by definition dissolved in the matrix. The result is reduced solubility of the gas in the polymer liquid state compared to that in the glassy state due to the loss of immobilized void space, and a decrease in the concentration of dissolved gas in the matrix with increasing T .

3.2.3 Free Volume Theory of Vrentas

Because of the nature of polymers, free volume theories remain one of the more preferred types of theories to describe a polymer's thermodynamic state. As discussed in Chapter 2, free volume theories are based on the existence of a specific amount of unoccupied volume within a compounds specific volume inherent to all chemical species.

In the liquid state, polymers are able to relax somewhat faster than the time scale of measurements. Upon impregnation by a gas, they are able to redistribute their free volume and attain a state of minimum free energy. In

other words, they are in equilibrium and standard thermodynamic relationships may be used.

The non-equilibrium nature of glassy polymers inhibits them from attaining an equilibrium state within the measurement time frame. As such, they can not be accurately modelled by conventional free volume theories. One of the most recent models for the description and prediction of glassy polymer-penetrant mixture properties is that of Vrentas^{38,46,47,53,56,57}. The model uses the volumetric behaviour of pure polymers and polymer-penetrant mixtures to predict the solubility of penetrants in glassy polymers.

The gas sorption theory of Vrentas extends the Flory-Huggins model to account for the non-equilibrium nature of the glassy polymer state through the e^B factor seen in equation 3.4 and 3.5.

$$\frac{p_1}{p_1^0} = \tau \phi_1 \exp(\phi_2 + \chi \phi_2^2) e^B \quad [3.4]$$

$$B = \frac{M_1 \omega_2^2 (C_{PP} - C_P) (dT_{gm}/d\omega_1)}{RT} \left[\left(\frac{T}{T_{gm}} \right) - 1 \right] \quad [3.5]$$

Equation 3.4 is restricted to $T < T_{g,m}$, and reduces to the Flory-Huggins equation when $T = T_{g,m}$, and thus $B = 0$, and if the gases are assumed to behave ideally. The penetrant pressure is denoted as p_1 , p_1^0 is the pure penetrant vapour pressure

at the measurement temperature; τ is a fugacity correction for non-ideality in the penetrant gas phase; ω_1 is the mass fraction of penetrant; $(C_{pg}-C_p)$ is the measure of the change in the polymer heat capacity at the transition; χ is the Flory-Huggins interaction parameter; and R and T have the usual meaning. The parameters ϕ_1 and ϕ_2 are the volume fractions of penetrant and polymer respectively, defined as

$$\phi_1 = \frac{\omega_1}{(\omega_1 + q\omega_2)} \quad [3.6]$$

$$\phi_2 = \frac{q\omega_2}{(\omega_1 + q\omega_2)} \quad [3.7]$$

and

$$q = \frac{V_2^\circ}{V_1^\circ} \quad [3.8]$$

where V_i° represents the specific volume of each component in its pure liquid state at the measurement T .

At high enough pressures, the correction for non-ideality in the gas phase can be significant. Equations 3.9 to 3.11 below show the correction for such factors through τ , where ν and ν° are the fugacity coefficients for the measurement and standard state, respectively.

$$\tau = (\nu^\circ/\nu) e^{-\nu} \quad [3.9]$$

$$v = \frac{f_1}{P_1} \quad , \quad v^o = \frac{f_1^o}{p_1^o} \quad [3.10]$$

$$y = \frac{\left(\frac{M_1 V_1^o}{RT} \right)}{(p_1^o - p_1)} \quad [3.11]$$

According to the Vrentas model, the sorption of gaseous penetrants by polymers is governed by the pure component properties C_p , C_{pg} , and V_2^o of the polymer, M_1 , p_1^o , and V_1^o of the penetrant, and the properties of the mixture (ie. the relationship between ω and $T_{g,m}$, and the value of χ). The values of V_1^o and p_1^o are not generally available for gases above their critical temperature but may be estimated from the vapour-liquid saturation curve or empirical equations such as those of Prausnitz⁵⁸.

The Vrentas model assumes the relationship seen in equation 2.1, such that the value of $(dT_{g,m}/d\omega_1)$ in equation 3.4 is constant. From Chapter 2, Figures 2.11 to 2.14, it can be seen that this equation is only applicable over a moderately small concentration range as the concentration of penetrant approaches 0.

The value of χ is representative of the strength of interactions occurring between the two components. From the Flory-Huggins theory, the χ parameter is defined by the relation

$$\chi = \frac{-W\sigma}{kT} \quad [3.12]$$

where W is defined as

$$W = W_{11} + W_{22} - 2W_{12} \quad [3.13]$$

and W_{11} , W_{22} , and W_{12} represent the pure component interactions for 1 and 2, and the interaction between components 1 and 2 respectively. The parameter σ is representative of the number of nearest neighbour interactions. Empirically, χ may be found from solubility parameter values by the following equation³⁸

$$\chi = 0.35 + \frac{M_1 V_1^0}{RT} (\delta_1 - \delta_2)^2 \quad [3.14]$$

where δ_1 and δ_2 are the solubility parameters for the gas and polymer, respectively.

For values of $\chi \leq 0.4$, the "unlike" interactions are at least as strong as the "like" interactions, and the penetrant may be considered a "good solvent". Conversely, when $\chi > 0.8$, the penetrant may be considered as a "poor solvent". If χ is large enough, phase separation or non-mixing will be seen.

As a consequence of the thermodynamic basis of the Vrentas theory, it predicts the sorption behaviour and volumetric behaviour strictly for samples prepared in a

reproducible manner. Commonly, this is done as follows⁵⁷:

The polymer-gas mixture is brought to an equilibrium state by heating it to a temperature above the glass transition temperature of the mixture, and then cooling it slowly to the measurement temperature. In this way only can a reproducible and definable state of the polymer be obtained.

To understand the predicted behaviour of this model, an analysis of the second derivative of p with respect to ω_1 (as ω_1 approaches 0) in equation 3.4 should indicate the dominant factors affecting the value and sign of the result. From this we see that

$$\frac{1}{p_1^0} \left(\frac{\partial^2 p_1}{\partial \omega_1^2} \right) = 2e^{(1+\chi)} e^{B_0} \left[-(1+2\chi) + \left(\frac{M_1}{RT} \right) (C_p - C_{pg}) A \left[\left(\frac{AT}{T_g^2} \right) + 2 \left(\frac{1-T}{T_{g2}} \right) \right] \right] \quad [3.15]$$

where B_0 is the value of B at $\omega_1 = 0$. For a glassy polymer-penetrant mixture ($T < T_{g,m}$), the sign of the second derivative of pressure with respect to ω will depend on the values of χ and A .

According to Vrentas⁴⁶, if χ is small, the second term in the brackets on the right hand side of the equation will dominate, and the sign of the result will be positive. This indicates a concave shaped sorption isotherm as is typically exhibited in glassy polymers.

One of the possible benefits of this model is that it

can predict some of the anomalous sorption behaviour seen in the literature. If χ is large, the equation predicts a convex curvature towards the pressure axis, similar to sorption behaviour seen for gaseous penetrants in rubbery polymers, even though the sorption involves a glassy polymer. So the theory predicts that sorption isotherms for good solvents show concave curvature towards the pressure axis, and for poor solvents will show convex curvature. However, it should be noted that sorption isotherms for slightly soluble gases in glassy polymers have, for the most part, shown typical concave behaviour^{49,59}.

3.3 Experimental

3.3.1 Apparatus

The apparatus used for solubility measurements was based on a design by Koros et al⁵⁰. The system was built and commissioned at the National Research Council of Canada. A schematic of the apparatus is shown in Figure 3.3. The system was designed to measure pressure changes over time to obtain equilibrium solubility data for gases in polymers.

The system consists of two volumes of approximately 12 mL each, to be referred to as the sample volume 1 [V_1] and sample volume 2 [V_2]. Two high pressure valves (1 and 2) were used to isolate V_1 and V_2 . These valves (NUPRO, model SS-4UW-TW) had an all-metal internal construction which eliminated possible extraneous sorption by polymeric seals

Figure 3.3 Schematic of gas sorption apparatus.

commonly used in valves. The cells were constructed from 3/4" VCR fittings. Stainless steel tubing of 1/4" o.d. was used for the gas inlet, while 1/8" o.d. tubing was used in the measurement side to minimize volumes.

The system was connected to a vacuum line, a pressure gauge [PG], a gas inlet, and pressure transducers [PT1 and PT2] (Setra, model 204) for the sample volumes V_1 and V_2 , respectively. The two pressure transducers were rated to 200 and 68 atm respectively. A pressure outlet was also incorporated for extra flexibility in the system.

A polymer film sample holder was built into the VCR nut of volume V_2 to accommodate polymer films of approximately 12 mm x 32 mm (Figure 3.4). Film samples were mounted onto threaded posts and held in place by nuts. The sample holder held a maximum of about 2.5 g of sample; for a 100 μ m film this represents about 30 pieces.

The transducers were calibrated with respect to vacuum and to room temperature saturation vapour pressure of carbon dioxide. Transducer PT1 registered a pressure of -0.2 atm under vacuum and +0.2 atm above the vapour pressure of CO_2 consistently. Using a gas reservoir [GR] of a known volume, the volumes of various parts of the system were accurately calibrated by the gas expansion technique using helium. The volumes were calculated to within ± 0.005 mL, with corrections made for valve volumes.

Figure 3.4 Film sample holder for gas sorption apparatus.

The entire system was isolated in an air bath to keep all experiments isothermal at temperatures of 35.0, 52.5 and 70.0°C. A temperature controller (Omega Systems, model 4201A-PC2) was used to keep the system at the desired temperature (± 0.1 °C). At higher temperatures, heaters connected to variacs were used to supplement the thermal output of the controller. Fans and/or squirrel cage blowers were used to circulate the air inside the bath. Several thermocouples were initially used to monitor temperature fluctuations over time and space inside the bath. All thermocouples, including the temperature controller, were calibrated with ice water and boiling water.

The system was monitored by an IBM compatible PC fitted with an IEEE interface (iotech) which recorded transducer readings over time from a Hewlett-Packard (model HP-3478A) 5½ digit digital voltmeter [DVM]. The frequency of transducer readings, which was dependant upon the time to complete sorption equilibrium, was varied from 5 to 30 seconds. The software used to collect the data was developed at the National Research Council of Canada.

3.3.2 Polymer Sample Preparation

3.3.2.1 Film Making

The polymer-gas systems studied were the same as those used in the high pressure calorimetry measurements. Polymer solutions of PS and PMMA were made in brown glass bottles to

5% (wt/vol). Polymer films were made by pouring a given amount of a polymer solution over a pool of filtered mercury in a 150 mm crystallization dish, and covered with a 170 mm watch glass that fit to the lip of the dish with no gaps. Using a volatile solvent for polymer solutions can cause problems with bubble nucleation in this type of film making process. However, if the solutions are well covered so that evaporation can proceed slowly (over 2-3 days), bubble nucleation will not occur. Dichloromethane was found to be the best solvent for making good quality polymer films.

Once the solvent was judged to have evaporated sufficiently, the film was removed from the dish. A stainless steel ring of approximately 130 mm diameter was used to cut away the outer edge of the film which tended to have a non-uniform thickness.

About 35 ml of solution was required to produce a film of 100 μm thickness. Film thicknesses were limited to a minimum of about 70 μm due to structural integrity problems encountered with thinner films during the annealing sequence. Films used ranged from 70 to about 200 μm depending on the diffusion rate for the given polymer-gas pair.

3.3.2.2 *Annealing and Conditioning of Film Samples*

The films were sandwiched between glass plates and annealed in a vacuum oven. The oven temperature was slowly

increased over several hours to about 20 °C below the pure polymer T_g , where it was held for about 24 hours. Then the temperature was raised slowly to about 3-5°C above the T_g of the pure polymer and held for another 24 hours. The samples were then cooled slowly to below the T_g , and let to cool to room temperature for a final 24 hours. In this manner, it was assumed that all the solvent was removed and that the polymer was free from any orientational strains that may have been produced during the evaporation sequence. This served to eliminate any history effects that may be frozen into the polymer, bringing the polymer film to a standard state before conditioning (see below).

Annealed films were weighed to obtain reasonably accurate values for the average thickness. They were then cut into the desired size (12 mm x 32 mm). Accurately known amounts of the film (1.5-2.0 g) were placed in the sample cell. The samples were contacted with the desired gas for at least twice as long as the amount of time required for sorption equilibrium to be accomplished. This was done at the lowest measurement temperature, and at a gas pressure just below the onset of the glass transition as defined in Chapter 2. This conditioned the polymer to an equilibrium solubility state, and produced a consistent reference state for solubility measurements by eliminating any time-dependant or concentration-dependant effects that may be induced in the polymer by sorbed gases.

3.3.3 Procedure

While under vacuum, valve 2 to the polymer sample compartment was closed. The sample volume V_1 was then filled with the required amount of gas to produce the desired pressure increase in V_2 , and valve 1 was closed. This was allowed to equilibrate thermally for at least 30 minutes. The readings from transducer PT1 were collected for several minutes before valve 2 was opened. This valve was left open throughout the measurements, and the readings from PT1 were collected.

Sorption experiments were done in both a sequential and random format. Sequences of increasing gas pressure experiments, without re-evacuating the polymer sample, were found to be as accurate as random solubility measurements. This allowed for a more efficient use of time since complete desorption of the solubilized gas can take twice as long as the sorption process.

Calculation of the gas sorbed by the polymer was done by two methods. First, mass balance calculations used the transducer readings from PT1 before opening valve 1, and at equilibrium solubility. Second, by extrapolating the sorption profile to time zero, a value for the initial pressure immediately after valve 1 was opened could be accurately made. The method of back-extrapolating to initial pressures may be seen in Figure 3.5. Solubility calculations were then done using the pressure difference

between the back-extrapolated initial pressure and the equilibrium solubility pressure.

Figure 3.5 Method of back-extrapolating to initial pressures for solubility measurements. The normalized transducer readings from PT1 and PT2 are shown versus time for PS-CO₂ at about 25 atm, 35.0°C.

3.4 Discussion

3.4.1 Methods of Measuring Solubility

In the measurement of solubility isotherms for gases in polymers, several methodologies are available. Some of the more prevalent methods are pressure decay as used here, gravimetry, and permeability. Pressure decay and gravimetry measure the sorption or desorption of gases by polymers via changes in pressure and sample weight, respectively. They are both direct methods of obtaining gas solubility and are essentially limited by the accuracy of the measuring devices and by the equation of state used. Permeability measurements, on the other hand, obtain solubility coefficients (s) indirectly since the permeability coefficient (P) is related to s by

$$P = D s \quad [3.16]$$

where D is the diffusion coefficient for the gas. The accuracy of indirect methods is usually not as good as that of direct methods.

In general, the solubility of gases in polymers will increase as the temperature decreases. Because of this, more accurate solubility data could be determined at low temperatures. Also, the reduction in the glass transition temperatures was significant enough that at higher temperatures, the pressure range over which sorption data could be obtained was limited. As will be apparent from the results, emphasis was placed on obtaining good low

temperature solubility data over the entire pressure range. From this, trends in solubility due to temperature effects could be studied.

3.4.2 Apparatus Limitations and Design Considerations

In pressure decay sorption measurements, the accuracy of the equation of state is paramount since quantitation of the amount of gas sorbed usually involves the difference of two large numbers (initial and final moles of gas) to obtain a relatively small number (the amount sorbed). The publications of IUPAC⁶⁰ serve as the best source for accurate p-V-T data. For the gases used in this study, accurate equations of state and p-V-T data are available, however this must be a consideration when using pressure decay to measure solubilities of less common gases.

The design used for the sorption apparatus allows for accurate measurements of pressure changes. Volumes V_1 and V_2 are approximately equal, maximizing pressure changes in the sample chambers. The apparatus developed here was used in a single-volume configuration where valve 2 (see Figure 3.3) would be left open for the duration of the experiment.

Initially, the apparatus was built to be used specifically in a dual-volume configuration, where valve 2 would be left open initially for only a short amount of time to introduce the gas to the polymer, and then closed. This provides for larger pressure changes and thus better

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PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

PRECISIONSM RESOLUTION TARGETS

accuracy in the measurements. However, the limiting factor was found to be the correlation between the two transducers when mass balance calculations were done. An error of $>0.5\%$ between the two transducers would contribute a large error in the final result. This was especially true for measurements of gases with low solubility, such as CH_4 .

