INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI®

UNIVERSITY OF ALBERTA

SOLUBILITY PROPERTIES OF LDPE AND LLDPE LIQUIDS AND THEIR MELT MISCIBILITY BY INVERSE GAS CHROMATOGRAPHY

BY

Maria Dulce Lamego Vieira da Silveira

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

IN

CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL AND MATERIALS ENGINEERING

EDMONTON, ALBERTA

SPRING, 2001

0-612-69808-4

UNIVERSITY OF ALBERTA

RELEASE FORM

NAME OF THE AUTHOR	Maria Dulce Lamego Vieira da Silveira
TITLE OF THESIS	Solubility Properties of LDPE and LLDPE Liquids and their Melt Miscibility by Inverse Gas Chromatography
DEGREE	Master of Science
YEAR THIS DEGREE GRANTED	2001

Permission is hereby granted to the University of Alberta to reproduce single copies of this thesis and to lend or sell such copies for private, scholarly or scientific research purposes only.

The author reserves all other publication rights in association with the copyright in the thesis, and except as hereinbefore provided neither the thesis nor any substantial portion thereof may be printed or otherwise reproduced in any material form whatever without the author's prior written permission.

Maria Dulce Lamego Vieira da Silveira
Maria Dulce Lamego Vieira da Silveira
7008- 97 Avenue
Edmonton, AB, Canada
T6B 1C7
Date: 12/20/00

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read and recommend to the faculty of Graduate Studies and Research for acceptance, a thesis entitled **Solubility Properties of LDPE and LLDPE Liquids and their Melt Miscibility by Inverse Gas Chromatography** submitted by **Maria Dulce Lamego Vieira da Silveira** in partial fulfillment of the requirements for the degree of **Master of Science in Chemical Engineering.**

Dr. Phillip Y. K. Choi (supervisor)

Dr. U. Sundararaj

Dr. P.Y. Ben Jar

Date: 12/05/2000

ABSTRACT

The technique of inverse gas chromatography (IGC) has been used to measure the Hildebrand solubility parameters (δ) of a commercial LDPE and eleven experimental LLDPEs, which have different solid-state density, average molecular weights, and molecular weight distribution. In particular, two approaches, one developed by Choi *et al.* [*J. Coll. and Inter. Sc.i*, 180, 1 (1996)] and the other by DiPaola-Baranyi and Guillet, [Lloyd DR, Ward TC, Schreiber HP, Pizana CC, ACS Symposium Series, *Inverse Gas Chromatography Characterization of Polymers and other Materials*, Chapter 9, American Chemical Society, Toronto (1988)] were adopted. And it was found that the former method yielded different δ_2 values, allowing the calculation of the Flory-Huggins interaction parameters (χ), while the latter did not. Nevertheless, they both gave solubility parameter values which are significantly lower than those obtained by PVT measurements. The measured parameters were then used to calculate the corresponding Flory-Huggins interaction parameters $\chi_{LDPE\text{-}LLDPE}$ and $\chi_{LLDPE\text{-}LLDPE}$ at four elevated temperatures. Our results suggest that both LDPE/LLDPE and LLDPE/LLDPE blends are thermodynamically miscible at most of the temperatures of interest. Additionally, the miscibility behavior of both LDPE/LLDPE and LLDPE/LLDPE blends seems to be insensitive to the properties (e.g., average molecular weight, branch content, polydispersity, melt index) of the LLDPEs used.

ACKNOWLEDGMENTS

I am grateful to my supervisor Dr. Phillip Choi for his guidance and support during the course of my research and also for his efforts in guiding me to write this thesis.

I express my sincere gratitude to my husband, Jarbas, who always supports me during all my endeavors.

I would also like to thank NSERC and NOVA Chemicals Corporation for their financial support given during the research.

Above all, I express my deep gratitude to my mother, Sonia and grandmother, Dulce whose unconditional love and support have been the driving force behind all my accomplishments in life.

TABLE OF CONTENTS

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

LDPE	Low-density polyethylene
LLDPE	Linear Low-density polyethylene
HDPE	High-density polyethylene
IGC	Inverse Gas Chromatography
DSC	Differential Scanning Calorimetry
DMA	Dynamic Mechanical Analysis
SAXS	Small-Angle X-ray Scattering
SANS	Small-Angle Neutron Scattering
SALS	Small-Angle Light Scattering
GPC	Gel Permeation Chromatography
C^{13}NMR	Nuclear Magnetic Resonance using carbon 13
PVT	Pressure – Volume – Temperature
MD	Molecular Dynamics
χ	Flory-Huggins Interaction parameter
δ	Hildebrand Solubility parameter
MW_{et}	Molecular weight of the ethylene repeat unit
$Mn,_{pol}$	Number molecular weight average of a polymer
ΔG_{mix}	Gibbs free energy of mixing
ΔH_{mix}	Molar heat of mixing
ΔS_{mix}	Combinatorial entropy of mixing
n	Number of moles

ϕ	Volume fraction
V	Molar volume
R	Gas constant
r_1	Solvent's molar volume / ethylene repeat unit molar volume
B_{12}	Binary interaction energy coefficient
T	Temperature
x	Degree of polymerization
N_g	Total number of lattice sites
$f(\phi)$	Function of the volume fraction
μ	Chemical potential
V_g^0	Specific retention volume
t_N	Net retention time
F	Carrier gas flow rate
t_0	Marker's retention time
t_R	Retention time
w	Acentric factor
W_l	Mass of the polymer coated in the column
J	James- Martin correction factor for the pressure gradient across the column
P_i	Column inlet pressure
P_o	Column outlet pressure
c_1^l	Solvent concentration in the liquid phase
c_1^g	Solvent concentration in the gas phase
v_2	Polymer specific volume