Two transducers were used, even though only one was really required. The second transducer [PT2] served to check on the integrity of the system, and on the precision of the first transducer. Some measurements were done interfacing both transducers to a multiplexer [DA/C] which allowed for the measurement of both transducers PT1 and PT2 in sequence.

Most of the measurements were done simply by monitoring PT1 throughout the time required for complete sorption. This eliminated the requirement for a multiplexer, simplified readings, and reduced the errors in the final results. The quoted precision of the transducers was $\pm 1\%$ full scale, however actual measurements proved this to be a liberal estimate. It should be noted that since pressure differences were being measured, absolute accuracy of the transducers was not critical.

Initial testing of the system included extensive pressure testing for leaks, drifts in operating temperatures, anomalous sorption, and hysteresis in the transducers. Of these, drifts in the operating temperature

contributed the most significant errors.

3.4.3 Calculation Methodology

The densities of polymer samples were obtained using a helium pycnometer. These measurements were done at the National Research Council of Canada. A value of $2.5 \times 10^{-4} \text{ K}^{-1}$ for the thermal expansion coefficient of the glassy state was used to estimate volumes at the measurement temperatures. As well, swelling data from Wissinger¹⁶ was used to correct for volume changes due to sorbed gases. Swelling data was available only for CO_2 with PS and PMMA ($.10\% \text{ atm}^{-1}$, and $.12\% \text{ atm}^{-1}$); extrapolations from this for swelling effects due to C_2H_4 were based on a constant concentration effect. Polymers were assumed to swell insignificantly with CH_4 . Swelling estimates were imperative for volume corrections required in the calculations used for concentrations of gases sorbed by pressure decay.

Equilibrium pressure readings were collected over several minutes before starting a sorption run. Average equilibrium values for both initial and final pressures were used for mass balance calculations, while an extrapolated initial pressure was used along with the equilibrium final pressure for sorption measured directly from pressure changes.

The results from mass balance calculations and initial

pressure calculations showed good agreement for highly soluble gases such as CO_2 (Figure 3.6). However, for CH_4 which has a much lower solubility, the results by mass balance were dramatically affected by experimental errors. The mass balance technique was also found to incorporate larger uncertainties due to non-linearities in transducer readings over long pressure ranges, and larger errors from the equation of state particularly as the critical region was approached. In using the extrapolated initial pressure, linearity over only very small pressure ranges was required by the transducer.

The publications of IUPAC were used to obtain molar volume data (V_1^0) for each gas at the measurement conditions. For most temperatures and pressures used, the uncertainties in the molar volume data are quoted to be $< 0.1\%$. However, as the critical region is approached, these uncertainties rose to about $\pm 0.2\%$. Values for V_1^0 at a specific T and p were calculated by a linear average from tabulated data. This increased the inherent errors by a factor of 2 at least. Because of these inherent errors in using tabulated data for molar volumes, sorption calculations based on extrapolated initial pressures, in general, provided more precise solubility data than mass balance calculations. All sorption isotherm data quoted in Appendix III were obtained by the method of back-extrapolation.

Figure 3.6 Comparison of solubility data for CO_2 in PMMA at 35.0°C . The circles are values calculated by mass balance, dots are by back-extrapolation to initial pressure, and the solid lines are data from the literature. (1, Koros et al⁵¹; 2, Sanders et al⁶¹)

For sequential runs, the calculated moles sorbed during each successive runs was cumulative; errors in the data would also be cumulative. In Figure 3.6, the data shown is from both sequential and random solubility measurements, so these errors were assumed to not contribute to a significant extent.

In most cases the agreement with limited amount of data available in the literature was reasonable considering the wide range of factors affecting the accurate determination of solubilities and the inherent differences from one polymer sample to the next. The data in Figure 3.6 also indicates that concentration- and time-dependant effects on the polymer were sufficiently eliminated by the conditioning procedure. Comparisons of results from this study with those available in the literature are shown in Figures 3.6 to 3.8.

The pressure limit for solubility measurements was governed by the onset of glass transition. This was estimated from the data obtained in Chapter 2. The solubility quoted is given as mL of gas at standard T and p, per gram polymer. These trends shown in Figure 3.6 to 3.8 are linearly proportional to a molality concentration. Values for the molar volumes at STP used to calculate these values were obtained from IUPAC tables as well.

Figure 3.7 Pressure-solubility relations for C_2H_4 in PMMA at 35.0°C . The solid line represents data from Koros et al.⁶².

Figure 3.8 Pressure-solubility relations for CO₂ in PS at 35.0°C. The solid line represents the data of Wissinger¹⁷.

3.4.4 Factors Affecting the Data

One of the main factors affecting the study of solubilities in polymers is the irreproducibility of data due to the state of the polymer. This is a result of differences in the ways in which polymer samples are prepared. Irreproducible results may be due to stress orientation of the matrix, causing a redistribution of the free volume in the matrix. Residual solvents in the polymer matrix may also affect gas solubility through specific solvent-gas interactions. The result is that polymer samples cannot simply be compared on the basis of type, but must also be compared on the basis of history to have some idea as to the relative thermodynamic states of the glassy polymers. It is therefore of utmost importance that consistent annealing and conditioning of the polymer be carried out on every sample. Unconditioned or improperly conditioned samples will result in hysteresis in the isotherms, especially when gases which swell the polymer matrix are used.

3.4.5 Solubility Data

Pressure measurements were taken at pre-selected time intervals (5 to 30 seconds) depending on the polymer-gas system studied. The measurements were used to verify sorption equilibrium and for subsequent analysis of sorption rates of gases into the polymers. A typical pressure-time

profile is shown in Figure 3.9.

Solubility data were collected for CO_2 , C_2H_4 , and CH_4 in PS and PMMA. The solubility isotherms for all the systems studied can be seen in Figures 3.10 to 3.15. The isotherms show the typical concave curvature seen for glassy polymers, even for CH_4 where errors in the data are relatively large. The gas solubility and concave behaviour is reduced at higher temperatures in agreement with what is seen in the literature.

The errors in all figures showing solubility data were based on errors in the molar volume data, sample volumes, and fluctuations in temperature. While low pressure measurements had a higher error due to transducer imprecision, the measurements of higher pressures were affected to a larger extent by temperature fluctuations. The result is an estimated constant error of 5% for all solubility data for CO_2 and C_2H_4 . Since larger errors in the molar volume data are obtained at higher pressures, larger pressure steps were used to counteract this effect on the accuracy of the measured solubility. The errors for PS- and PMMA- CH_4 data are significantly larger due to the small pressure changes observed for these systems.

The solubilities for all three gases in PS at 35.0°C can be seen in Figure 3.16. It is interesting to note that the solubilities of CO_2 and C_2H_4 are essentially the same in PS, within experimental error. For these same gases in PMMA

Figure 3.9 Typical sorption rate profile; shown here is C_2H_4 in PS at $52.5^\circ C$.

Figure 3.10 Solubility isotherms for CO_2 in PS at 35.0 (circles), 52.5 (dots), and 70.0°C (triangles). The lines shown are calculated from Equation 3.1, fitted to the data using a non-linear least-squares regression analysis.

Figure 3.11 Solubility isotherms for CO₂ in PMMA at 35.0 (circles), 52.5 (dots), and 70.0°C (triangles). The lines shown are calculated from Equation 3.1, fitted to the data using a non-linear least-squares regression analysis.

Figure 3.12 Solubility isotherms for C_2H_4 in PS at 35.0 (circles), 52.5 (dots), and 70.0°C (triangles). The lines shown are calculated from Equation 3.1, fitted to the data using a non-linear least-squares regression analysis.

Figure 3.13 Solubility isotherms for C_2H_4 in PMMA at 35.0 (circles), 52.5 (dots), and 70.0°C (triangles). The lines shown are calculated from Equation 3.1, fitted to the data using a non-linear least-squares regression analysis.

Figure 3.14 Solubility isotherms for CH_4 in PS at 35.0 (circles), and 70.0°C (dots). The lines shown are calculated from Equation 3.1, fitted to the data using a non-linear least-squares regression analysis.

Figure 3.15 Solubility isotherm for CH_4 in PMMA at 35.0 (circles), 70.0°C (dots). The lines shown are calculated from Equation 3.1, fitted to the data using a non-linear least-squares regression analysis.

Figure 3.16 Solubility of various gases in PS at 35.0°C; C₂H₆ (circles), CO₂ (dots), and CH₄ (triangles).

Figure 3.17 Solubility of various gases in PMMA at 35.0°C; C_2H_4 (circles), CO_2 (dots), and CH_4 (triangles).

(Figure 3.17) the solubility of CO_2 is substantially higher than that of C_2H_4 . It should again be noted that the trends in the data reflect the relative number of moles of gas in the polymer.

There are some interesting trends in Figures 3.18 and 3.19. Considering the chemical similarity of CO_2 and PMMA (carbonyl groups present in both), it was not surprising to see that CO_2 solubility in PMMA is significantly higher than in PS. Based on a corresponding states argument, it might be expected that the solubility of CO_2 would be slightly higher for CO_2 than C_2H_4 in both polymers. Therefore, it is interesting to see that the solubility of C_2H_4 is essentially the same in both polymers, and that the solubilities of CO_2 and C_2H_4 in PS are essentially identical.

Clearly there are some types of preferential interactions occurring in these polymer-gas systems. Based on the differences in the chemical make-up of both these polymers, it may be extrapolated that there are no significant specific interactions with C_2H_4 and either polymer. The high solubility for CO_2 in PMMA is thus attributed to strong favourable interactions between the polymer and gas. From the solubility data in PS, there would appear to be some weak repulsive interactions occurring between CO_2 and PS which act to produce a solubility similar to C_2H_4 in PS. Unfortunately, the amount of information available is not sufficient to allow for the

Figure 3.18 Solubility of CO₂ in PS (circles) and PMMA (dots) at 35.0°C.

Figure 3.19 Solubility of C_2H_4 in PS (dots) and PMMA (triangles) at $35.0^\circ C$.

quantitative differentiation of the relative interaction strengths of any particular polymer-gas pair.

An interesting trend is noted when the trends in solubility isotherms are compared to T_g - p profiles of Chapter 2. For all polymer-gas combinations, the two sets of experimental data show the same trends for the depression in T_g with pressure, and in approximately the same ratios, as that seen for the solubility with pressure. It was shown in Chapter 2 that preferential interactions do not affect the glass transition temperature of the mixture. From the results seen here it appears that preferential interactions affect the solubility of a gas in a polymer at a given pressure. Thus, the behaviour of T_g with p can be rationalized by the dependence of gas solubility on p .

Due to the scatter in the solubility data for CH_4 , not a great deal of information may be obtained from analysis of its solubility isotherms. A qualitative comparison of solubilities shows that CH_4 has approximately the same solubility in both polymers at a given T and p , and that solubility is reduced somewhat by increases in temperature, as expected. It is worth noting that while there was no solubility data available to compare with the CH_4 at the same temperatures, data obtained from the literature for CH_4 in PS at 25 and 30°C shows significantly higher solubilities than those measured here^{49,61}.

3.4.6 Heats of Sorption

Heats of sorption may be obtained from the temperature dependence of solubility. Values were obtained for the systems PS-CO₂ and -C₂H₄, and for PMMA-CO₂. Accurate determinations for PMMA-C₂H₄ could not be made. Imprecision, and the lack of sufficient data at higher temperatures, inhibited sorption enthalpies from being obtained for polymer-CH₄ systems as well.

The van't Hoff plots for PS-C₂H₄ at 5 and 15 atm pressure are shown in Figure 3.20. The solubility values used in this figure were obtained from the line of best fit for the sorption isotherms in Figures 3.10 to 3.15. The linearity in the trends of $\ln(s)$ with $1/T$ over the T range and between the two pressures suggests an essentially frozen polymer configuration, unchanged by the presence of the gas at moderate pressures. The average heat of sorption over the pressure and temperature range studied was found to be -19.5 kJ mol⁻¹ for PS-CO₂, -21.6 kJ mol⁻¹ for PS-C₂H₄, while that for PMMA-CO₂ was found to be -22.5 kJ mol⁻¹. The uncertainties in the data used, especially at the higher temperatures, are expected to contribute significantly to the errors in the measured heats of sorption (eg. $\pm 10\%$). The correlation of the data (r^2) to the lines of fit from the van't Hoff expression are $>.98$. The magnitudes of the heats of sorption determined from this study agree reasonably well with the limited data available in the

Figure 3.20 van't Hoff plot for C_2H_6 in PS at 5 (triangles) and 15 atmospheres (dots).

literature^{51,54}. In all cases, exothermic trends for the heats of sorption were seen.

3.4.7 Analysis by the Dual-Mode Model

The fit of the dual mode equations to the data is fairly insensitive to the values of b and c_H' . This is especially true for limited data sets or data sets which contain significant scatter, and prohibits them from being used to accurately determine dual mode parameters. With the exception of the data sets obtained for sorption isotherms at 35.0°C, an accurate analysis of the data using the dual-mode model was not possible. The dual mode parameter values obtained from this study are compared with literature values in Table 3.1. A qualitative analysis of the changes in the solubility trends with temperature will be made based on a dual mode formalism. It should be noted that the lines of best fit to the solubility isotherms shown in Figures 3.10 to 3.15 were obtained from a dual-mode fit of the data.

The values for the dual mode parameters shown in Table 3.1 were determined from a non-linear regression analysis of the data. Since the experimental data from this study at 35.0°C is a compilation of several sets of sequential sorption routines, the dual mode parameter values determined are assumed to be reasonably accurate. For all polymer-gas systems, the correlations of the data (r^2) to the dual-mode equation are $\approx .7$.

Table 3.1: Dual mode parameters determined for CO_2 and C_2H_4 in PS and PMMA at 35°C from this study and the literature.

polymer	gas	k_D	b	c_H'
PS	CO_2	.379	.133	9.43
PS	C_2H_4	.370	.106	12.7
PMMA	CO_2	.930	.654	4.14
PMMA	C_2H_4	.347	.402	10.6
PMMA ⁵¹	CO_2	1.14	.218	14.9
PMMA ⁶¹	CO_2	.916	.236	12.6
PMMA ⁶¹	C_2H_4	.531	.259	7.09
PMMA ⁶²	CO_2	.944	.158	19.7
PMMA ⁶²	C_2H_4	.461	.189	12.4

***Note:** dimensions of k_D is mL of gas @ standard temperature and pressure per gram of polymer per atmosphere pressure, c_H' is in mL @STP per g polymer, and b is in reciprocal atmospheres.

In comparing these values to those obtained from the literature, a large range of values are seen for all parameters. This includes several values quoted from one group (see Table 3.1). This is a manifestation of the problems associated with obtaining a reproducible "state" for the glassy polymer. Thus comparisons of the dual mode parameters between polymer-gas systems are qualitative at best.

The parameters for both gases in PS are remarkably similar, with the exception of c_H' . The value of c_H' , the void volume or hole saturation constant is higher for C_2H_4 in both polymers. This is a result of the larger degree of curvature seen in C_2H_4 isotherms relative to CO_2 . Since

these polymer samples were conditioned with the gases before testing, it would seem that C_2H_4 was able to introduce more void volume into the matrix than CO_2 . It should be noted, however, that these trends do not agree with those seen in the literature based on the dual mode parameter values shown in Table 3.1.

Qualitatively, it may be seen from Figures 3.10 to 3.15 that one of the effects of temperature is to reduce value of k_D , indicating a reduction in the amount of gas dissolved in the bulk matrix. The increased linearity of the isotherms at higher temperatures reflects a relative decrease in the Langmuir population compared to the dissolved population. This coincides with more negative heats of sorption expected for the adsorbed populations.

The main downfall of the dual mode model is its lack of predictive ability. The three parameters required (k_D , c_H' , b) cannot be obtained from fundamental molecular properties or empirical correlations. The validity of the basic premise of the dual-mode model, the existence of two completely separate kinds of populations, has been questioned by several authors. Some suggest that a spectrum of sites should exist whose interaction energies would depend on the local site geometry^{63,64}, while others have attempted to use a continuous site model for Langmuir gas sorption in glassy polymers⁶⁵. However, it is worth noting that none of these models have proven in any case to be

superior to the dual-mode equation at correlating the experimental data⁶⁶.

3.4.8 Analysis by the Vrentas Free Volume Model

Prediction of the solubility of gases in polymers by the Vrentas model requires mostly pure component properties. The only mixture-based parameters required are the Flory-Huggins χ parameter, which can be calculated from solubility parameters (δ), and the plasticization strength parameter (A) of the penetrant in the polymer.

Despite the seemingly limited amount of information required for the calculation of the solubility isotherms, the difficulty remains in obtaining accurate values for the required parameters. For gases above their critical point, information is required on the hypothetical liquid state for both components (V_1° , p_1° , and V_2°). Values for the required parameters for PMMA, PS, C_2H_4 and CO_2 used to test the Vrentas free volume theory are shown in Tables 3.2 and 3.3.

Table 3.2 Pure component parameters required for Vrentas solubility calculation at 35.0°C*.

	δ (J/cm ³) ^{1/2}	V_1° (cm ³ /g)	M_1 (g/mol)	p_1° (atm)	f_1° (atm)
CO ₂	12.3	0.80	44.01	81.5	52.5
C ₂ H ₄	13.5	0.43	28.05	86.1	56.2
CH ₄	11.6	0.31	16.04	-	-
PS	18.6	1.0	-	-	-
PMMA	19.4	1.1	-	-	-

* All values from Prausnitz⁵⁸ at 25°C except f_1° ⁶⁷.

Table 3.3 Mixture parameters required for solubility calculation at 35.0°C.

	χ	q	$A(K)$
PS-CO ₂	0.90	1.25	1300
PS-C ₂ H ₄	0.47	2.33	2200
PMMA-CO ₂	1.04	1.38	1100
PMMA-C ₂ H ₄	0.51	3.55	1700

The values for δ and V_i° for all gases and polymers were determined from information found in the publication of Prausnitz⁵⁸; the hypothetical liquid vapour pressures (p_i°) were determined by extrapolation of the vapour-liquid saturation line to the measurement temperature; the fugacities of the hypothetical liquid state were calculated according to Prausnitz⁶⁷; χ values were calculated from equation 3.17; and values for A were determined from Figures 2.11 to 2.14 of Chapter 2. The predicted c-p profiles from equation 3.4 are compared to the data obtained in this study in Figures 3.21 to 3.24. Insufficient data were available for the prediction of CH₄ sorption data (ie. no A term available from Chapter 2). The corrections for the non-ideal nature of the gas according to the Vrentas model (equations 3.9 to 3.11) were found, by graphical comparison, to reduce the goodness of the fit to the experimental data, and so are not used.

Figure 3.21 Comparison of experimental data (dots) to that predicted by the Vrentas model (line) for CO₂ in PS at 35.0°C.

Figure 3.22 Comparison of experimental data (dots) to that predicted by the Vrentas model (line) for C_2H_4 in PS at 35.0°C.

Figure 3.23 Comparison of experimental data (dots) to that predicted by the Vrentas model (line) for CO₂ in PMMA at 35.0°C.

Figure 3.24 Comparison of experimental data (dots) to that predicted by the Vrentas model (line) for C₂H₄ in PMMA at 35.0°C.

For the determination of gas solubility from the Vrentas equations, the values for $T_{g,m}$ were calculated using equation 2.1 (page 22). A reasonable fit of the Vrentas predictions to the data from this study is found for PS-CO₂. However, the solubility values for CO₂ in PMMA were significantly under-predicted, while those for C₂H₄ in both polymers were over-predicted. These discrepancies seem to arise from the value used for χ . The smaller χ is, the more compatible the two phases are supposed to be. From solubility measurements it is expected that CO₂ will be interacting preferentially with PMMA relative to C₂H₄. Yet, the value determined from equation 3.14 produces a smaller χ value for PMMA-C₂H₄. The discrepancy in the results may be due to incorrect δ values used to calculate χ . The values for A are assumed to be fairly accurate since they were obtained from the experimental data of this study.

Based on a qualitative comparison of experimental data to that calculated from the Vrentas equations, the values of χ appear to be too small for the polymer-C₂H₄ systems, and too large for the PMMA-CO₂ system. The value of χ obtained from equation 3.14 (page 68) cannot be used to accurately reproduce solubility data for these polymer-gas systems.

Since the solubility parameter (δ) is related to the energy of vapourization of the substance, it cannot be truly defined for either SFs or polymers. Solubility parameter values for SFs may be determined from empirical equations⁶⁸

based on the density of the SF, while those for polymers can be obtained from experimental data for polymer-penetrant systems⁵⁸. The χ values used here are assumed to be more accurate than those used in the literature for PS-CO₂ (2.0), which was estimated from solubilities in the polymer melt⁴⁷.

It is worth noting that although the A parameters were not available for CH₄, values for χ could be obtained for these mixtures from solubility parameter data. The values were found to be 0.44 and 0.47 for PS- and PMMA-CH₄ systems, respectively. It is expected from this information, and a rough estimate of A from Chapter 2, that the solubilities would have been over-predicted for these systems as well.

In all cases, the trends in the calculated solubility seem to over-predict the concave curvature for the solubility isotherms. This is not likely to be due to the use of parameter values for 25°C rather than 35°C (Table 3.2) since it may be assumed that these values will not change dramatically over such a small temperature range. It is likely partially a result of the assumed ideal nature of the gas, and of the values used for A and χ used in the Vrentas equations.

The concave curvature in the sorption isotherms predicted by the Vrentas model agrees with the general trends seen in experimental data for highly soluble gases. However, most sorption isotherm profiles of poor solvents in glassy polymers show typical concave curvatures towards the

pressure axis as well, whereas the Vrentas model predicts a convex curvature. From the experimental data in this study, CH_4 would be considered a poor solvent, and Figures 3.14 and 3.15 do not substantiate a convex behaviour.

One exception to these observations has been the PMMA-water data quoted in the literature by Vrentas⁴⁶. The discrepancy in the sorption data observed for water in PMMA may be attributed to a critical adsorption pressure phenomenon described by Zhou et al^{69,70}. There appears to exist a critical pressure required for some non-adsorbing species such as noble gases, below which little if any Langmuir character is seen. Once the critical pressure is reached, sorption in the glassy polymer starts to take on its familiar concave curvature towards the pressure axis. It is possible that this phenomenon could be mistaken for a genuine convex curvature in the sorption isotherm associated with rubbery polymers only. The solubility of gases used here are likely too large to allow for this phenomenon to be verified. The discrepancy between the Vrentas theory predictions and literature data for very low solubility gases obviously needs to be addressed further, but is beyond the scope of this work.

Another discrepancy arises from the parameter A. At a constant χ value, the theory predicts that low values of A will produce sorption isotherms consistent with sorption in rubbery polymers (eg. convex curvature), and high values

will produce typical glassy polymer sorption isotherms concave to the pressure axis⁴⁷. A part of this discrepancy is due to the fact that, according to the model, the plasticizing strength of the gas alters the shape of the sorption isotherm. Traditionally, sorption isotherms in glassy polymers are consistently concave to the pressure axis at low pressures regardless of the solubility or plasticizing strength of the gas. Also, the plasticizing strength of the gas has been shown to decrease with increasing concentration. Thus the use of a parameter whose value cannot reflect the changing nature of sorption with concentration will not be able to model the system adequately.

Unfortunately, there was no data available to estimate the variation of χ with T , so fitting the model to solubility data at higher temperatures, or determining ΔH_s values from the Vrentas theory, was not possible. There was also insufficient data to model the sorption profiles of CH_4 , which would have allowed for a test of the low solubility predictions of the model.

The Vrentas model does not contain any fitting parameters; ideally it should be able to predict volumetric and sorption behaviour from the pure component parameters. Although there is the requirement for two parameters to characterize the mixture, Vrentas^{38,46,47} notes that these parameters are not meant to be fitting parameters since

their values are available for a number of systems. However, in a number of situations using less common gases and polymers, it is likely that they would have to be estimated.

The applicability of a model which depends on hypothetical states, for which properties of only a few substances may be easily estimated, is a weakness of the model. It may thus be more applicable to systems where the penetrant is not a supercritical fluid. Its application for the prediction of solubilities of the systems tested here is limited at best.

3.4.9 Sorption Rate Data

A factor that need be considered in obtaining precise sorption rate data is the measurement time. An equilibration time of 3 to 6 hours was determined to yield the most reproducible results. The film thicknesses were tailored to produce the desired times to equilibrium. For the most part, films of about 100 μm were used. However, for CO_2 and CH_4 which had fairly fast diffusion into PS, thicker films were required (eg. 200 μm).

For all calculations of diffusion coefficients, Fick's law was assumed to describe the rate of sorption of the gas. Because of the use of sequential sorption data, where concentration increments were moderate, the values determined for D were assumed to represent the actual D at

each concentration.

3.4.9.1 Methods of Determining Diffusion Coefficients

There are a few different methods to calculate D from sorption rate data⁷¹⁻⁷³. These will be outlined in this section, along with a brief discussion of their strengths and downfalls.

A. Short-Time Slope

The change of the concentration of a penetrant in a polymer film with time follows the analytical relationship derived from Fickian physics

$$\frac{M_t}{M_\infty} = \frac{4}{\pi} \sqrt{\frac{Dt}{L^2}} \quad [3.17]$$

A plot of the mass sorbed at time t (M_t) over the mass sorbed at equilibrium (M_∞) versus $t^{1/2}/L$ is referred to as a reduced sorption plot. Here, only the slope of the initial linear portion of the sorption curve is required to obtain the diffusion coefficient.

B. Half-Time Sorption

The diffusion coefficient may be quantitatively estimated by

$$D = \frac{0.049 L^2}{t_{1/2}} \quad [3.18]$$

where $(t_{1/2}/L^2)$ is the time of sorption at one half equilibrium solubility normalized to film thickness.

C. Moment Analysis

By integrating over the sorption curve,

$$\tau_s = \int_0^{\infty} \left(1 - \frac{M_t}{M_{\infty}}\right) dt \quad [3.19]$$

where τ_s may be used to determine D through

$$D = \frac{L^2}{12\tau_s} \quad [3.20]$$

for sorption in a film.

The diffusion coefficients for all system were calculated by all three methods outlined above and tabulated in Appendix IV. The results from all three methods compare reasonably well considering the inherent errors that each method has as a result of experimental technique.

The results of short-time slope are chosen to represent the systems best for a few reasons. First, half time sorption measurements are dependant upon a single point in the sorption profile and are thus more prone to errors than the other methods. Second, the use of moment analysis requires accurate data for the entire sorption profile. Third, the determination of the short-time slopes from reduced sorption profiles reduces can reduce errors in calculations of D since anomalies in the pressure readings may be eliminated⁷³.

Sorption curves and reduced sorption plots produced from the sorption rate data assumed that the mass sorbed over time was directly proportional to the change in pressure. The error incorporated because of this assumption was $< 0.5\%$ at the highest pressures used.

For PS-C₂H₄ and PMMA-CO₂, the trends in D with penetrant concentration can be seen in Figures 3.25 and 3.26. It is expected that the errors in the trends of D with c are large since the results portrayed are two calculated properties. The values obtained agree reasonably well with the very limited data available in the literature^{65,74}.

Based on the data obtained at 35.0°C, the effect of penetrant concentration in the polymer matrix was very moderate at lower concentrations, but rose dramatically as the penetrant concentration approached the glass transition "concentration", so that there was an exponential-like rise in the measured diffusion coefficients for most of the gases. The trends of D with p for these same two systems (Figures 3.27 and 3.28) are similar to those seen with p , except with slightly less curvature. These trends observed in D with c or p are unlike those seen for solubility or glass transition temperatures in this study, where the measured parameters show their largest effects in the lower concentration/pressure regions. It is likely a reflection of the volumetric properties of the polymer-gas mixture. From the literature, trends in swelling with p are fairly

Figure 3.25 Diffusion coefficients versus concentration for C_2H_4 in PS at 35.0 (circles), 52.5 (dots), and 70.0°C (triangles). Lines of fit are shown to indicate trends in the data.

Figure 3.26 Diffusion coefficients versus concentration for CO₂ in PMMA at 35.0 (circles), 52.5 (dots), and 70.0°C (triangles). Lines of fit are shown to indicate trends in the data.

Figure 3.27 Diffusion coefficients versus pressure for C_2H_4 in PS at 35.0 (circles), 52.5 (dots), and 70.0°C (triangles). Lines of fit are shown to indicate trends in the data.

Figure 3.28 Diffusion coefficients versus pressure for CO_2 in PMMA at 35.0 (circles), 52.5 (dots), and 70.0°C (triangles). Lines of fit are shown to indicate trends in the data.

monotonic for PS- and PMMA-CO₂ mixtures¹⁷.

Further evidence of the dependence of D on volume were based on the observed increases in D with increasing T, opposite to the effect of temperature on penetrant solubility. It was seen that increases in temperature dramatically affect the rate of penetrant diffusion in the matrix. Also, when comparing diffusion coefficient isotherms, there appears to be a larger effect of concentration at higher temperatures. Because of the limited amount of data, and the scatter in D values at higher temperatures, little further may be said concerning this point.

3.4.9.2 *Activation Energies of Diffusion*

Arrhenius plots may be used to obtain activation energies of diffusion for gases in the glassy polymer. A plot of $\ln(D)$ versus $(1/T)$ for PMMA-CO₂ at 5 and 15 atm is shown in Figure 3.29. The lines fit to the data were used to obtain the average activation energy of diffusion over the temperature range studied.

The activation energy of diffusion obtained from this data agree well with the literature data for diffusion rates of CO₂ in glassy PMMA⁵⁴. The activation energies for the systems studied are: 28 kJ mol⁻¹ for PS-CO₂, 33 kJ mol⁻¹ for PMMA-CO₂, 28 kJ mol⁻¹ for PS-C₂H₄, and 35 kJ mol⁻¹ for PMMA-C₂H₄. The values for D were taken from the lines of fit to

Figure 3.29 Arrhenius plot for CO_2 in PMMA at 5 (circles) and 15 (dots) atm. The lines drawn indicate the average value of the activation energy of diffusion over the temperature range studied.

the data (eg. as in Figures 3.27 and 3.28). Errors in the calculated activation energies are expected to be at least $\pm 10\%$ due to uncertainties in the data. The correlation (r^2) between the data and the line of fit from the Arrhenius expression is $>.98$.

The magnitude of the activation energies of diffusion is indicative of the glassy state of the polymer. As with heats of sorption being more exothermic for the glassy state, activation energies will also be relatively larger due to the extra energy required to activate the adsorbed populations for transport. The larger activation energies seen for penetrant in PMMA agrees with the trends observed in diffusion rates, which were significantly smaller for all gases in PMMA. Activation energies could not be determined for CH_4 due to insufficient accurate data.

4.0 EXTRACTIONS FROM POLYMERS USING SUPERCRITICAL FLUIDS

4.1 Introduction

Plastics have become one of the most widely used groups of materials in our man-made environment. Because of their high strength to weight ratio and low production costs, economics have driven their replacement of traditional materials such as wood, glass, and metal⁷⁵.

Most plastics require additives to improve or tailor the polymer's properties for a specific use. As well, during the production of polymers, additives and stabilizers are used to improve the material's resistance to degrading processes (eg. light, heat, and oxidation). The result is a final product which may contain a wide variety of chemicals incorporated in the matrix.

Recently, the purity of plastics has come into question. The concern is mainly over the more mobile compounds from the plastics migrating, and accumulating in significant quantities, in the contained substance. This is especially true in cases of human-contact uses (eg. hospital equipment, beverage containers).

Methods for determining the types and concentrations of chemicals in the polymer matrix are varied^{76,77}. Traditional methods such as dissolution/reprecipitation of the polymer and soxhlet extraction can be time consuming and incomplete. Non-destructive spectrophotometric techniques such as UV and IR have been employed, however they tend not to be

sufficiently sensitive, and yield information only on functional groups and not on chemical species. Quantitative differential thermal analysis has been used to determine the total amount of chemicals present in the matrix, but this method is not very sensitive and cannot differentiate between chemical types. While high resolution NMR has proven to be successful in elucidating and quantifying chemicals in polymers, the costs incurred in obtaining results from this technique may not be justified.