M	Molecular weight
B_{11}	Second virial coefficient of the solvent in the gas phase
P_1^0	Solvent's saturated vapor pressure
A, B, C	Antoine's constants
T_c	Critical temperature
P_c	Critical pressure
$f^{(0)}, f^{(1)}$	Modified version of the fugacities defined by Pitzer-Curl
T_r	Reduced temperature
V_0	Common reference molar volume
ΔE_{vap}	Internal energy change of vaporization
ΔH_{vap}	Enthalpy of vaporization
χ_H	Enthalpic contribution to the Flory-Huggings interaction parameter
χ_S	Entropic contribution to the Flory-Huggings interaction parameter
χ_{12}^{∞}	Infinite dilution solvent-polymer Flory-Huggings interaction parameter
χ_S^{∞}	Infinite dilution entropic contribution to the Flory-Huggings interaction parameter
N	Number of molecules
Φ^*	Fraction of sites
ΔG^c	Combinatorial Gibbs energy
ΔS^c	Combinatorial entropy
r	Number of segments in a polymer molecule
γ	Activity coefficient
α	Activity

CHAPTER 1

1 INTRODUCTION

Despite the fact that polymer blends have been known for some time, such systems have only received increased attention for the last three decades, owing to the pressing need for a faster and less expensive way of developing new materials having desirable processing and performance properties. Consequently, there has been much interest in developing reliable and convenient experimental methods that can be used to better characterize and understand how different polymers interact in a blend [1-4].

The properties of polymer blends strongly depend on the miscibility of their constituent polymers. In general, miscibility occurs when specific interaction forces exist between the backbones of the polymers in a blend [5]. These interactions may be in the form of hydrogen bonding, acid-base type, dipole moments, etc. Miscibility of polymers can be determined experimentally by measuring their Flory-Huggins interaction parameter (χ). In this regard, there are a few methods available and these include melting point depression measurements using Differential Scanning Calorimetry (DSC), Small-Angle Neutron Scattering (SANS) and Inverse Gas Chromatography (IGC) [5-11]. Among these techniques, IGC has become popular in recent years due to its simplicity, rapidity and availability of the GC equipment. In addition, IGC experiments can provide miscibility information at elevated temperatures (e.g. 200°C) while the other techniques, except for SANS, cannot [3].

There are two common approaches used to infer miscibility by IGC. The first one is to measure the Flory-Huggins interaction parameter between the polymers directly for a blend. In this case, both concentration and temperature dependence of χ can be obtained. Another approach is to measure the Hildebrand solubility parameters (δ) of the pure polymers and then use the measured δ values to calculate the Flory-Huggins interaction parameters between the polymers. Since the latter approach focuses on determining δ of the pure components, the resultant χ is only temperature dependent. Both methods are currently being used. The work presented here utilized the second one as the first approach suffers from a serious problem: the measured interaction parameters depend on the nature of the solvents used in the experiment.

Among the large number of polymer blends that have been studied over the past few decades, polyethylene blends have still been a topic of great interest among industries and research centres because by using various catalysts, polyethylene with different molecular structures can be made [12-20]. Despite considerable efforts that have been made on the subject, there is still no consensus on the miscibility of these blends. In fact, different groups of researchers have proposed different views on the issue ranging from complete phase separation [21-29] to complete homogeneity [9-11] for blends of high-density polyethylene (HDPE) and low-density polyethylene (LDPE) as well as of HDPE and linear low-density polyethylene (LLDPE). In the case of HDPE/LLDPE, all researchers have generally accepted that the branch content (i.e., average number of branches per thousand backbone carbons) of LLDPE is the major factor that controls miscibility [26-28].

LDPE/LLDPE blends have also been frequently studied and researchers found that the blends retain the superior mechanical properties of LLDPE as well as the processability of LDPE [1,20]. As postulated by Speed [30], LDPE/LLDPE blends are of considerable market interest for a variety of reasons. Typical commercial applications require combinations of LLDPE with some amounts of LDPE through slip, antiblock and color masterblatches as well as mixtures of LLDPE with high fractions of reprocessed LDPE scrap. Blending LDPE into LLDPE reduces haze and increases melt tension to give better bubble stability. It also improves toughness and melt drawdown properties compared to LDPE base resin.

Regarding the miscibility of LDPE/LLDPE blends, as in the HDPE/LDPE case, no consensus has been reached. Based upon frequency relaxation spectra and rheological functions, Utracki and Schlund [31] deduced that LDPE and LLDPE did not mix in the molten state. With the use of Small-Angle Light Scattering (SALS) technique, Moonhor *et al.* [32] found that the blend is miscible in the amorphous phase, but not in the crystalline phase. Through extensive studies on thermal and relaxation behavior of polyethylene blends, Lee and Cho [33] investigated LDPE/LLDPE miscibility using DSC and Dynamic Mechanical Analysis (DMA) and found that such blends are miscible in the amorphous phase but not in the crystalline one.

Hu *et al.* [34] studied several polyethylene blends including LDPE/LLDPE ones by DSC, Small Angle X-ray Scattering (SAXS) and other techniques. They found that for the LDPE/LLDPE system, DSC showed two distinct endothermic peaks indicating that there are separate crystalline phases in the blend. The light-scattering patterns led them to believe that when LDPE/LLDPE blends are cooled from the molten state, LLDPE first crystallizes forming spherulites and LDPE crystallizes subsequently within the spherulites previously formed by the LLDPE.

To date, miscibility studies of polyethylenes have only focused on temperatures slightly above their melting points (up to 165°C) rather than typical processing temperatures (approx. 200°C) [21-28]. The objective of this current work is to broaden the understanding of the phase behavior of polyethylene blends at four elevated temperatures (170, 190, 210 and 230°C) with the use of IGC. In particular, we attempt to correlate molecular structures of polyethylenes with their solubility properties and miscibility.