4.2 Theory

4.2.1 Introduction to Supercritical Fluid Extraction

Within the last decade, some of the major benefits of supercritical fluids (SFs) in chemical analysis and materials processing have been realized. The major benefit of supercritical fluids over traditional extraction solvents are their superior transport properties. Unlike extractions from most other solid materials, the chemical species to be removed from polymers are contained within the matrix. In the case of extractions from polymers, SFs may have a further benefit. Compared to liquids, high pressure gases can be quickly sorbed by a polymer. As a result, SFs have been used to extract a variety of chemicals from many types of polymers^{8,15,78-83}.

4.2.2 Thermodynamics and Kinetics of Extraction from Polymers

Compounds contained within the matrix must be able to diffuse through it to be extracted, so the kinetics of diffusion as well as thermodynamics of solubility and partitioning of the solute between the SF and polymer phases must be considered. It is generally accepted though that extractions from polymers are limited by the kinetics of solute diffusion through the matrix^{78,84}. Also, for extractions from polymers, consideration must be given to the effects that SFs have on the polymer's properties. The roles that both kinetics and thermodynamics play in the extraction process will be discussed.

The different physical processes that contribute to the rate of extraction of chemicals from polymers may be seen in Figure 5.1. Kinetic processes that can affect the rate of extraction will include (1) the rate of SF impregnation of the matrix, (2) the diffusion of chemical species through the polymer matrix to the surface of the particle, (3) the rate of desorption of the chemicals from the surface of the polymer, and (5) the rate of diffusion of the free solute species in the SF. The thermodynamics of the system will govern only process (4), the partitioning of the chemical species between the polymer and SF phases.

Although it would seem that the partitioning may be outnumbered by the variety of kinetic processes that may be

Figure 4.1 The factors involved in extractions from polymers. These are impregnation of the polymer by the SF (1), migration of the solute in the polymer (2), desorption from the polymer surface (3), partitioning between the polymer and SF phases (4), and solute diffusion through the SF (5).

involved in the extraction, this in no way means that the kinetics must dominate.

As a first approximation, it is generally considered that the impregnation of the polymer particle by the SF (factor 1, Figure 4.1) and the rate of diffusion of the chemical species through the SF phase (factor 5) are not rate determining steps. The rate of extraction will be governed by the remaining factors.

A significant difference in extractions from polymers compared to that from other matrices is that changes in the conditions of extraction affect the state of the matrix. This section will deal with what is known about the effects of temperature, pressure, solvent, solute, and matrix character on the extraction efficiency. The intention of this chapter is to delineate the relative roles of the kinetic and thermodynamic factors governing SF extractions from polymers.

4.2.2.1 *The Effect of Pressure on Extraction*

In the vicinity of the critical point, the density of a SF changes rapidly with pressure. This results in an increase in the loading capacity of a solvent for a given solute, which can lead to an improvement in extraction efficiency. The density of the SF will also affect the rate of solute dissolution. Thus the molecular weight and nature of the solute will dictate to what extent the solvent can

accommodate the solute, so that higher molecular weight species and more polar species will be more efficiently extracted by a more dense fluid^{1,78,82}. These factors are partially responsible for the phenomenon of selective extractions using SF solvents.

The opposing effects that gas pressure may have on a polymer matrix must be addressed as they pertain to extraction rates. Pressure acts to densify the polymer, likely reducing the rates of diffusion of species within the matrix. The dominant effect, however, is the increased gas solubility in the polymer which plasticizes the polymer and increases the mobility of species in the matrix. The result of all these factors is that increases in pressure will generally lead to an improvement in extraction efficiency. Figure 4.2 shows the effect of temperature in the extraction of diisooctyl phthalate, chlorinated polythene wax, and Topanol CA from PVC powder at 460 atm for 30 minutes, at 5 mL/min SF flow.

4.2.2.2 *The Effect of Temperature on Extraction*

In a reverse manner to pressure, increases in temperature will decrease the density of the SF, all else equal. To a first approximation, this will result in a decrease in the solute solubility, and a reduction in extraction efficiency. However, solubility studies have shown that the increased activity of the solute due to an

Figure 4.2 The effect of pressure on amount extracted; all other parameters constant⁷⁹.

Figure 4.3 The effect of temperature on amount extracted; all other parameters constant⁷⁹.

increase in temperature can counter the effects of the lower density¹. Therefore, solute volatility must also be considered when the optimization of extraction conditions is the goal.

From the matrix point of view, an increase in temperature will reduce the solubility of the gas in the matrix. However, it will also act to increase the mobility of compounds within the matrix and improve transport properties in the solvent. Thus increases in temperature generally also have a beneficial effect on extractions from polymers. The results in Figure 4.3 are for similar extractions as shown in Figure 4.2, showing the effect of pressure in extractions at 95 °C for 15 minutes.

4.2.2.3 *Matrix Effects*

The nature of polymer and solute will affect the rates of diffusion of species through the matrix. Increases in the surface area of the sample (ie. grinding) will improve the extraction rate⁷⁹, indicating that diffusional processes have a significant role in governing extraction rates.

It has been observed that plasticization of the matrix by SFs can induce crystallization in semicrystalline polymers. Crystallinity will reduce extraction efficiencies by impeding the migration of compounds through polymers. Since only amorphous polymers are being considered in this study, such effects will not be discussed further.

4.2.2.4 Solute/Solvent Effects

The wide variety of compounds that may be present in polymers dictates that both diffusion and solubility factors must be considered. Such compounds may range from high molecular weight and highly polar substances such as stabilizing and functional additives, to residual solvents, monomers and low molecular weight oligomers. While common SFs like CO_2 can dissolve low molecular weight substances quite easily, the solubility limits and rates of dissolution of highly polar or high molecular weight substances can play a major role in determining the overall efficiency of an extraction¹.

The effect of solvent type has been studied in extractions from sands and soils¹, but has not been addressed to any significant extent insofar as extractions from polymers are concerned. Limited study of the effects of cosolvents such as methanol in extractions from polymers has been done⁷⁹.

A note of caution is warranted at this point. In seeking better methods of extracting substances, SF solvents other than CO_2 are frequently used without due consideration for possible hazards. N_2O is considered as a possible alternative since it has similar critical conditions to CO_2 , and contains a permanent dipole which may provide for a superior solvating fluid. However, its highly oxidative nature raises concerns when using this solvent with

oxidizable substances. Since hydrocarbon polymers are inherently oxidizable, the use of N_2O as an extractant for any polymer is not recommended.

4.2.2.5 *Factors to be Studied*

Despite the potential for SFs in the area of quantitation of compounds present in polymers, only a handful of papers may be found on the subject^{14,21,79,80,82,83}. Studies on the effects of T and p are the most prevalent; work in this area on samples similar to the ones used in this study have been published^{14,15}. For this reason, no detailed work on the effects of T or p were performed.

The main goal of SF extractions in this study was to determine the relative extraction efficiencies of two different SFs whose effects on a polymer's physical properties had been well characterized. The detailed studies of effects on the glass transition, solubility, and diffusion effects studied here opened the door for a comprehensive study of relative effects of the gases CO_2 and C_2H_4 on SF extractions from polymers. Extractions were performed on PS only.

Compounds that are of environmental and health concern are those present in significant quantities, and which may migrate rapidly through the matrix. Since rates of diffusion are inversely proportional to the molecular sizes of the compounds²¹, smaller or lower molecular weight

species are generally of highest concern. For this reason, extractions performed on PS will focus on the quantitation of monomer, and the semi-quantitative analysis of dimer, and trimer.

4.2.3 Modelling Extractions from Polymers

As mentioned, the extraction of species from polymer via traditional methods can be time consuming and incomplete. While extractions using SFs can drastically reduce time requirements, exhaustive extractions may still take several hours¹⁵. One solution to this problem is to model the rate of extraction so that exhaustive extractions are not required. The "hot-ball" model of Bartle et al⁷⁸ uses the mathematics of Fickian diffusion to predict compound concentrations in the polymer matrix. It is referred to as the "hot-ball" model simply because it assumes a physical equivalence to the solution of heat flow out of a hot sphere placed in a cold fluid. Some inherent assumptions of the model must be addressed.

The first assumption specifies that all polymer particles are spherical in shape, and that the solute is distributed uniformly throughout the matrix. The second assumption requires the concentration of solute in the solvent to be nil at all times. Strictly speaking, this model is applicable only for dynamic extractions where all of the solute diffusing to the surface is immediately swept

away by the solvent. Finally, the migration of material through the matrix is assumed to follow Fickian diffusion.

The Fickian equation for the diffusion of a compound through a spherical geometry is

$$\frac{m}{m_0} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left(\frac{1}{n^2} \right) \exp \left(\frac{-n^2 \pi^2 D t}{r^2} \right) \quad [4.1]$$

which is basically a sum of exponential decays^{71,78}. Here, m_0 is the total amount of a species present in the matrix initially, m is the amount left in the matrix at time t , D is the effective diffusion coefficient of the compound being extracted from the matrix, and r is the radius of the spherical polymer particle. Unless specifically stated otherwise, the term D and references to diffusion-limiting processes will represent the rate of migration of the solute through the polymer only.

As indicated by Bartle et al⁷⁸, at sufficiently long time periods the sum in equation 4.1 may be replaced by a single exponential decay. A plot of $\ln(m/m_0)$ versus time will be linear in this region (Figure 4.4). The slope of this plot is equal to $-1/t_c$, where t_c is the characteristic time of extraction.

$$t_c = \frac{r^2}{\pi^2 D} \quad [4.2]$$

The value of t_c is related to the initial time required for the rate of extraction to fall to a simple exponential

Figure 4.4 Hot-ball model analysis; plot of $\ln(m/m_0)$ versus t_r for the basic model (a), compared to an enhancement of solute extracted (b), and inhibition to extraction (c)⁸¹. The m parameters are used to quantify the total solute concentration in the polymer from equation 4.3.

dependence on time. Ideally, a plot of $\ln(m/m_0)$ versus time should be linear when $t > \frac{1}{2}t_c$. This relationship is commonly exhibited for real samples^{78,85}. The parameter t_r refers to the reduced time of an extraction, and is equal to the ratio of t to t_c .

The intercept of this linear portion on the y-axis will ideally be equal to -0.5. This however is rarely the case for real samples. Intercepts that are not equal to this indicate a deviation from the ideal model. According to Bartle et al⁷⁸, reasons for the deviation from the expected value are due to irregularities in the shapes of the particles, solubility limitations, and non-uniformities in the solute concentration. These will act to raise or lower the intercept based on how they affect the initial amount of compound extracted from the polymer.

The phenomenology of the diffusion of solute out of the particle, according to the hot-ball model, is as follows. During the initial period of extraction, a steep concentration gradient is present at the surface of the particle, and solute desorbs from the particle at a rate faster than a simple exponential decay. In the ensuing time period, the step in the concentration gradient inside the particle becomes progressively less steep, until such a time that a smooth concentration gradient is set up and the rate of diffusion of solute remaining in the polymer particles decreases exponentially with time. It is this phenomenology

that is responsible for the intercept being equal to -0.5 in the ideal case.

From equation 4.1 above, Bartle et al⁷⁸ were able to formulate an analytical expression to calculate the total amount of solute (m_0) in the polymer

$$m_0 = m_1 + \left(\frac{m_2^2}{(m_2 - m_3)} \right) \quad [4.3]$$

where m_1 is the initial amount extracted from time zero to time 1, and m_2 and m_3 are the amounts of solute extracted during two subsequent equal extraction time periods (see Figure 4.4). This equation above can quantitatively predict the total amount of solute present so long as the mass collected during the time m_1 incorporates the initial non-exponential period of decay in the solute concentration within the polymer particle (ie. $m_1 = m(t_x)$, where $t_x > \frac{1}{2}t_c$). This may be verified from a plot of $\ln(m/m_0)$ versus t as in Figure 4.4.

The basic shape of the extraction curve will not be affected by non-idealities in the system such as non-spherical particle shape (Figure 4.5). Such factors affect only the steepness of the initial portion of the extraction rate profile and characteristic times of extraction. The result is that the time to exhaustive extraction will vary with changes in system parameters relative to the "hot-ball" ideal state. The accuracy of the final result using equation 4.3 will depend on the precision of the

Figure 4.5 Comparison of extraction profiles predicted by the Hot-Ball model (a), with an enhancement of extraction (b), and an inhibition of extraction (c). The dashed lines show the expected result from the hot-ball model in (b) and (c).

quantitation technique used for measuring solute collected in the extracts, and the extent to which the extraction was carried out. Understandably, more precise results can be obtained from longer extractions^{14,84}.

Bartle et al^{84,85} extended the basic diffusion-limited model to take into account the possible effects that a solubility limitation may have on the extraction. The extension assumes that the solvation properties of the fluid affect the solute solubility in the SF and the partitioning of the solute between the two phases equally. The equation produced is

$$\frac{m}{m_0} = 6 \sum_{n=1}^{\infty} \frac{\left(\frac{hr}{a_n}\right)^2}{(hr(hr-1) + a_n^2) \exp\left(\frac{-a_n^2 D_{eff} t}{r^2}\right)} \quad [4.4]$$

where a_n are the roots of the equation

$$a \cot(a) = 1 - hr \quad [4.5]$$

The difference between the two models is the use of the parameter h , defined as

$$h = \frac{KCF}{A_s D_{eff}} \quad [4.6]$$

where F is the flow rate of solvent, A_s is the surface area of the particles, C is the solubility of the solute in the solvent, D_{eff} is the effective diffusion coefficient for the extraction process (incorporating all contributing kinetic factors), and K represents a constant for a particular

temperature and polymer-solute system. The parameter h is a compilation of the factors which affect the extraction process (Figure 4.6).

Figure 4.6 Hot-ball model plots of $\ln(m/m_0)$ versus t_r . Curve 2 is for high values of h , indicating a diffusion-limited extraction; curve 1 has a low value for h and is indicative of other factors, such as partitioning, playing a dominant role⁶⁵.

4.3 Experimental

4.3.1 Apparatus

The apparatus used to perform extractions from polymer samples is shown in Figure 4.7. The system was designed and commissioned at Carleton University. It uses a Milton-Roy Mini-pump reciprocating piston pump [P] (type: NSI-33R; model: 920231) rated to 400 atm. All tubing used was either 1/8" or 1/16" stainless steel HPLC tubing (Chromatographic Specialties) coupled with Swagelok fittings. A section of coiled and flattened 1/8" tubing was placed in-line, after the pump, to suppress pressure pulses from the pump. A Span Instruments flow-through pressure gauge [PG] was used to monitor pressure, and a VALCO six-port switching valve [V] was used to monitor the flow of SF through the system.

The extraction cell [C] was designed and constructed at the Science and Technology Centre, Carleton University. The cell body (ca. 12 cm long X 2 cm o.d.) was made from 410 stainless steel fitted with removable threaded caps constructed of hardened SS and sealed with teflon gaskets. The internal cell space was designed to accommodate two soxhlet thimbles (12 mm X 50 mm) with a minimal amount of void volume. Into the top of each cell cap was tapped a 1/4" NPT thread, to which were fitted 1/4" NPT to 1/16" Swagelok unions.

The flow of the SF was controlled by crimping the end of 1/16" ss tubing. These restrictors were preferred over

Figure 4.7 Schematic of supercritical fluid extraction apparatus. The meanings of the captions are given in the text.

fused silica capillary tubing as they gave more reproducible flow rates. A bubble flow meter [FM] was used to measure gas flow rates from the restrictor.

Extracts were trapped in glass vials [T], heated by rubberized heating tape (Omega), and filled with methanol (Fisher Scientific, HPLC grade). They were analyzed by HPLC-UV (Varian model 9010 and 9050 respectively) fitted with an autosampler (Varian model 9095). The chromatographic method used a 20 μ L injection volume with a mobile phase of pure methanol flowing at 1.5 mL/min. A wavelength of 247 nm was determined to be optimal for use in the detection of styrene. A GC-MS (Varian Saturn II) was used to identify some of the solutes trapped, and to test for non UV-absorbing species in the extracts.

Polymer samples used were the same as those quoted in previous sections. The polymer samples were freeze ground and sieved to +30-60 mesh size to obtain a standard size fraction; the granules of polymer were between 0.5 and 1.0 mm diameter.