1.1 REFERENCES

1. Utracki LA, *Polymer Alloys and Blends – Thermodynamics and Rheology*, Academic Press: NY (1989)
2. Olabisi O, Robenson LM, Shaw MT, *Polymer-Polymer Miscibility*, Academic Press: NY (1979)
3. Lloyd DL, Ward TC, Schreiber HP, Pizana CC, ACS Symposium Series, *Inverse Gas Chromatography Characterization of Polymers and other Materials*, American Chemical Society, Toronto (1988)
4. Shigetaka S, Yasuro H, Hisatsugo K, *Macromolecules*, 21, 3454 (1988)
5. Al-Saigh Z, Chen P, *Macromolecules*, 24, 3788 (1991)
6. Venkataraman N, Burns CM, Huang RYM, Llyod DR, *Polymer Blends and Composites in Multiphase Systems*, American Chemical Society, 4 (1984)
7. Hill MJ, Barham PJ, Keller A, Rosney CCA, *Polymer*, 32, 1384 (1991)
8. Hill MJ, Barham PJ, *Polymer*, 36, 1523 (1995)
9. Alamo RG, Londono JD, Mandelkern L, Stehling FC, Wignall GD, Macromolecules, 27, 411 (1994)
10. Agamalian M, Alamo RG, Kim MH, Londono JD, Mandalkern L, Wignall GD, *Macromolecules*, 32, 3093 (1999)
11. Alamo RG, Graessley WW, Krishnamoorti R, Lohse DJ *et al.*, *Macromolecules*, 30, 561 (1997)
12. Gopalan M, Mandelkern L, *The Journal of Physical Chemistry*, 71, 3833 (1967)

13. Londono JD, Wignall G.D, Alamo R.G, Mandelkern L, *Materials Research Society Symp.*, 376, 281 (1995)

14. Alamo GR, Viers B.D, Mandelkern L, *Macromolecules*, 28, 3205 (1995)

15. Thein Kyu, Shi-Ru Hu, Stein R.S, *J.of Polym. Sci., Part B,* 25, 71 (1987)

16. Thein Kyu, Shi-Ru Hu, Stein R.S, *J.of Polym. Sci., Part B,* 25, 89 (1987)

17. Zhao H, Zhongli L, Huang B, *Polymer*, 30 (2), 140 (1998)

18. Lee H, Cho K, Ahn T.K, Choe S, Kim I, *J.of Polym. Sci., Part B,* 35, 1633 (1997)

19. Prasad A, *Polymer Engineering and Science*, 38, 1716 (1998)

20. Birley W, Datta N.K, *Plastics and Rubber Processing and Application*, 2, 237 (1982)

21. Barham PJ, Hill MJ, Keller A, Rosney CCA, *J. of Materials Science Letters*, 7, 1271 (1988)

22. Hill MJ, Barham PJ, Keller A, Rosney CCA, *Polymer*, 32, 1384 (1991)

23. Hill MJ, Barham PJ, Keller A, *Polymer*, 33, 2530 (1992)

24. Hill MJ, Barham PJ, *Polymer*, 33, 4099 (1992)

25. Hill MJ, *Polymer*, 35, 1991 (1994)

26. Hill MJ, Barham PJ, van Ruiten J, *Polymer*, 34, 2975 (1993)

27. Hill MJ, Barham PJ, van Ruiten J, Goldbeck-Wood G, *Polymer*, 34, 2981 (1993)

28. Hill MJ, Barham PJ, *Polymer*, 35, 1802 (1994)

29. Tashiro K, Stein R.S, Hsu S.L, *Macromolecules*, 25, 1801 (1992)

30. Speed C.S, *Plast. Eng*, July, 39 (1982)

31. Utracki LA, Schlund B, *J. Polym. Eng. Sci.*, 27, 1512 (1987)

32. Moonhor R, Thein K, Stein R, *J. Polym. Sci., Part B,* 25, 105 (1987)

33. Lee H, Cho K, Ahn T, Choe S, Kim I, Park I, Lee B, *J. Polym. Sci.,Polym. Phys. Edn.*, 35, 1633 (1997)

34. Hu S, Kyu T, Stein R, *J. Polym. Sci.,Polym. Phys. Edn.*, 25, 71 (1987)

CHAPTER 2

2 INVERSE GAS CHROMATOGRAPHY (IGC)

As mentioned in Chapter 1, IGC is one of the most common techniques used to characterize polymer blends. The term "inverse" was adopted due to the low volatility of polymers that makes them unsuitable for study by conventional gas chromatography (GC) where the mobile phase is the focus of study. In IGC, the chromatographic column that consists of the pure polymer coated on the solid support (i.e., stationary phase) is under study. IGC has been applied extensively to a variety of homopolymers, copolymers and polymer blends. And a wealth of information such as interaction parameters, contact energy parameters, molar heats of sorption and mixing of solvents can be obtained [1]. With appropriate correlations, all these parameters can be obtained experimentally by measuring the retention times of the injected pure solvents, weight of the coated material, flow rates of the carrier gas, and its inlet and outlet pressures and column temperature. This chapter will review the basic theories on how IGC is used to characterize miscibility of polymers based upon the measured δ.

2.1 Polymer Blend Thermodynamics

An important thermodynamic term for describing the miscibility of polymer blends is the Gibbs free energy of mixing ΔG_{mix} that is given by:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{1}$$

where ΔS_{mix} is the combinatorial entropy of mixing and ΔH_{mix} is the enthalpy change of mixing.