Extractions were performed with CO_2 and C_2H_4 . It was necessary to cool the head of the reciprocating pump when using CO_2 to prevent vapour-lock in the check valves. This cooling was not required when pumping C_2H_4 due to its lower critical temperature and sufficient fluid density at room temperature. Extra caution should be taken when using C_2H_4 as a SF solvent due to its flammability. Since C_2H_4 at

ambient conditions is slightly less dense than air, it can be easily and safely directed up a fumehood vent without problem.

4.3.2 Procedure

Approximately 3 g of polymer sample was accurately weighed (Mettler, model AE160) into two 12 mm X 50 mm cellulose extraction thimbles (Whatman, single thickness). With the thimble tops folded over, they were placed upright into the cell. The top cell cap was tightened onto the cell using an adjustable torque wrench (Norbar) set to 55 ft*lbs. The cell was placed into a water temperature bath and equilibrated for at least 30 minutes. A second section of coiled tubing was used here to ensure that the fluid entering the cell was thermally equilibrated. Once sufficiently equilibrated, the main valve from the gas cylinder [G] was opened and pumping of fluid into the cell commenced immediately. The time required to achieve a pressure of 305 atm was about 2 minutes for CO₂, and about 4 minutes for C₂H₄. Time "zero" for the extraction was set when the pressure was within 5 atm of the final value, at which time the switching valve [V] was opened. Sampling times varied from 5 minutes to 2 hours depending on the length of the extraction run, system conditions, and the stage at which the sample was taken.

Samples were collected in clean, pre-weighed (empty)

glass vials, which were filled with about 20 mL of methanol. The samples, once removed from the extraction system, were covered and left to cool in a dry, dark place. Once cooled, they were re-weighed to obtain an accurate volume of extract, and then analyzed by HPLC. Calibration of the detector for styrene (I) was done by multipoint external standards made new every day. Samples were tested in a random order on the HPLC.

Extractions were done at least in duplicate for each set of conditions. The conditions for extractions can be seen in Table 4.1

Table 4.1: Extraction conditions used in this study

Type	T (°C)	p (atm)	ρ (g/mL)	gas flow (mL/min)	T_r	p_r	ρ_r
CO ₂	60.0	305	.836	90	1.09	4.20	1.79
C ₂ H ₄	60.0	305	.388	120	1.18	6.15	1.81
C ₂ H ₄	35.0	210	.389	90	1.10	4.25	1.80

A "standard" set of conditions (60 °C and 305 atm) was used for both C₂H₄ and CO₂. Gas flow rates were 120±10 mL/min for C₂H₄ and 90±10 mL/min for CO₂ under these conditions. A set of extractions was also completed for C₂H₄ at 35 °C and 210 atm; this corresponded to essentially the same reduced temperature and pressure as CO₂ at standard conditions. The reduced parameters (T_r , p_r , ρ_r) correspond

to the actual parameter values (T , p , ρ) normalized by their respective values at the critical point (T_c , p_c , ρ_c). The terms "standard" and "reduced" will be used to specify the extraction conditions used for C_2H_4 . It should be noted that the terms "standard" and "reduced" conditions will be used interchangeably when referring to CO_2 as these conditions are the same in both cases.

Extractions which incorporated an initial "static" conditioning period (ie. no gas flow) of 1 hour were completed at standard conditions with both SFs. Most extractions were carried out for three to four hours; at least one exhaustive extraction ($t > 8$ hours) was also performed with each SF.

4.4 Discussion

For reasons of clarity, this section will be presented as follows. First, a discussion of extractions from PS using SFs (section 4.4.1) and an analysis of significant sources of experimental errors will be presented (section 4.4.2). Then, the data from extractions at various conditions will be compared (section 4.4.3). An analysis of the data by the hot-ball model will follow (section 4.4.4). Finally, a summary of results, and conclusions obtained based on knowledge obtained from the previous chapters, will be presented (section 4.4.5). By reporting the information in such a manner, hopefully a clearer picture of extractions of compounds from polymers using SFs will be given.

4.4.1 Background

Some initial work in the area of SF extractions from PS has been done previously in our laboratory^{14,15}. These extractions were on commercial PS samples (Styron 688) which contained large amounts of additives (>1000 ppm). These samples were pellets (2mm diameter X 3mm length), used as supplied by Dow Chemicals Canada. For proprietary reasons, the types of additives cannot be named; they were however significantly higher molecular weight species than the monomer.

The procedure used here was basically the same as used previously with the exception of grinding the sample and

performing exhaustive extractions. Strictly UV absorption was used to quantify monomer previously. Results indicated that the amounts of chemicals extracted, other than monomer, were below the limit of detection. The amounts of styrene (I) extracted however were significant. After 6 hours, more than 0.15 mg of monomer was apparently extracted from a 1 g sample. A "hot-ball" analysis indicated this to be about 30% of the total amount present in the matrix¹⁴. Samples used in the present study were additive-free.

4.4.2 Experimental Errors

The main source of experimental uncertainty in the quantitation of compounds extracted by this procedure is associated with the detection method. Here, HPLC-UV was used which provided a detection limit of about 0.1 ppm for styrene in methanol. Reproducibility in the chromatograms was about $\pm 5\%$. These errors will not be indicated on the forthcoming figures for reasons of clarity. While the limits of detection in terms of concentration are not known for dimer (II) and trimer (III), it is known that they were frequently much closer to their limits of detection than the monomer, and thus will likely have higher experimental uncertainties.

The amount of monomer determined in the extract will likely be less than the amount actually extracted due to losses during trapping. These losses were estimated from

test runs using a 20 ppm standard styrene solution as the trapping solvent under similar conditions used during a standard CO₂ extraction. Over a 30 minute time period approximately 10% of the amount of styrene initially present was lost. Quantification of the amount of a given solute in a polymer must therefore take this into consideration, especially when using heated traps and high gas flow rates for relatively volatile compounds. While sample grinding can improve extraction rates, concerns over reduction in compounds present in the matrix due to the grinding process must be considered if accurate quantitation is the goal.

Blank extractions were done on empty soxhlet thimbles, staggered between other runs, to determine if there were interferences or carry-over of material from one run to the next. None were observed.

The flow rate of gas through the restrictor was kept constant by heating the trap solvent. If not heated, expanding CO₂ at the tip of the restrictor would solidify, causing sporadic flow. All trap solvents were preheated before use. The error in the measured flow of gases from the trap was significant due to problems in keeping the trapping system gas-tight.

As indicated in the experimental section, the flow rates used at standard conditions were not the same for CO₂ and C₂H₄. This was not deemed to be critical since it is assumed that the extraction process is diffusion limited, so

that the important factor in the extraction rate should be time⁷⁸.

4.4.3 Extraction Results

4.4.3.1 Reproducibility

The results of four separate extractions under identical conditions with CO₂ are shown in Figure 4.8 to indicate reproducibility in the extraction results. Agreement is good between all results. Deviations in the results may be attributed to small variations in the extraction conditions, precision in the quantitation method, and minor procedural changes which took place initially from run to run. The deviations in the results from one run to the next are expected to increase with extraction time due to compounding of errors.

4.4.3.2 Compounds extracted

Initial extractions were carried out with long collection time periods. During these runs, conditions of flow rate and collection time were optimized. HPLC-UV indicated three major absorption peaks at 247 nm (Figure 4.9). The first elution peak was confirmed as (I) through external standards. The second and third chromatographic peaks were essentially equally spaced apart in elution time, and were thus inferred to be (II) and (III). This seemed to be confirmed by GC-MS (Figure 4.10). Other compounds in the

Figure 4.8 Comparison of several extraction runs with CO_2 at standard conditions showing reproducibility. Deviations are expected to increase with time due to compounding of errors.

Figure 4.2 Chromatograms showing relative amounts of I, II, and III extracted as time progressed. Sample (a) was collected 2 hours into the extraction, (b) at 4 hours, and (c) at 8 hours.

Figure 4.10 Total ion trace (a) and selected ion traces for monomer (104, b), dimer (208, c), and trimer (312, d) from GC-MS chromatogram of extract.

extracts were also seen by GC-MS. It is known that they are not the result of solvent impurities, but no attempts were made to identify them since it was not certain that they were obtained from the extraction process.

It was determined from the chromatographic analysis that samples collected early during an extraction contained mostly monomer. As time proceeded, the samples contained increasing amounts of II and III collected relative to I (Figure 4.9, a to c). This observation is consistent with a diffusion-limited extraction process from polymers.

An interesting phenomenon was the appearance, from the HPLC chromatograms, that more III was being collected than II. From GC-MS chromatogram, however, significantly larger peaks were obtained for II. It is assumed that the extinction coefficient for these oligomers will increase with the number of monomeric units since the phenyl substituents are the cause of the sorption of light. This may be responsible for producing the smaller peaks for dimer in the UV absorption signal. A second option is that these compounds were not dimer and trimer as designated. This possibility is not likely, nor of great concern since only semi-quantitative discussions of the results for II and III will be made.

4.4.3.3 Comparison of SF type at "standard" conditions

The comparison of CO_2 and C_2H_4 at standard conditions (305 atm, 60 °C) may be seen in Figures 4.11, indicating the relative amounts of I collected during the extraction runs. Similar trends were seen in the cumulative amounts of II and III collected. In comparing the trends observed in Figure 4.11, it is obvious that under these conditions C_2H_4 is initially superior to CO_2 at extracting monomer from PS. However, it also appears that a greater amount of I is extracted using CO_2 . It is also noteworthy that the PS granules contacted with C_2H_4 at standard conditions were fused to a solid mass, unlike those contacted with CO_2 which remained more or less as granules. The implications of this will be discussed further in the section 4.4.3.7.

The higher flows of gases used for C_2H_4 extractions (ca. 25%) indicates that the actual residence time per mole of C_2H_4 is slightly less than for CO_2 . However, a comparison of molar volumes under these conditions (eg. 52.6 mL/mol for CO_2 and 72.2 mL/mol for C_2H_4) indicates that the flow rate for C_2H_4 (0.39 mL/min) at these conditions was almost twice as much as for CO_2 (0.21 mL/min). While this seems to account for the difference in the extraction rates seen in Figure 4.10, it should be stressed again that extractions of polymers are generally thought to be limited by the diffusion rate of solutes through the polymer. In this case, the time of extraction will be the important factor.

Figure 4.11 Comparison of extraction profiles for styrene by C_2H_4 (squares) and CO_2 (dots) at standard conditions. Two extractions are shown for each SF.

4.4.3.4 Comparison of SF type at "reduced" conditions

Extractions were also done with C_2H_4 under the same reduced conditions as a standard CO_2 extraction. This required a pressure of 210 atm and a temperature of 35 °C. It should be noted that under reduced conditions the flow rate of C_2H_4 gas was identical to that of CO_2 at standard conditions (eg. 90 ± 10 mL/min).

When the two SF solvents are compared under similar reduced conditions, the extraction rates for I are remarkable similar (Figure 4.12). Similar trends were also seen for II and III. In this case, the granules of PS were similar in appearance after contact with either SF. This implies that a standard set of reduced conditions should provide equal extraction efficiency regardless of the SF solvent.

Since the flow of gas from the restrictor is now the same for both solvents, the contact time per mole of solvent is also the same. The difference between the flow rates of the two SF fluids through the cell now varies from 0.21 mL/min for CO_2 to 0.29 mL/min for C_2H_4 .

4.4.3.5 Static conditioning

Static extraction periods of one hour were performed with both CO_2 and C_2H_4 at standard conditions (Figure 4.13 and 4.14). While no significant gain in extraction efficiency was obtained in the case of CO_2 , a major effect

Figure 4.12 Comparison of extraction profiles of styrene by C_2H_4 (triangles) and CO_2 (squares) at reduced conditions.

Figure 4.13 Comparison of extraction profiles of styrene by CO_2 at standard condition, with (squares) and without (triangles) a one-hour static conditioning period. Time axis represents the time of dynamic extraction.

Figure 4.14 Comparison of extraction profiles of styrene by C_2H_4 at standard condition, with (squares) and without (triangles) a one-hour static conditioning period. Time axis represents the time of dynamic extraction.

due to static conditioning was observed for C_2H_4 . When considering the extra hour of extraction time utilized in the static mode, the overall efficiency of extraction was reduced in both cases. This indicates that there is no benefit in the use of a static extraction period in this case for the removal of even relatively highly mobile species from the polymer matrix.

4.4.3.6 *Comparison of extraction rate profiles*

The differential extraction profiles of both CO_2 and C_2H_4 (Figures 4.15 and 4.16) indicates that about 30 minutes is required to reach the peak extraction rate from the polymer particles for both SFs at standard conditions. This occurs despite the higher flow rate of C_2H_4 through the cell and the larger amounts of compounds extracted. The time to reach the peak extraction rate was found to be slightly longer (ca. 50 minutes) under reduced conditions for C_2H_4 . However, the flow rates for C_2H_4 under reduced conditions are still higher than those seen for CO_2 at standard conditions (section 4.4.3.4, pg 163).

In a dynamic extraction, the initially trapped solution of SF and solute will have had minimal contact time with the polymer. Since 20-40 minutes is the approximate time required to flow through one cell volume, it is possible that the observed trends are the result of a cell-flush effect. It should be noted that the results from runs

Figure 4.15 Differential extraction profile for styrene by CO_2 at standard conditions indicating the time to peak extraction rate.

Figure 4.16 Differential extraction profile for styrene by C_2H_4 at standard conditions indicating the time to peak extraction rate.

containing a static extraction period do not substantiate the cell-flushing idea. During these extractions, the first sample taken almost inevitably contained the highest amount extracted.

4.4.3.7 Exhaustive extraction results

Exhaustive extraction results for I and II by CO_2 and C_2H_4 are compared in Figure 4.17 and 4.18, respectively. For CO_2 , it is seen that the extraction of I is almost complete after 8 hours, however II (and III) continued to be removed at a substantial rate (Figure 4.18). This is unlike that seen for C_2H_4 . It appears as though the amounts of solute extractable by CO_2 are larger than those with C_2H_4 .

While it had appeared initially that C_2H_4 was a superior extractant, the previous results suggest that it cannot completely remove all of the solute. Losses during the trapping of extracted solutes may be ruled out since, for CO_2 , the amounts of II and III continue to rise after I has been essentially completely removed. The results of the exhaustive extraction performed at standard conditions for C_2H_4 indicate that the amounts of I, II, and III levelled off at the same time, and all at amounts significantly below that observed with CO_2 , and even below that seen with C_2H_4 at reduced conditions when Figures 4.11 and 4.12 are compared.

Figure 4.17 Comparison of exhaustive extraction profiles of styrene by CO₂ (dots) and C₂H₄ (triangles) at standard conditions.

Figure 4.18 Comparison of exhaustive extraction profiles of styrene dimer by CO_2 (dots) and C_2H_4 (triangles) at standard conditions.

4.4.4 "Hot-Ball" Model Analysis

4.4.4.1 Basic Model Analysis

An analysis using the "hot-ball" model from previous work using equation 4.3 indicated the amount of monomer contained in a similar polymer sample to be 470 ± 40 ppm^{14,15}. Analysis of all runs performed in this study amenable to the use of this model (8 runs) indicate a concentration of I in the polymer matrix of 320 ± 20 ppm. Although this is significantly lower than that seen from previous results, it should be noted that the analysis done previously was by UV detection only. Those results might be expected to be high as a result of other compounds and/or oligomers extracted which absorb in the same region. Losses during trapping and due to grinding are not likely to produce such a large effect. Since the PS used in the two analyses were different commercial samples from the same supplier, the agreement between the two results is good.

Plots of $\ln(m/m_0)$ versus time can be used to determine extraction efficiency relative to the ideal model. The value of the intercept relative to the ideal case (-0.5) will give some indication of the non-ideal nature of the extraction, while the slope of the linear portion will be representative of the rate of the extraction. The values determined for the time to reach linearity ($\frac{1}{2}t_c$) were used as a double check on the time period m_1 of extraction used to calculate m_0 from equation 4.3 (pg 143).

There are any number of factors that may be rationalized as the cause of non-idealities in the extraction rates, but the most likely causes are partitioning and diffusional effects. Other factors, such as polymer particle geometry and non-uniform solute distribution in the matrix, will not be discussed here.