Flory and Huggings, with the use of the concept of a quasi-crystalline lattice as a model for liquids, independently derived an expression for the combinatorial entropy of mixing for linear flexible chain molecules [2,12]. The Flory-Huggins quasi-lattice theory can be found in Appendix B.

In the case of a binary mixture:

$$\Delta S_{mix} = -R(n_1V_1 + n_2V_2)\left[\frac{\phi_1 \ln\phi_1}{V_1} + \frac{\phi_2 \ln\phi_2}{V_2}\right] \tag{2}$$

where n_1 and n_2 are the numbers of moles of components 1 and 2; ϕ_1 and ϕ_2 are their volume fractions; and V_1 and V_2 are their molar volumes. The enthalpy change of mixing is assumed to have a form of the Van Laar expression:

$$\Delta H_{mix} = (n_1V_1 + n_2V_2)B_{12}\phi_1\phi_2 \tag{3}$$

where B_{12} is a binary interaction energy coefficient and can be related to the Flory-Huggins interaction parameter between components 1 and 2, χ_{12}, by the following expression:

$$\frac{B_{12}}{RT} = \frac{\chi_{12}}{V_1} \tag{4}$$

By replacing the ΔH_{mix} and ΔS_{mix} terms in equation (1) by equations (2) to (4), one obtains the following expression:

$$\Delta G_{mix} = RT\left[n_1 \ln\phi_1 + n_2 \ln\phi_2 + n_1\phi_2\chi_{12}\right] \tag{5}$$

It is obvious, based upon equation (2), that even though positive contribution of the combinatorial entropy favors mixing, its value is diminished as the molar volumes of the components become larger. As a result, miscibility can only be achieved by having negative polymer-polymer interaction parameters, χ_{12}, if both components are high molecular weight polymers (i.e., exothermic heats of mixing).

However, in order to satisfy stability considerations for a binary system, the following criterion is also required:

$$\frac{\partial^2 \Delta G_{mix}}{\partial \phi_2{}^2} > 0 \tag{6}$$

This requirement guarantees that the mixture is in a stable region. The $\partial^2\Delta G_{mix}/\partial\phi_i{}^2 = 0$ expression describes the spinodal curve which divides the stable and non-stable regions where spontaneous demixing occurs.

Another expression for ΔG_{mix} which is defined in terms of the degree of polymerization, x, is [3,13]:

$$\Delta G_{mix} = RT\left[\frac{\phi_1}{x_1}\ln\phi_1 + \frac{\phi_2}{x_2}\ln\phi_2 + \phi_1\phi_2\chi_{12}\right] \tag{7}$$

where x_1 and x_2 are the degrees of polymerization defined based upon the volume of the lattice site chosen.

The difference in chemical potentials of the solvent in the solution and pure solvent states $\Delta\mu_1$ can be obtained by differentiation of the molar Gibbs free energy of mixing with respect to the amount of the solvent, n_1, in the solution. With the use of the solvent's molar volume as the reference volume (i.e., $x_1 = 1$) and $\phi_1 = n_1 x_1 / N_g$, one obtains:

$$\frac{\partial \Delta G_{mix}}{\partial n_1} = \Delta\mu_1 = RT\left[\chi_{12}\phi_2^2 + \ln(1-\phi_2) + \left(1-\frac{1}{x_2}\right)\phi_2\right] \tag{8}$$

where N_g is the total number of lattice sites.

The inflection point of the function $\Delta\mu_1 = f(\phi_2)$ and its extreme values characterize the spinodal curve:

$$\frac{\partial \Delta\mu_1}{\partial \phi_2} = RT\left[2\chi_{12}\phi_2 - \frac{1}{(1-\phi_2)} + \left(1-\frac{1}{x_2}\right)\right] \tag{9}$$

At the critical point, the second derivative of the function $\Delta\mu_1 = f(\phi_2)$ becomes zero and the maximum, minimum and inflection point are all equal to zero:

$$\frac{\partial^2 \Delta\mu_1}{\partial \phi_2^2} = RT\left[2\chi_{12} - \frac{1}{(1-\phi_2)^2}\right] = 0 \tag{10}$$

Solving both equations (9) and (10) for χ_{12} and equating the results, after some manipulation, one obtains the value for $\chi_{12,crit}$:

$$\chi_{12,crit} = \left[\frac{\left(1 + x_2^{1/2}\right)^2}{2x_2} \right] \tag{11}$$

As $x_2 \rightarrow \infty$, equations (11) becomes:

$$\chi_{12,crit} = \frac{1}{2} \tag{12}$$

According to the above equation, if χ_{12} is less than $\chi_{12,crit}=0.5$, the polymer and solvent are miscible in all proportions. However, if $\chi_{12} > \chi_{12,crit}$, phase separation occurs.

Instead of using the solvent's molar volume as a reference, one can adopt the molar volume of the repeat unit of the polymer in question as the reference volume, equation (5) would now read:

$$\Delta G_{mix} = RT \left[n_1 \ln\phi_1 + n_2 \ln\phi_2 + \frac{V_1}{V_0} n_1 \phi_2 \chi_{12} \right] \tag{13}$$

where V_0 is the reference volume. In this work, polyethylene is of interest. Therefore, V_0 is the ethylene molar volume at temperature T. Let's define $r_1 = V_1 / V_0$ for simplification.

Following the same procedure as described before, one would find:

$$\frac{\partial \Delta\mu_1}{\partial \phi_2} = RT\left[2r_1\chi_{12}\phi_2 - \frac{1}{(1-\phi_2)} + 1 - \frac{V_1}{V_2}\right] \tag{14}$$

Taking the second derivative of equation (14):

$$\frac{\partial^2 \Delta\mu_1}{\partial \phi_2{}^2} = RT\left[2r_1\chi_{12} - \frac{1}{(1-\phi_2)^2}\right] \tag{15}$$

By setting equations (14) and (15) to zero and solving for $\chi_{12,crit}$:

$$\chi_{12,crit} = \frac{1}{2r_1}\left(1 + \sqrt{\frac{V_1}{V_2}}\right)^2 \tag{16}$$

Since $V_2 >> V_1$,

$$\chi_{12,crit} = \frac{1}{2r_1} = \frac{V_0}{2V_1} \tag{17}$$

It is worth noting that if V_1, the solvent molar volume, is used as the reference volume, equation (17) will be reduced to equation (12), i.e., $\chi_{12,crit} = 0.5$.

In the case of binary polymer blends, the $\chi_{23,crit}$ is given by:

$$\chi_{23,crit} = \frac{1}{2}\left(\sqrt{\frac{V_0}{V_2}} + \sqrt{\frac{V_0}{V_3}}\right)^2 \tag{18}$$

Equation (18) can be further simplified using $V_o = MW_{et} * v_2$; $V_2 = Mn,_{pol2} * v_2$; $V_3 = Mn,_{pol3} * v_3$, where MW_{et} is the molecular weight of the ethylene repeat unit; $v_2 = v_3$ and they are the specific volume of polymer 2 and 3, respectively, which will be further discussed below. And $Mn,_{pol2}$ and $Mn,_{pol3}$ are the number average molecular weights of polymers 2 and 3, respectively:

$$\chi_{23,crit} = \frac{1}{2}\left(\sqrt{\frac{MW_{et}}{Mn,_{pol2}}} + \sqrt{\frac{MW_{et}}{Mn,_{pol3}}}\right)^2 \tag{19}$$

It should be pointed out that the concept for χ_{crit} is derived based upon two linear polymers. Since in this work we are dealing with two branched polymers, LDPE and LLDPE, χ_{crit} values obtained using either equation (18) or (19) can only be used as an ad hoc reference, rather than an absolute one. The polymer specific volume in the liquid state for polyolefins can be obtained by the empirical expression developed by Rudin *et al.* [6]:

$$v_2 = 1.282 + 9 * 10^{-4}(T - 150) \tag{20}$$

where T is in °C. It is worth noting that according to the above expression, the melt density of the polyethylene is only a function of temperature and is independent of its branching characteristics. In other words, both LDPE and LLDPE share the same melt density at the same temperature.

Having reviewed the basic solution thermodynamics theories, which are pertinent to our work, we now turn over attention to the GC theories.

The specific retention volume, V_g^0, is commonly used to describe the elution behavior of a solvent injected into a GC column and is also important for obtaining thermodynamic properties of the stationary phase. It is defined as [4]:

$$V_g^{\,0} = \frac{t_N * F * J * 273.15}{W_l * T} \tag{21}$$

where t_N is the net retention time obtained by the difference between the retention times of the solvent and of a marker; F is the carrier gas (helium) flow rate at the experimental temperature T; W_l is the mass of the polymer coated in the column; and J is the James-Martin correction factor for the pressure gradient across the column. J can be obtained by [1]:

$$J = \frac{3}{2}\left\{\frac{\left[\left(\frac{P_i}{P_0}\right)^2 - 1\right]}{\left[\left(\frac{P_i}{P_0}\right)^3 - 1\right]}\right\} \tag{22}$$

where P_i and P_0 are the chromatographic column inlet and outlet pressures, respectively.

The specific retention volume is also related to the partition coefficient (i.e, the ratio of the concentration of the solvent in the liquid phase to that of the gas phase) by the following expression [4]:

$$V_g{}^0 = \left(\frac{c_1{}^l}{c_1{}^g}\right) * \left(\frac{273.15}{T}\right) \tag{23}$$

where $c_1{}^l$ and $c_1{}^g$ refer to the solvent concentrations in the liquid and gas phases, respectively.

In a chromatographic column, the equilibrium between the stationary and mobile phases is usually fast reached. However, the column temperature should be at least about 50°C above the glass-transition temperature for amorphous polymers and slightly above the melting temperature for semicrystalline polymers to avoid surface adsorption and kinetic effects interference with the value of $V_g{}^0$. At equilibrium,

$$\mu_1{}^l = \mu_1{}^g \tag{24}$$

where $\mu_1{}^l$ and $\mu_1{}^g$ are the chemical potentials of the solvent in the liquid and gas phases.

Under infinite dilution situation (i.e., both $c_1{}^l$ and $c_1{}^g$ are very small), the chemical potential of the solvent in the gas phase relative to the reference state (i.e., $\Delta\mu_1{}^g$) is then obtained by:

$$\Delta\mu_1{}^g = RT\ln\left(\frac{RTc_1{}^g}{M_1}\right) \tag{25}$$

where M_1 is the molecular weight of the solvent.

The chemical potential of the solvent in the liquid phase relative to the reference state (i.e., $\Delta\mu_1^l$) is given by [16]:

$$\Delta\mu_1^l = RT\left(\ln\alpha_1 + \ln P_1^0 + P_1^0 * \frac{(B_{11} - V_1)}{RT}\right) \tag{26}$$

where B_{11} is the second virial coefficient of the solvent in the gaseous phase; α_1 is the activity of the solvent in the liquid state; V_1 is its molar volume; and P_1^0 is its saturated vapor pressure at temperature T. P_1^0 can be calculated by Antoine's equation as:

$$\log P_1^0 = A - \frac{B}{(T+C)} \tag{27}$$

where T is in degrees Celsius and the constants A, B and C are taken from reference [5].