Plots of $\ln(m/m_0)$ versus t for extractions using C_2H_4 and CO_2 at the same reduced conditions can be seen in Figures 4.19 and 4.20, respectively. The linear portions of the plots yield a slightly larger value for C_2H_4 than CO_2 (-1.0×10^{-2} and -8.4×10^{-3} respectively); in both cases the intercept is significantly higher than the ideal case ($+.24$ and $+.10$, respectively). Based on these results, it may be concluded that some factor is acting to reduce the rate of extraction during the initial part of the extraction process. This will be discussed further in section 4.4.5.

By plotting $\ln(m/m_0)$ versus time for the dynamic extraction portions of CO_2 extractions which incorporated a static conditioning period (Figure 4.21), it can be seen that the profile more closely resembles the ideal case, with an intercept at about $-.25$. Although strictly speaking the hot-ball model is only applicable to completely dynamic extractions, its ability to delineate factors affecting extraction conditions is formidable.

Since it is logical to assume that partitioning effects should be constant in both dynamic extractions and static

Figure 4.19 Hot-ball model analysis of the extraction of styrene by C_2H_4 at reduced conditions.

Figure 4.20 Hot-ball model analysis of the extraction of styrene by CO_2 .

Figure 4.21 Hot-ball model analysis of the extraction of styrene by CO_2 with one hour static conditioning.

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conditioning periods at a given set of conditions, then the concave curvature towards the time axis observed during the initial portion of a strictly dynamic extraction must be attributed to some diffusion-limiting effect.

The profile of $\ln(m/m_0)$ versus time for C_2H_4 at standard conditions shows a significantly different result than previously seen. Although initially the profile appears similar to some standard "real case" results from the literature^{78,85}, a close analysis indicates that two separate linear portions exist in the profile (Figure 4.22). This is substantiated by the determination of $(\frac{1}{2}t_c)$ equal to 25 minutes for the initial linear portion which extends for about 60 minutes. It seems that two separate processes were occurring; an initially fast process of extraction which fell off rapidly to be replaced by a much slower one. So while C_2H_4 appears to be a superior extractant initially, it would seem that some process occurs after an initial extraction period which severely hinders the ability of C_2H_4 to quantitatively remove I from the polymer.

4.4.4.2 Analysis of Modified "Hot-Ball" Model

Modifications to the hot-ball model were made by Bartle et al^{84,85} to account for the non-idealities in extractions from polymers. The stipulations put forth in the modification are that a finite concentration of solute exists in the solvent at the solvent-polymer interface. The

Figure 4.22 Hot-ball analysis of the extraction of styrene by C_2H_4 at standard conditions.

assumptions are that the rate of extraction is limited by the rate of deportment of the solute from the polymer surface, which encompasses both the kinetic and thermodynamic factors, and the flow rate of the solvent.

There undoubtedly exists a concentration gradient of solute, in the SF, in the vicinity of a polymer particle. Since the diffusion rate for compounds in SFs are undoubtedly much higher than in the polymer, arguments based on solvent saturation at the polymer-SF interface would appear to be unsubstantiated.

While the flow rate does have some effect on the efficiency of an extraction, it has been shown in published works that the flow rate of solvent has little effect on the rate of extraction even for non-polymeric matrices¹.

Another implicit assumption of this modification suggests that the steady-state of the system is rapidly established. Results from this study refute this assumption, in that it has been shown that there exists an initiation time to maximum extraction rate from the polymer which is finite and measurable. The time required to reach the steady state can dramatically affect the initial extraction efficiency, which is when the majority of solute is usually removed.

It was also assumed in the formulation of the modified equations that partitioning effects are a direct reflection of changes in the solubility of the solute in the SF. While

this assumption may be applicable for extractions from the surfaces of soils or sands where the matrix is unaffected by the SF, this assumption is likely not valid in the case of extractions from polymers. This fact is based on the evidence of previous chapters which indicate that the state of the polymer is dramatically affected by T and p.

The extension of the diffusion-based "hot-ball" model to accommodate a solubility limitation will now be addressed. From the amounts of styrene extracted, it may be estimated that the maximum possible concentration of monomer in CO_2 would be about 10 ppm. This is based on 10 ppm monomer extracted (over 10 minute period) from a 3 g polymer sample into 5 mL of solvent (flow accumulation for 10 minutes) at a density of about 0.9 g/mL. This is well below the estimated miscibility of about 0.1 mole fraction I in CO_2 at 60°C and 305 atm⁸⁵. Similar arguments may also be made for the concentrations of I in C_2H_4 . Thus other factors which affect the extraction rate dominate over a solubility limitation in this case.

From equation 4.6 and Figure 4.6, it may be seen that an increasing value for C acts to increase the rate of solute extraction from the matrix. If this parameter is considered as a reflection of the partitioning between the two phases, then its use is justified. Also, increases in the diffusion rate of the solute through the matrix reduce the time of extraction by reducing the characteristic time

of extraction (equation 4.2). However, the use of A_s appears to contradict an increase in extraction efficiency with increasing surface area, while the use of F seem to be unnecessary since extractions from polymers and solids in general is independent of flow rate. It would seem that the latter two parameters of the modified hot-ball model do not properly represent the extraction process. It may be of more benefit simply to use the basic model and rationalize non-idealities in the extractions based on known facts.

4.4.5 Overview of Extraction Results

For extractions from most solid matrices, it is assumed that the solubility of the solvent in the matrix is nil¹. This is not the case with polymer matrices. Data obtained here and in the literature indicates that the solubility of high pressure gases can be substantial, and that their effects on the matrix can be as significant as those due to liquid solvents.

The trends in the reduction of T_g with pressure (Figures 2.9 and 2.10) suggest that for a good many SF extractions, the polymer-gas mixture will be in a liquid state. The presence of the gas in the polymer plasticizes the matrix allowing for dramatic increases in the migration rates of species in polymer.

The kinetic factors generally governing extraction rates are the rate of solute diffusion in the polymer and

the rate of desorption of solute from the matrix surface. Based on the strong plasticization strength that CO_2 has on PS, it is expected that the migration rate of styrene through the matrix should be high. It was determined in Chapter 3 that the interactions between CO_2 and PS are weak and possibly even unfavourable. The value of χ (0.90) for PS- CO_2 substantiates this conclusion. Since it may be assumed that styrene will interact strongly with PS, this suggests that the rate of desorption of styrene from the polymer surface could also be a limiting factor.

However, for extractions from PS using CO_2 , the incorporation of an initial static conditioning period did not affect the rate of extraction of styrene (Figure 4.13). Clearly then kinetic factors can be ruled out. The results obtained indicate a thermodynamically governed extraction process. In this case, the rate of extraction of styrene from PS by supercritical CO_2 is governed by the partitioning of styrene from the polymer into the solvent phase.

From the extractions at standard conditions which contain a static conditioning period, the partition coefficient for styrene between the SF phase and the PS phase may be estimated. Here, the partition coefficient is defined as the mass of solute per gram solvent (ppm styrene in SF), divided by the mass of solute per gram in the PS phase. This may be estimated accurately for CO_2 as 0.080 at standard conditions. For C_2H_4 however, it is not known

whether saturation of styrene in the SF phase was attained. The partition coefficient is thus estimated to be approximately 0.25 from the data available.

For extractions from PS using C_2H_4 , a rather significant increase in the initial rate of extraction is seen when using a static conditioning period (Figure 4.14). This indicates that kinetic factors are contributing significantly to the rates of extraction in this case. As with CO_2 , C_2H_4 is a strong plasticizer of PS, and appears to interact only minimally with PS. Both solute diffusion rate through the polymer and desorption rate from the polymer surface may be contributing factors here.

While significantly larger amounts of styrene were collected during the initial stages of extractions which contained a static conditioning period, the differences in the amounts extracted at the two conditions shown in Figure 4.14 are less than would be expected if diffusion of styrene through the matrix was the sole contributing factor.

Based on the chemical similarities of styrene and C_2H_4 , it is assumed that the interactions between them will rival the interactions between styrene and PS. This agrees with the fact that the extraction of styrene by C_2H_4 is not limited to any significant extent by the partitioning of styrene between the two phases. This is further substantiated by the partition coefficients calculated for CO_2 and C_2H_4 at "standard" extraction conditions.

One of the main factors affecting extractions from polymers that tends to be overlooked is the changes in the matrix that will occur at high pressures such as those used in SF extractions, and the effects that this has on extraction rates. A comparison of extractions by C_2H_4 at "standard" and "reduced" conditions (Figures 4.11 and 4.12) can be used to exemplify this. If it were to be assumed that gas pressure effects on the matrix were negligible, so that the extraction process was limited by the thermodynamics of distribution of the solute between the two phases, then the increase in extraction efficiency observed on going from 35°C and 210 atm. (reduced conditions) to 60°C and 305 atm (standard conditions) for C_2H_4 would be a direct result of the increase in the chemical potential of the solvent.

The increase in the solubility of styrene in C_2H_4 upon changing extraction conditions (reduced to standard) is estimated to be roughly 4 fold using EOS based calculations¹. This agrees reasonably well with increases seen in the extraction rates in Figures 4.11 and 4.12. However, since the extraction of styrene from PS using C_2H_4 was shown to be limited to a large extent by kinetic factors, it is implied that large changes in the properties of the plasticized matrix also affects the rate of extraction on going from "reduced" to "standard" conditions. The point is that it cannot be realistically assumed that

the changes in the state of the polymer matrix will not affect the extraction rate.

In all extractions performed here, there was seen a time lag from the start of an extraction to the time of maximum extraction rate. This was shown through extraction rate profiles (Figure 4.15 and 4.16) and a hot-ball model analysis (Figure 4.19 and 4.20) of the data. The time to reach the maximum rate was about 30 minutes for CO_2 at "standard" extraction conditions. Since all extractions which incorporated an initial static period (both CO_2 and C_2H_4) showed maximum extraction rates from the very first sample, the cell-flush idea was eliminated as the major cause of the time-lag.

Tests performed previously on PS samples¹⁵ of considerably larger particle size (ie. 2 to 3 mm thick as compared to 0.5 to 1 mm thick in this study) showed a time lag of approximately 120 minutes to achieve the maximum extracted rate. Based on the relative sizes of the particles used, and the relationship between the time to equilibrium sorption and sample thickness (t proportional to L^2), a time of 20 to 40 minutes is expected for complete impregnation of the polymer samples by the SF for this study. Thus, the time lag to peak extraction rate is a result of the initial time required for the SF to completely plasticize the polymer matrix. Not until the polymer is completely plasticized by the SF can the solute migrate from

the matrix at its maximum rate.

The determination of significant impregnation times of the polymer by the SF indicates that kinetic factors of some magnitude are always present in SF extractions from polymers. This fact also inhibits the hot-ball model from providing a realistic description of the extraction process since one of the basic assumptions of the model is that such processes are assumed to be instantaneous.

The initial lag time for extraction seen for CO_2 and C_2H_4 at standard conditions were very similar, while that for C_2H_4 at reduced conditions was approximately twice as long. Not only does this further substantiate the time requirement for impregnation of the polymer, but it has significant implications towards the plasticization effects of these SFs at the extraction conditions.

From Chapter 3, it was seen that diffusion coefficients for C_2H_4 in PS were about an order of magnitude smaller than for CO_2 . Since the solubilities of the gases in the polymer are very similar in the glassy state the change in the rates of impregnation, and relative rates of impregnation, for the two SFs into the polymers is thought to be mostly due to the superior plasticization strength of C_2H_4 as compared to CO_2 at the conditions of extraction. The higher molar volume of C_2H_4 compared to CO_2 suggests that C_2H_4 swells the liquid polymer to a larger extent⁸⁷.

The stronger plasticization effect of C_2H_4 was not

without cost. At standard extraction conditions, a reduction in the rate of styrene removal was seen at longer times. This resulted in a reduced efficiency of C_2H_4 to quantitatively remove styrene as compared to CO_2 . A hot-ball model analysis of this data (Figure 4.22) suggests that the initially fast extraction process was replaced by a much slower rate of extraction. Losses of solute during trapping sequences and partitioning effects have been eliminated as causes of this result. The observed effects on the extractions were thus attributed to sintering or fusing of the ground polymer particles.

The samples removed after contact with CO_2 under standard conditions and C_2H_4 under reduced conditions were fused together; the individual granules of polymer, however, were still discernible. The sample removed after contacting with C_2H_4 at standard conditions was a solid mass, without any observable trace of individual granules remaining.

The phenomenology of monomer removal from PS by C_2H_4 at "standard" conditions is as follows. The deportment of styrene was initially fast due to strong plasticization effects and a high affinity of styrene for C_2H_4 . At longer times, the rate was reduced as the polymer began to flow and fuse to a solid mass. The rate of extraction was then limited by the diffusion rate of styrene through the fused polymer. In such cases then, it may be more efficient to use lower T and/or p to optimize the extraction conditions.

The initially granulated sample which fused to a solid mass proved to be difficult to remove from the extraction cell after depressurization because of sample expansion due to foaming.

Generally, interpretations of the hot ball model do not consider solvent effects on the diffusion rates of solutes in the matrix. Since the extended model does have the ability to accommodate these effects through the D parameter in the equation for h (equation 4.6), it should be able to model effects of changes in diffusion rates on the $\ln(m/m_0)$ versus t profiles. The effects of such changes in h , and thus $\ln(m/m_0)$ would depend on the magnitudes of both D and C , and on how they change with changes temperature, pressure, and gas-polymer-solute type.

In summary, it has been shown here that the determination of the amount of monomer in PS can be done in a quantitative manner without the need for exhaustive extractions. The factors affecting the extraction rate, other than minor effects due to sample constitution, are the partitioning of the solute between the polymer and SF phases, the rate of diffusion of the solute through the polymer, and the desorption of the solute from the surface of the polymer. At relatively moderate pressures of CO_2 and C_2H_4 , PS is plasticized sufficiently that at ambient conditions it will be in a liquid state. While rates of solute diffusion in the polymer are dramatically enhanced by

the plasticization of the polymer by the SF, diffusional limitations to extractions must also include the initial impregnation of the polymer by the SF. Only with sound knowledge of the effects of SFs on the polymer matrix can the factors affecting the extraction rate be determined.

5.0 CONCLUSION

5.1 Summary

The modifications made to the calorimeter allowed for the measurement of the glass transition in polymer-gas systems to very high pressures. Proper annealing and preparation of the polymer-gas mixture allowed for reproducible calorimetric measurements of the effect of gas pressures on the glass transition temperature. A comparison with literature data from other methods used to determine the glass transition temperature shows fairly good agreement.

At a given pressure, CO_2 and C_2H_4 were equally efficient at plasticising PS ($-0.9^\circ\text{C}/\text{atm}$). The effect on PMMA for C_2H_4 was identical to its effect on PS, while CO_2 was a much stronger plasticizer of PMMA ($-1.2^\circ\text{C}/\text{atm}$). On the other hand, CH_4 showed only mild plasticizing strength for both polymers, and approached a $T_{g,m}$ minimum around 350 atm.

Chow's equation relates changes in the glass transition temperature to the moles of penetrant sorbed. It was found to fit the data from this study well at all gas concentrations. The value of z from Chow's equation was determined to be constant for each polymer. For PS, a value of $z=2$ was used, while a value of $z=1$ was required for PMMA. Based on the fit to the data, there may be some validity in assuming z to be a polymer specific.

The relative plasticizing strengths at a given pressure are affected only by the solubility of the gas in the polymer. This indicates that the plasticization of a polymer is not directly affected by specific polymer-gas interactions. This leads to the conclusion that $T_{g,m}$ is a colligative property. The use of equations based on a constant penetrant mass fraction effect to model $T_{g,m}$ was shown to be inaccurate even at moderate gas concentrations. Such relationships may be useful only in cases where the concentration of penetrant approaches zero.

Some thermal scans obtained at intermediate pressures seemed to indicate that a complex phenomenon may be occurring in this region. The retrograde vitrification phenomenon may be responsible for these observations, but could not be verified due to limitations associated with thermal scanning methods in defining this region.