And B_{11} was determined by an improved approach developed by Tsonopoulos [11] to properly account for the nonideality in vapor-liquid equilibria :

$$B_{11} = \left(f^{(0)} + wf^{(1)}\right) * \frac{RT_c}{P_c} \tag{28}$$

where $f^{(0)}$ and $f^{(1)}$ are a modified version of the fugacities defined by Pitzer-Curl [11]; w is the acentric factor; T_c is the solvent critical temperature; and P_c is the solvent critical pressure. The modified Pitzer-Curl fugacities are determined by:

$$f^{(0)} = 0.1445 - \frac{0.33}{T_r} - \frac{0.1385}{{T_r}^2} - \frac{0.0121}{{T_r}^3} - \frac{0.000607}{{T_r}^8} \tag{28a}$$

$$f^{(1)} = 0.0637 + \frac{0.331}{{T_r}^2} - \frac{0.423}{{T_r}^3} - \frac{0.008}{{T_r}^8} \tag{28b}$$

where T_r is the reduced temperature.

$\ln\alpha_1$ is related to the Gibbs free energy change on mixing through the following expression [17]:

$$RT\ln\alpha_1 = \left(\frac{\partial \Delta G_{mix}}{\partial n_1}\right)_{n_2,P,T} \tag{29}$$

The partial derivative can be evaluated with the derivation of equation (5), which leads to:

$$\left(\frac{\partial \Delta G_{mix}}{\partial n_1}\right)_{n_2,P,T} = RT\left[\ln\phi_1 + 1 - \frac{V_1}{V_2} + \chi_{12}\right] \tag{30}$$

By combining equations (25), (26), (29) and (30), and after some manipulation, the expression for χ_{12} reads [4]:

$$\chi_{12} = \ln\left(\frac{273.15Rv_2}{Vg^0 V_1 P_1^0}\right) - \left(1 - \frac{\mathrm{V}_1}{\mathrm{M}_2 v_2}\right) - \frac{P_1^0(B_{11} - V_1)}{RT} \tag{31}$$

Under infinite dilution conditions, for high molecular weight polymers, the second term of the right hand side of equation (31) approaches 1. So, the final expression, the one used in most of the IGC literature, is [1]:

$$\chi_{12} = \ln\left(\frac{273.15Rv_2}{V_g{}^0 V_1 P_1{}^0}\right) - 1 - \frac{P_1{}^0(B_{11} - V_1)}{RT} \tag{32}$$

Traditionally, when the Flory-Huggins lattice theory is applied to a solvent-polymer system, the molar volume of the solvent is used as the reference volume to define the size of the lattice. The problem is that it is difficult to compare the interaction strengths between different solvents with the same polymer since χ_{12} are calculated based upon different lattice sizes. As a result, the apparent differences in the interaction parameters among different solvents with the same polymer do not necessarily come completely from the differences in the intermolecular interactions but also, the lattice sizes that were used.

Zhao and Choi [10] proposed a common reference volume approach by which, the interaction strengths between the different solvents with the polymer can be properly compared. Their approach was incorporated into this work. Therefore, equation (32) should be modified to:

$$\chi_{12} = \frac{V_0}{V_1}\left[\ln\left(\frac{273.15Rv_2}{V_g{}^0 V_1 P_1{}^0}\right) - 1 - \frac{P_1{}^0(B_{11} - V_1)}{RT}\right] \tag{33}$$

where V_0 is the common reference volume (molar volume of the ethylene repeat unit in this work). Note that if V_1 is used as the reference volume, the term V_1/V_0 in the above expression will become 1 and equation (33) will reduce to equation (32). Once the solvent-polymer interaction parameters are determined, the Hildebrand solubility parameters of the pure polymers can then be obtained by the procedure described below.

First, the solubility parameters of the solvents (δ_1) have to be determined. δ_1 is defined as follows [11]:

$$\delta_1 = \left(\frac{\Delta E_{vap}}{V_1} \right)^{1/2} \tag{34}$$

where ΔE_{vap} is the internal energy change of vaporization. Assuming that the solvent vapor behaves as an ideal gas:

$$\delta_1 = \left(\frac{\Delta H_{vap} - RT}{V_1} \right)^{1/2} \tag{35}$$

where ΔH_{vap} is the enthalpy change of vaporization of the solvent at temperature T. In this way, the solubility parameters of low-molecular weight species can be determined in a straightforward manner by direct measurement of ΔH_{vap}.

The temperature dependence of δ can be obtained from the following empirical correlation [8]:

$$\left(\frac{\delta_{1,T_2}}{\delta_{1,T_1}} \right)^2 = \left(\frac{V_{1,T_1}}{V_{1,T_2}} \right)^{2.27} \tag{36}$$

where $\delta_{1,Ti}$ and $V_{1,Ti}$ are the Hildebrand solubility parameter and molar volume of the solvent at T_i. All the $\delta_{1,T1}$ used came from [7] and were determined by their respective heat of vaporization at 25°C.

Once the solubility parameters of the solvents used are determined, the next step is to determine the solubility parameter of the polymer. In this work, two approaches were adopted and their results were compared. The first is the one developed by Choi *et al.* [14]. The essence of their method is that the solubility parameter of the polymer of interest is determined by averaging the solubility parameters of the solvents that exhibit $\chi_{12} < \chi_{12,crit}$. This new approach is an attempt to better quantify the well known rule of "like dissolves like". The rationale is exactly the same as that of the solvent swelling experiments except that one uses a more objective indicator, the interaction parameter, instead of the degree of swelling, to judge miscibility. It is worth noting that solvents with different δ can dissolve the same polymer. The more solvents we used, the better the chance of determining the sphere of miscibility of the polymer-solvent system. And the average of the solvents' δ constitutes the best estimate of δ_2. To better understand the method, let's take a look at one example:

As can be seen in Table 1, only δ_1 values of solvents that show $\chi_{12} < \chi_{12,crit}$ will be used in the calculation of δ_2 (in this case, for A-2 at 170 ^{0}C). δ_2 is determined by averaging all selected values of δ_1 and the uncertainties associated with the computed δ_2 correspond to the standard deviation of the δ_1 values considered:

$$\delta_2 = \frac{13.4 + 12.5 + 14.1 + 12.2 + 14.7 + 14.4}{6} = 13.5(MPa)^{1/2}$$

It is interesting to note that solvents that have comparable δ (benzene and toluene in Table 1) do not necessarily show similar χ_{12} values. At this point, it is not clear to us the reason for such observation. Further investigation is needed.