The solubilities of the gases CO_2 , C_2H_4 , and CH_4 in glassy PS and PMMA were measured by pressure decay. Solubility isotherms generally follow a concave curvature in a plot of gas solubility versus pressure. At 35.0°C and 50 atm, the solubility of CO_2 in PS reaches about 30 mL of gas (at STP) per gram of polymer, while in PMMA it attains a solubility of about 50 mL/g. The solubility of C_2H_4 in both polymers is about the same (about 30 mL/g), while the solubility of CH_4 in both polymers at these conditions was found to be just slightly above 5 mL/g. The trends in gas

solubilities suggests that preferential polymer-gas interactions may have a significant effect on the solubility of a gas in a glassy polymer at a given pressure. Based on the results of Chapter 2, it is shown here that the changes in the trends in the glass transition temperature with pressure are a result of the relationship between gas solubility and pressure.

The calculated heats of sorption for these gases in PS and PMMA agreed well with the limited data in the literature. More exothermic heats of sorption are expected for the glassy state relative to the liquid state due to the sorption of gases into "frozen" void space in the matrix. The result is a reduction in the gas solubility with increasing temperature.

The dual mode model fit the experimental data very well. The strong plasticizing strengths of most of the gases studied limited the amount of data that could be obtained, especially at higher temperatures. Reasonable values for the dual mode parameters could only be obtained from this study at 35.0°C. The values obtained from a non-linear curve fit to the experimental data agree somewhat with those seen in the literature. The trends in values for the hole saturation constant, however, are opposite to that seen in the literature. These results may be attributed to the difficulty in obtaining a consistent glassy state for measurements even with seemingly identical polymer samples.

The Vrentas theory uses the concept of free volumes to predict the solubility of gases in amorphous glassy polymers. The theory requires a consistent experimental preparation procedure to allow for the estimation of the free volume of the glassy polymer-gas mixture. The theory was able to somewhat reproduce solubility data, but only at very low pressures (eg. < 10 atm). This may be due in part to the assumed ideal nature of the gases even at high pressures, and the adherence of the Vrentas theory to a gas plasticization effect based on the penetrant mass fraction. The exception to this was the PS-CO₂ system, where the Vrentas equations were able to reproduce solubility data reasonably well to significantly high pressures. Some of the discrepancies in the solubility predictions stem from inappropriate solubility parameter values used for the polymer-gas pair.

The diffusion of gaseous penetrants into glassy polymers were determined through sorption rate measurements. The effects of gas concentration in the polymer matrix were very moderate at lower concentrations, but rose dramatically as the gas concentration approached the glass transition "concentration", so that there was an exponential-like rise in the measured diffusion coefficients for most highly soluble penetrants. It was seen that increases in temperature increased the rate of penetrant diffusion in the matrix. The effect of increases in gas concentration may

also be enhanced by increases in temperature. All of these trends observed are unlike that seen for all other measured parameters (ie. solubility parameter, $s=c/p$, and $T_{g,m}$) which show their largest effects at lower temperatures, and in the lower concentration regions. The observed effects on D are assumed to be due to the volumetric properties of the polymer-gas mixture.

The extraction of styrene from polystyrene was performed using CO_2 and C_2H_4 at a variety of run conditions in attempt to elucidate the factors affecting SF extractions from polymers. The concentration of monomer in PS was determined to be 320 ± 20 ppm. This does not account for losses during trapping of the solute or from the grinding of the polymer particles. The result agree reasonably well with previous data for a similar PS sample.

At "standard" run conditions, the extraction of styrene from PS by CO_2 is governed mostly by the partitioning of styrene between the two phases. At a given T and p , C_2H_4 will initially extract more styrene from PS than will CO_2 . The factors determining the efficiency of extraction for C_2H_4 were found to be mostly kinetic in nature. These factors appear to be the diffusion rate for styrene through the polymer, and the rate of desorption of styrene from the surface of PS.

The calculated partition ratios for styrene between PS and C_2H_4 and CO_2 were 0.25 and 0.080, respectively. These

values reflect the preference of styrene for C_2H_4 as compared to CO_2 , and further substantiates the aforementioned factors which governed the extraction of styrene from PS using these two SFs.

At higher temperatures and pressures, the overall efficiency for extraction may be better with CO_2 than with C_2H_4 . This is a result of the effect C_2H_4 has on the PS matrix. Because of its higher molar volume, it is better able to swell the liquid polymer. The reduction in matrix viscosity results in the sintering or fusing of the PS particles. Such effects can severely inhibit the extraction process and produce a two-stage extraction process. In this scenario, the second stage of extraction is much slower, governed by the migration of compounds through the fused polymer.

While the basis for hot-ball model may not provide an accurate picture of the extraction process from polymers, its equations can be used to determine factors affecting the extraction rate. Modifications to the model have been proposed to further account for factors which affect the rate of extraction of solutes, such as changes in the rate of diffusion of the species in the matrix and thermodynamic limitations to the extraction rate. The model, however, still does not consider the impregnation process of the polymer by the SF, which has been shown to be the limiting process during the initial stages of extraction.

5.2 Future Work

Based on this work, suggestions for further research into the area of supercritical fluids and polymers include:

- An in-depth study of the retrograde vitrification phenomenon. Because of the high solubility of CO₂ in PMMA, this system would be a likely candidate for such a study.
- The quantification of polymer-gas interactions would determine the extent to which such interactions affect the solubility of gases in polymers. Inverse gas chromatography has shown some promise in this respect.
- A study of the effects of low solubility gases on the glassy polymer, and the critical adsorption pressure phenomenon may help to better understand the ways in which polymers and gases interact.
- Extractions of various species from polymers in attempts to determine the roles of thermodynamics and kinetics in the quantification of extraction efficiency. This would help in developing analytical methods for the determination of the concentrations of solutes in the polymer.

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APPENDIX I. Production of Microcellular Plastics

High pressure gases can cause foaming of the polymer matrix during depressurization steps of processes in which the two phases come into contact. If the solubility of the gas is sufficient to fully plasticize the matrix, and depressurization is faster than the rate of diffusion of the gas in the matrix, then nucleation of gas may occur producing a foam⁸⁸. A recent patent was awarded for a process using only supercritical fluids to produce foamed polymers⁸⁹.

The 'popping' or foaming of polystyrene has become an important commercial process due to the widespread use of styrofoam for applications ranging from cups and plates to household insulation. The use of specific chemicals, called foaming or blowing agents, allow for the production of a homogeneous cellular structure of the polymer matrix. This results in materials savings, as well as giving the polymer desirable physical properties such as low weight, and better thermal, electrical, and sonic insulating power.

Blowing agents may be of either the *chemical* or *physical* type. Physical blowing agents are simply chemicals, in the polymer-rich phase, which are made to change from liquids to gases under the proper conditions. They usually require the presence of a nucleating agent to allow for the production of homogeneous bubble or cell

sizes. Chemical blowing agents are chemicals that decompose upon heating, forming gaseous products.

Typically polystyrene is foamed commercially in one of two ways. The first process incorporates a foaming agent into the polymer matrix during mixing at high pressures and temperatures in an extruder. Blowing agents used in for this process include CFCs and other low molecular weight, highly volatile solvents that liquefy easily under pressure. This process can produce styrofoam sheeting and other types of products that may be formed via extrusion through a die. This of course limits this processes applicability. The second process uses the high solubility of hydrocarbons such as pentane to impregnate the polymer matrix. The trapped solvents are then used to foam the sample by heating it, thus vapourizing the solvent and foaming the molten polymer. This process enables the polystyrene to produce forms or shapes more easily, and is used in the production of styrofoam cups, etc... .

Ideal foaming agents should be inert in most respects (ie non-flammable, non-corrosive, thermally and chemically stable), yet still be environmentally safe. Thus hydrocarbon solvents and CFCs are being considered for replacement. It will as well be desirable to replace chemical blowing agents for commercial foaming processes. The most favourable compounds for foaming will be inert gases such as nitrogen, carbon dioxide, argon, etc... .

The following pages outline a qualitative study performed on the use of supercritical CO_2 as a physical blowing agent for PS. It should be noted that this study was completed before any patents or literature information had been published on the subject.

Procedure

The procedure for foaming polystyrene pellets using supercritical CO_2 was varied extensively. The following procedure indicates the parameters used to produce the maximum pellet expansion observed:

A measured polystyrene pellet was placed into a soxhlet extraction thimble. The top of the thimble was folded over to reduce pellet disturbance, especially during pressurization/depressurization steps. The thimble was then placed in the high pressure cell, and the cell connected to the system which consists of a tank of CO_2 with a dip-tube, a piston pump, a flow-thru pressure gauge, a high pressure valve, a thermostating device, and a thermocouple (see SF extraction apparatus, Figure 4.6). The system was purged with CO_2 for approximately 1 minute.

The cell was placed inside the temperature thermostating device; used here was a small electrical oven. The oven was then turned on for the cell to reach the desired temperature, taking about 30 minutes to reach equilibration. As the equilibration temperature was being

reached, the pump was turned on at such a time that both the pressure and temperature reach the desired levels almost simultaneously.

Once a given amount of time has elapsed, the pump was shut off and the pressure reduced by opening a fitting at the end of the system, enabling the depressurization from say 300 atm to about 60 atm (CO_2 vapour pressure at room temperature) to take of the order of 30 to 40 seconds. As the pressure drops, the cell was removed from the oven. Once the pressure had fallen sufficiently, the top fitting to the cell was removed and then the cell cap as quickly as possible so that the sample temperature would not reach the glass transition temperature (T_g) before it is removed. Note that the CO_2 tank was left open during the pressure reduction steps, allowing for increased cooling of the sample before removal by gas flow into the cell.

The use of a soxhlet extraction thimble seems to be of prime importance to allow the sample to be cooled and frozen into a foamed product.

Discussion

The proceeding discussion will deal with variables and parameters that affect the product obtained during our foaming process.

Depressurization

As with conventional foaming procedures, it is the depressurization that enables the foaming additive to vapourize, causing the observed phenomenon. In our process, the added CO₂ does not vapourize, but phase separates from the polymer matrix in which it was once dissolved. This is accompanied by large changes in the gas diffusion rate through the matrix and in the fluid density, producing the same result as conventional foaming processes. Unlike conventional physical blowing agents, which require nucleating agents such as talc to produce the desired effect, supercritical CO₂ can produce a homogeneously foamed polymer matrix without these.

Contact Time

The length of contact time between the solid polymer phase and the fluid CO₂ phase has a direct relationship, as one might expect, on the degree of impregnation of the polymer. So long as the polymer sample has been fully impregnated by the fluid, reproducible degrees of foaming can be obtained in the final product. Clearly then smaller

individual pellet sizes would be preferred for faster impregnation and production. For pellets of ca. 2 → 3 mm. diameter as commonly used in our experiments, a contact time of about one hour was required at a temperature of 120°C for reproducibly foamed pellets to be produced, with a volume expansion of about 10 fold.

Temperature

A temperature above the T_g of the pure polymer seemed to produce the best results for the use of supercritical CO_2 as a foaming agent. At about 80°C, some minute swelling and trapped bubbles were seen. Significant amounts of foaming (eg. at least 5 fold increase in volume) were not apparent until about 110°C. The maximum amount of foaming was seen at about 130°C. Much above this temperature, drastic reductions in the amount of foaming was seen. It is assumed with the temperature too high, the increased fluidity of the molten polymer reduced its ability to sustain bubbles in the matrix. This seems to indicate that the optimum temperature for foaming is a balance between several effects.

Pressure

From 130 atm to as high as 350 atm, there appeared to be little difference in the final product size, but a definite correlation of cell size inside the foamed polystyrene sample and the pressure maintained during the

run. At the highest pressures cells were extremely small, reaching as low as ca. 0.05 mm. in diameter. At the lowest pressures, cells of up to 2 mm. diameter were produced. Pressures in between these extremes produced decreasing cell sizes which correlated well with increasing pressure. It is however unclear exactly what effect the pressure directly had on final product character, as it was also possible to produce products at low pressures with smaller cell sizes than commonly seen, and vice versa. It is worth noting that in almost all cases the cell size produced was quite homogeneous.

It is thought that the rate of depressurization has a large effect on cell size. At higher pressures the rate of change in pressure is much larger than at lower pressures. This would allow for the fluid phase to nucleate and form bubbles at a much faster rate due to a more rapid decrease in the fluid solubility and diffusion rate with decreasing pressure. More rapid nucleation would produce a larger number of very small bubbles; similarly, slower nucleation, as expected at lower pressures, would produce a smaller number of larger bubbles. The concentration of gas in the polymer may also affect the final cell sizes as well.

Molding

Sliced polymer pellets and multiple pellets were used to test for aggregation during foaming. In both cases, so long as sufficient time was given for the polymer to become molten and completely impregnated, the product observed was a single foamed conglomerate of the initial polystyrene pieces.

Polymer Types

This process was discovered on polystyrene samples assumed to be impure. Using polystyrene samples of known integrity, both clean and impure (level of impurities < 2%) no noticeable changes in the final product from that observed during initial testing.

Most polystyrene samples tested were in the molecular weight (M_w) range of $2 \times 10^5 \rightarrow 3 \times 10^5$. A very high molecular weight sample (1.5×10^6) was obtained and tested. The product proved to be as easy to foam as lower molecular weight polymer samples, albeit at slightly higher temperatures (ca 150°C). Therefore this process may be of significance to polymers which are not typically processable by extrusion techniques.

Other amorphous polymers and copolymers were tested as well. Under similar conditions, polymers like poly(methyl methacrylate) and copolymer styrene/acrylonitrile (70/30) proved to foam as well, while styrene/butadiene/acrylonitrile

(high butadiene content), poly(ethylene terephthalate), and polyvinylchloride did not foam at all.

SF type

During extraction testing, it was discovered that C_2H_4 proved to be superior to CO_2 at producing a foamed PS matrix. At $60^\circ C$ and 305 atm, the polymer sample expanded upon depressurization to occupy the entire inner volume of the extraction cell. CO_2 under these conditions had little effect on the matrix. It is thought that the high solubility and slow diffusion rates for C_2H_4 (compared to CO_2) in PS are responsible for its superior foaming power.

Conclusion

The general trend over the past decade has been one of increasing concern for the environment, and thus the replacement of non-"environmentally friendly" chemicals for "better" ones. The process of foaming polymers using supercritical CO_2 has been shown to be reproducible, applicable to a wide range of molecular weights, and a wide range of polymer types. The use of supercritical C_2H_4 may also provide some benefit over commonly used foaming agents.

APPENDIX II. Tables of Glass Transition Data

Table II-1: Glass Transition values for PS-CO₂

p(atm)	T _b (°C)	T ₁ (°C)	T _g (°C)	T ₂ (°C)	T _i (°C)
0.0	86.6	96.2	97.8	99.4	104.3
5.3	85.6	92.1	94.3	96.8	102.4
9.3	82.8	87.2	89.6	91.6	97.9
15.1	78.1	82.6	85.3	88.1	95.8
22.7	66.8	74.3	78.0	81.5	90.0
35.7	60.7	64.0	68.4	73.1	79.3
51.5	48.8	50.6	53.8	57.1	68.7
72.2	-	43.9	46.1	47.8	-

Errors in all values < 0.5°C

Table II-2: Glass transition values PS-C₂H₄

p(atm)	T _b (°C)	T ₁ (°C)	T _g (°C)	T ₂ (°C)	T _i (°C)
0.0	86.6	96.2	97.8	99.4	104.3
5.5	82.4	90.4	92.3	94.6	100.9
11.7	76.8	83.1	86.7	89.7	97.7
27.2	60.2	64.7	68.6	72.4	72.4
34.0	55.9	59.4	63.4	71.9	74.8
49.0	39.9	44.9	53.4	59.6	59.6
78.0	24.8	29.7	39.8	50.3	68.8
80.4	30.8	31.6	38.1	51.8	79.3

Errors in all values < 0.5°C

Table II-3: Glass transition values for PS-CH₄

p(atm)	T _b (°C)	T ₁ (°C)	T _g (°C)	T ₂ (°C)	T _g (°C)
0.0	86.8	96.2	97.8	99.4	104.3
9.8	83.3	92.8	94.6	96.6	102.1
26.6	80.1	88.3	90.6	92.8	98.8
49.6	75.5	83.0	85.1	87.6	93.7
75.8	73.7	79.4	81.5	83.7	89.3
81.7	69.2	76.7	79.0	81.2	89.1
125	60.8	69.5	72.5	75.4	82.7
203	58.5	64.8	67.3	69.8	76.0
236	59.8	64.8	67.2	69.4	73.6
264	48.8	58.4	61.3	64.1	70.8
354	48.4	55.3	57.9	60.7	66.8

Errors in all values < 0.5°C

Table II-4: Glass transition values for PMMA-CO₂

p(atm)	T _b (°C)	T ₁ (°C)	T _g (°C)	T ₂ (°C)	T _g (°C)
0.0	77.3	87.7	90.7	93.8	100.3
8.8	65.3	76.0	80.5	85.1	91.3
18.2	55.3	63.8	69.2	74.5	78.9
22.3	53.8	59.5	63.7	67.9	72.6
29.5	53.8	55.4	59.7	63.9	67.9
37.2	45.3	47.2	50.8	57.2	63.4

Errors in all values < 0.5°C

Table II-5: Glass transition values for PMMA-C₂H₄

p(atm)	T _b (°C)	T ₁ (°C)	T _g (°C)	T ₂ (°C)	T _g (°C)
0.0	77.3	87.7	90.7	93.8	100.3
11.0	68.8	76.8	80.2	84.0	90.8
21.8	61.8	69.0	74.7	80.6	88.3
21.8	-	68.0	73.7	79.5	-
36.3	-	54.1	66.8	79.5	-
54.5	-	49.6	57.3	65.1	-

Errors in all values < 0.5°C

Table II-6: Glass transition values for PMMA-CH₄

p(atm)	T _b (°C)	T ₁ (°C)	T _g (°C)	T ₂ (°C)	T _g (°C)
0.0	77.3	87.7	90.7	93.8	100.3
11.4	75.6	85.0	88.0	91.3	97.6
24.5	72.1	83.1	87.2	91.5	92.8
48.4	67.3	80.3	84.3	88.3	95.0
97.0	67.8	76.5	80.8	85.1	85.8
152	64.5	71.2	75.5	79.8	83.5
218	64.8	68.5	73.5	77.7	77.7

Errors in all values < 0.5°C

Appendix III: Tables of gas solubility data

Table III-1: Solubility data for CO₂ in PS

T(°C)	p(atm)	C(mL/g)	S(mL/g*atm)
35.0	2.40	2.33	.971
35.0	2.80	3.54	1.26
35.0	4.80	3.86	.804
35.0	5.00	6.38	1.28
35.0	6.70	6.33	.945
35.0	7.00	4.64	.663
35.0	10.2	6.46	.633
35.0	15.4	12.0	.779
35.0	15.5	10.2	.658
35.0	16.0	12.4	.775
35.0	21.2	12.2	.575
35.0	23.9	14.6	.611
35.0	29.7	20.2	.680
35.0	31.1	18.6	.598
35.0	33.5	21.4	.639
35.0	43.0	24.6	.572
35.0	44.7	24.2	.541
35.0	52.6	28.6	.544
35.0	54.6	31.4	.575
52.5	2.95	2.32	.786
52.5	9.39	5.19	.553
52.5	19.6	9.00	.459
52.5	41.5	15.5	.373
70.0	3.03	1.39	.459
70.0	7.17	2.97	.414
70.0	9.64	3.78	.392
70.0	14.4	5.74	.399
70.0	24.0	8.76	.365

* Solubility values taken from several samples of PS of varying thickness. No systematic differences were seen in the determined values.

* Errors in solubility values are of the order of 5% based on procedural differences, fluctuations in temperature ($\pm 0.1^\circ\text{C}$), errors in volume calibrations and polymer swelling effects, and inherent errors due to the IUPAC equation of state.

Table III-2: Solubility data for CO₂ in PMMA

T(°C)	p(atm)	C(mL/g)	S(mL/g*atm)
35.0	2.56	4.49	1.75
35.0	5.24	8.53	1.63
35.0	6.83	9.84	1.44
35.0	14.6	18.9	1.29
35.0	20.5	21.5	1.05
35.0	21.9	24.2	1.11
35.0	30.7	32.1	1.05
35.0	37.0	38.3	1.04
35.0	37.6	38.3	1.03
35.0	39.5	40.7	1.03
35.0	44.9	46.4	1.03
35.0	50.6	51.5	1.02
52.5	2.66	3.35	1.26
52.5	8.21	7.77	.946
52.5	16.6	12.9	.777
52.5	26.8	18.8	.701
70.0	3.27	2.20	.673
70.0	5.82	3.48	.600
70.0	10.2	4.70	.461

* Errors in solubility values are of the order of 5%.

Table III-3: Solubility data for C_2H_4 in PS

T(°C)	p(atm)	C(mL/g)	S(mL/g*atm)
35.0	2.56	4.79	1.87
35.0	3.49	4.41	1.26
35.0	5.37	6.15	1.15
35.0	7.68	9.67	1.26
35.0	9.65	8.15	.845
35.0	14.7	12.8	.871
35.0	14.8	12.5	.845
35.0	16.4	15.7	.957
35.0	26.9	19.1	.710
35.0	32.9	23.6	.717
35.0	35.0	21.5	.614
35.0	42.9	30.6	.713
35.0	50.6	27.7	.547
52.5	2.76	3.58	1.30
52.5	2.96	3.26	1.10
52.5	10.1	5.71	.565
52.5	20.0	8.69	.435
52.5	42.9	18.4	.429
70.0	3.21	2.25	.701
70.0	10.1	4.16	.412
70.0	21.0	7.19	.342

* Errors in solubility values are of the order of 5%.

Table III-4: Solubility data for C_2H_4 in PMMA

T(°C)	p(atm)	C(mL/g)	S(mL/g*atm)
35.0	2.72	6.18	2.27
35.0	8.78	12.1	1.38
35.0	19.6	15.9	.811
35.0	32.4	19.8	.611
35.0	38.9	24.6	.632
35.0	54.0	29.7	.550
35.0	56.1	28.8	.513
52.5	2.87	2.25	.784
52.5	10.5	4.70	.448
52.5	21.0	8.04	.383
52.5	43.4	17.1	.394
70.0	3.45	1.34	.388
70.0	9.50	3.39	.357
70.0	19.2	6.97	.363

* Errors in solubility values are of the order of 5%.

Table III-5: Solubility data for CH₄ in PS

T(°C)	p(atm)	C(mL/g)	S(mL/g*atm)
35.0	8.80	1.94	.220
35.0	14.7	3.90	.265
35.0	17.0	2.90	.171
35.0	28.3	4.45	.157
35.0	31.9	5.55	.174
35.0	33.8	5.21	.154
35.0	41.5	5.28	.127
35.0	52.1	6.05	.115
35.0	57.8	7.46	.129
35.0	60.8	7.28	.120
70.0	15.9	1.36	.086
70.0	34.2	2.85	.083
70.0	55.2	6.19	.112

* Errors in solubility values are of the order of 15%.

Table III-6: Solubility data for CH₄ in PMMA

T(°C)	p(atm)	C(mL/g)	S(mL/g*atm)
35.0	6.03	1.01	.167
35.0	13.4	2.09	.156
35.0	25.2	2.42	.096
35.0	32.6	3.82	.117
35.0	51.4	4.91	.096
70.0	17.4	1.33	.076
70.0	34.4	2.54	.074
70.0	56.9	3.44	.060

* Errors in solubility values are of the order of 15%.

Appendix IV: Tables of diffusion coefficients

Table IV-1: Diffusion coefficients for CO₂ in PS

T(°C)	P(atm)	C(mL/g)	(X 10 ⁻¹¹ m ² sec ⁻¹)		
			D _{sts}	D _{ht}	D _{ma}
35.0	5.00	6.38	1.0	.70	.68
35.0	15.4	12.0	1.7	.89	.88
35.0	31.1	18.6	2.1	1.0	.75
35.0	44.7	24.2*	1.6	.75	.32
52.5	2.95	2.32	1.5	1.1	1.2
52.5	9.39	5.19	2.3	1.3	1.3
52.5	19.6	9.00	3.3	1.5	1.7
52.5	41.5	15.5*	1.9	.84	.23
70.0	3.03	1.39	2.8	2.0	2.0
70.0	7.17	2.97	3.2	1.7	1.8
70.0	9.64	3.78	-	1.8	-
70.0	14.4	5.74	4.4	1.9	2.0
70.0	24.0	8.76*	3.8	1.6	.88

D_{sts} - diffusion coefficient from short-time slope of reduced sorption plot

D_{ht} - diffusion coefficient from time to half sorption

D_{ma} - diffusion coefficient from moment analysis

* - two stage sorption observed; value for D_{sts} will differ since initial stage slope is used to calculate

Error estimate: ±10% in D_{sts} values

Table IV-2: Diffusion coefficients for CO₂ in PMMA

T(°C)	P(atm)	C(mL/g)	(X 10 ⁻¹² m ² sec ⁻¹)		
			D _{sts}	D _{ht}	D _{me}
35.0	2.56	4.49	.29	.26	.28
35.0	5.24	8.53	.39	.32	.37
35.0	6.83	9.84	.41	.33	.30
35.0	14.6	18.9	1.0	.65	.80
35.0	21.9	24.2	1.7	.87	1.2
35.0	30.7	32.1	3.0	1.4	1.8
35.0	37.6	38.3	4.6	2.2	2.8
35.0	44.9	46.4	6.8	3.2	3.0
35.0	50.6	51.5	6.2	5.0	6.5
52.5	2.66	3.35	.64	.52	.59
52.5	8.21	7.77	.92	.65	.74
52.5	16.6	12.9	1.4	.88	.93
52.5	26.8	18.8	2.7	1.5	1.7
70.0	3.27	2.20	1.4	1.1	1.1
70.0	5.82	3.48	1.6	1.2	1.3
70.0	10.2	4.70	2.0	1.3	1.4
70.0	14.4	9.23	2.3	1.4	1.4

Error estimate: ±10% in D_{sts} values

Table IV-3: Diffusion coefficients for C₂H₄ in PS

T(°C)	P(atm)	C(mL/g)	(X 10 ⁻¹² m ² sec ⁻¹)		
			D _{sts}	D _{ht}	D _m
35.0	3.49	4.41	.43	.34	.34
35.0	2.56	4.79	.40	.35	.36
35.0	5.37	6.15	.44	.40	.38
35.0	9.65	8.15	.46	.39	.34
35.0	7.68	9.67	.61	.49	.53
35.0	14.7	12.8	.60	.50	.42
35.0	26.9	19.1	.99	.66	.67
35.0	35.0	21.5	1.3	.85	.81
35.0	50.6	27.7	2.3	1.2	1.5
52.5	2.96	3.26	.88	.69	.72
52.5	10.1	5.71	1.6	1.1	.68
52.5	20.0	8.69	1.7	1.1	.41
70.0	3.21	2.25	1.5	1.1	.44
70.0	10.1	4.16	1.4	1.4	.68
70.0	21.0	7.19	2.0	1.2	1.0

Error estimate: ±10% in D_{sts} values

Table IV-4: Diffusion coefficients for C_2H_4 in PMMA

T(°C)	P(atm)	C(mL/g)	(X 10^{-14} m ² sec ⁻¹)		
			D _{sts}	D _{ht}	D _{me}
35.0	2.72	6.18	1.1	.90	1.2
35.0	8.78	12.1	1.4	1.1	1.6
35.0	19.6	15.9	3.8	2.2	3.0
35.0	32.4	19.8	4.6	3.3	4.8
35.0	38.9	24.6	11	5.2	6.2
35.0	56.1	28.8	6.7	3.9	7.3
52.5	2.87	2.25	1.7	1.7	2.0
52.5	10.5	4.70	2.4	2.0	2.4
52.5	21.0	8.04	3.1	2.4	2.6
52.5	43.4	17.1	4.2	3.5	4.8
70.0	3.45	1.34	8.2	7.3	5.7
70.0	9.50	3.39	6.3	7.5	5.1
70.0	19.2	6.97	17	12	9.6

Error estimate: $\pm 10\%$ in D_{sts} values

Table IV-5: Diffusion coefficients for CH₄ in PS

T(°C)	P(atm)	C(mL/g)	(X 10 ⁻¹² m ² sec ⁻¹)		
			D _{sts}	D _{ht}	D _{me}
35.0	14.7	3.90	2.2	2.2	2.3
35.0	31.9	5.55	3.1	2.7	3.2
35.0	57.8	7.46	2.0	3.2	3.0
70.0	15.9	1.36	7.0	6.8	5.3
70.0	34.2	2.85	5.8	9.0	9.6
70.0	55.2	6.19	5.1	4.6	7.2

Error estimate: ±10% in D_{sts} values

Table IV-6: Diffusion coefficients for CH₄ in PMMA

T(°C)	P(atm)	C(mL/g)	(X 10 ⁻¹³ m ² sec ⁻¹)		
			D _{sts}	D _{ht}	D _{me}
35.0	6.03	1.01	.40	.37	.43
35.0	13.4	2.09	.27	.36	.65
35.0	32.6	3.82	.81	.38	.58
35.0	51.4	4.91	.43	.62	1.2
70.0	17.4	1.33	5.0	3.0	3.4
70.0	34.4	2.54	6.9	3.9	3.8
70.0	56.9	3.44	6.0	3.1	2.5

Error estimate: ±10% in D_{sts} values

Appendix V. Glossary of Terms

component subscripts: 1 = gas or SF, 2 = polymer

A - plasticization strength of gas (K); equation 2.1

A_s - surface area of polymer particles; Hot-Ball model

B - non-equilibrium correction parameter; Vrentas model

b - hole affinity constant; Dual mode model

c_i - concentration of component i ; Dual mode model

c_H - concentration of gas in voids spaces; Dual mode model

c_H' - hole saturation constant; Dual mode model

c_o - concentration dissolved penetrant; Dual mode model

c_o - equilibrium conc of sorbed penetrant

C - Solubility limitation; modified Hot-ball model

C_p - heat capacity at constant pressure

$C_{p,g}$ - heat capacity of the polymer glassy state

D - diffusion coefficient

D_o - diffusion coefficient at zero penetrant concentration

D_{av} - average diffusion coefficient

E_D - activation energy for diffusion

F - flow rate of solvent; modified Hot-ball model

G - free energy of polymer-penetrant mixture

H - enthalpy

ΔH_s - heat of sorption

h - compilation term of factors affecting extraction rate; Hot-ball model

K - extraction constant; modified Hot-ball model

k_D - Henry's law constant; Dual mode model

- L - polymer film thickness
- M_n - number average molecular weight
- M_w - weight average molecular weight
- M_g - molecular weight of gas; Chow's equation
- M_p - molecular weight of the polymer repeat unit;
Chow's equation
- M_t - mass of gas sorbed at time t
- M_∞ - mass of gas sorbed at equilibrium
- m_i - mass of solute extracted from polymer; Hot-ball model
- P - permeability coefficient
- p - pressure
- p_1° - hypothetical liquid vapour pressure
- q - ratio gas/hypothetical liquid molar volumes;
Vrentas model
- S - entropy
- s - solubility coefficient
- T - temperature
- T_g° - thermodynamic glass transition temperature
- T_g - glass transition temperature
- $T_{g,m}$ - glass transition temperature of polymer-gas mixture
- T_b - temperature defining the beginning of the change in
heat flow to the polymer
- T_1 - onset temperature of the glass transition
- T_2 - completion temperature of the glass transition
- T_e - temperature defining the end of changes in heat flow to
polymer
- t - time
- t_c - characteristic time of extraction; Hot-ball model

- t_r - reduced extraction time; Hot-ball model
- V_i^0 - specific molar volume of component i
- W - interaction energy between different components
- w - mass of gas sorbed per gram of polymer
- x_i - mole fraction comp i
- y - fugacity correction factor; Vrentas model
- z - coordination number; Chow's equation
- α - thermal expansion coefficient
- β - polymer specific parameter; Chow's equation
- δ - solubility parameter
- ρ_i - molar density component i
- Φ_i - volume fraction component i
- θ - penetrant parameter; Chow's model
- κ - isothermal compressibility
- ω_i - mass fraction component i
- ν - fugacity coefficient
- ν^0 - fugacity coefficient of the hypothetical liquid
- χ - Flory-Huggins interaction parameter
- τ - fugacity correction; Vrentas model
- τ_s - characteristic time of diffusion; moment analysis

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