Table 1: Measured χ_{12} between A-2 (LLDPE) and Solvents Used and their δ_1 Values at 170° C.

Solvents	χ_{12}^{*}	$\chi_{12,crit}^{*}$	$\delta_1(MPa)^{1/2}$	**Solvents Selected for Study**
1-hexene	0.14	0.10	10.7	
1-octene	0.15	0.09	12.3	
benzene	0.24	0.16	14.7	
cyclohexane	0.34	0.13	13.1	
hexane	0.14	0.12	10.7	
n-dodecane	0.06	0.08	13.4	X
n-heptane	0.12	0.11	11.6	
n-nonane	0.08	0.09	12.5	X
n-pentadecane	0.05	0.07	14.1	
n-pentane	0.15	0.13	9.0	X
octane	0.10	0.11	12.2	
toluene	0.15	0.17	14.7	X
xylene	0.12	0.16	14.4	X

* values calculated with the ethylene repeat unit molar volume as a reference.

The second method, which is commonly used by IGC users, is the one developed by DiPaola-Baranyi and Guillet [1]. In particular, they interpret the Flory-Huggins interaction parameter as a residual free energy function rather than the original enthalpy parameter which, allows separation into enthalpic and entropic contributions:

$$\chi = \chi_H + \chi_S \tag{37}$$

The basis of the method is that the solubility parameters of the solvent δ_1, and polymer δ_2, are introduced in the form of Regular Solution theory [4] to account for enthalpic effects:

$$\chi_{12}^{\infty} = \left(\frac{V_0}{RT}\right) * (\delta_1 - \delta_2)^2 + \chi_s^{\infty} \tag{38}$$

where the subscript ∞ indicates that IGC data is collected at infinite dilution of solvent in the polymer and V_0 is the molar volume of the repeat unit of the polymer (in this case, ethylene). Rearrangement of equation (38) yields:

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi_{12}^{\infty}}{V_0}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_S^{\infty}}{V_0}\right) \tag{39}$$

A plot of the function on the left-hand side of equation (39) versus δ_1 should give a linear line with a slope of $2\delta_2 / RT$. One disadvantage of this method is that if the measured χ_{12}^{∞} values are negative, the data do not conform to the linear relationship.

In order to quantify miscibility of polymer blends, the Flory-Huggins interaction parameter between two polymers (i.e., χ_{23}) is sought. With the values of the Hildebrand solubility parameters of two different polymers, δ_2 and δ_3, the interaction parameters χ_{23} ($\chi_{\mathrm{LDPE\text{-}LLDPE}}$ or $\chi_{\mathrm{LLDPE\text{-}LLDPE}}$) can be calculated using a correlation based upon the combination of the Hildebrand solubility parameter and Flory-Huggins lattice theories [9]:

$$\chi_{23} = \frac{V_0}{R * T}(\delta_2 - \delta_3)^2 \tag{40}$$

where V_0 is the smallest molar volume of the repeat units of the polymers comprising the blend (in the present work, the molar volume of ethylene repeat unit) at temperature T; δ_2 and δ_3 are the respective Hildebrand solubility parameters of the constituent polymers; and R is the gas constant. The main assumptions underlying equation (40) are: no volume change on mixing, ideal entropy of mixing, weak forces of the induced dipole type (i.e., dispersive interactions), and Berthelot's rule for the cross interactions, which produces the perfect square form of the equation. It is worth noting that according to the Flory-Huggins lattice theory, one can obtain negative χ_{23}. It is only when it is combined with the Hildebrand solubility parameter theory that the resultant expression (i.e., equation (40)) forces χ_{23} to be positive. The major rationale for using this expression in the present work is because both experimental studies and theoretical work have suggested that equation (40) is valid for hydrocarbon polymer blends [15].

2.2 References

1. Lloyd DR, Ward TC, Schreiber HP, Pizana CC, ACS Symposium Series, Inverse Gas Chromatography, Characterization of Polymers and other Materials, American Chemical Society, Toronto (1988)

2. Prausnitz J, Ruiger N, Leichtinphaler, Azevedo EG., *Molecular Thermodynamics Fluid-Phase Equilibria*, 417-501, 3rd Edition, Prentice Hall International Series (1999)

3. Hans-Georg Elias, *Introduction to Polymer Science*, 223-233, 1st Edition, VCH (1997)

4. Al-Saigh Z, *Int. J. Polym. Anal & Charact*, 3, 249-291 (1997)

5. Reid RC, Prausnitz JM, Sherwood TK, *The Properties of Gases and Liquids*, McGraw-Hill (1997)

6. Rudin A, Chee KK and Shaw JH, *J. Polym. Sci, Part C*, 30, 415 (1970)

7. Barton FM, *CRC Handbook of Solubility Parameters and other Cohesion Parameters*, 123-133,303-308, CRC Press (1991)

8. Utracki LA, *Polymer Alloys and Blends - Thermodynamics and Rheology*, Hanser Publishers, Munich (1989)

9. Al-Saigh ZY, *Int. J. Polym. Anal. Charact.*, 3, 249 (1997)

10. Zhao L, Choi P, *Polymer, 42, 1075* (2000)

11. Tsonopoulos C, *AIChE Journal*, 20, 263 (1974)

12. Panayiotou C, *Macromolecules*, 20, 861 (1987)

13. Hill TL, *An Introduction to Statistical Thermodynamics*, 402-408, Dover Publicatio, NY (1986)

14. Choi P, Kavassalis TA, Rudin A, *J. Colloid and Inter. Sci*, 180, 1 (1996)

15. Schwizer KS, Curro JG, *Advances in Chemical Physics*, vol. XCVIII, 65-67, John Wiley & Sons, NY (1997)

16. Denbigh KG, *Principles of Chemical Equilibrium*, Cambridge University Press, 4th edition (1996)

17. Flory PJ, *Principles of Polymer Chemistry*, Cornell University Press: New York (1953)

CHAPTER 3

3 EXPERIMENTAL

3.1 Preparation of Coated Solid Support

Each polymer was first dissolved in xylene in the temperature range of 100 – 110°C. An inert solid support chromosorb W (60/80 mesh) was then added to the polymer solution at a polymer to solid support mass ratio of approximately 10%. This is to ensure that a ratio of at least 7% will be obtained in the final coated chromosorb. A lower ratio would not have enough polymer to coat all internal surfaces of the chromosorb, which will affect the measured retention time significantly. On the other hand, for ratios above 10%, the polymer coated on the solid support would form a thick layer, and it would be difficult for the solvents used for the IGC experiments to reach equilibrium promptly. Xylene was then slowly evaporated by gentle heating the slurry at about 100°C with constant stirring using a rotary evaporator. The dried coated support was then transferred to a vacuum oven and conditioned at 80°C for 4 hours in order to remove the residual solvent. The percent loading of the polymer on the support was determined by calcination of 1 to 1.5 g of the coated solid support in a furnace operated at a temperature of 850°C for 12 hours. Table 2 summarizes the total mass of the coated solid support, the mass of the polymer and the corresponding polymer / solid support ratio for each column.

Table 2: Total Mass, Mass of the Coated Polymer and Loading for Each Column

Polymer	**Total mass of the coated support (g)**	**Polymer Mass (g)**	**Loading (%w/w)**
A-1 (LLDPE)	0.6593	0.0599	9.0
A-2 (LLDPE)	0.5414	0.0379	7.0
A-3 (LLDPE)	0.5888	0.0529	8.9
A-4 (LLDPE)	0.5943	0.0507	8.5
A-5 (LLDPE)	0.6225	0.0521	8.4
A-6 (LLDPE)	0.5463	0.0380	7.0
M-1 (LLDPE)	0.6439	0.0553	8.6
M-2 (LLDPE)	0.5559	0.0445	8.0
M-3 (LLDPE)	0.6440	0.0515	8.0
M-4 (LLDPE)	0.5901	0.0460	7.8
M-5 (LLDPE)	0.5773	0.0433	7.5
S-216 (LDPE)	0.6863	0.0535	7.8

3.2 Column preparation

Columns were prepared with the use of stainless steel tubes (100 cm in length and approximately 0.18 cm inner diameter) that were acetone washed in the lab and then plugged at one end by inert glass wool and filled with the coated solid support. In order to achieve even packing, the column was constantly vibrated during filling. After the column was filled, the other end was also plugged with the same type of glass wool. Columns were conditioned with pre-purified Helium for 2 days at 60°C in a gas chromatograph in order to further eliminate any residual solvent before data collection. Helium was also used as a carrier gas in the actual experiments when various solvents were injected into the column and its flow rates were measured at the corresponding experimental temperatures with the use of a soap bubble flowmeter. In general, the flow rates ranged from 18 mL/min to 20 mL/min, as recommended by the GC manual [HP 4890D Gas Chromatograph Operating Manual, Hewlett Packard Company (1997)].

3.3 Instrumentation

All IGC measurements were carried out on a Hewlett-Packard 4890 gas chromatograph equipped with a flame ionization detector (FID). Very small volumes (~ 1 μL) of the vapor of the selected solvents were injected manually with 10μL Hamilton syringes with removable needle and Bevel tip #2 in order to satisfy the infinite dilution conditions for the solvent. For each solvent, 3 samples were injected with a reproducibility of 3% and their average retention times were used for subsequent calculations. Experiments were repeated at 170, 190, 210 and 230°C for each column. The inlet and outlet pressures of the column were measured with the manometers and are shown in Table 3.

3.4 Materials

LDPE with a code of S-216 and LLDPE with codes of A-1 to A-6 and M-1 to M-5 samples were obtained from NOVA Chemicals Corporation based in Calgary, Canada. The A-series LLDPEs were prepared by Ziegler-Natta catalysts while the M-series by single-site catalysts. Their average molecular weights, polydispersity, melt index and branch contents are listed in Table 4.

Table 3: Inlet and Outlet Pressures of Each Column at Each Temperature

Column	Manometric Inlet Pressure (KPa) at the experiment temperatures				Outlet Pressure (KPa)
	170°C	190°C	210°C	230°C	
A-1	150	150	160	160	96
A-2	150	150	160	170	96
A-3	160	160	160	160	96
A-4	150	150	150	160	96
A-5	140	145	150	150	96
A-6	130	140	140	140	96
M-1	100	110	110	110	96
M-2	140	150	160	165	96
M-3	120	130	135	140	96
M-4	100	110	120	125	96
M-5	100	105	110	115	96
S-216	150	150	170	170	96

The M_n and the M_w values were obtained by GPC (Gel Permeation Chromatography). Branch Content values were obtained by ^{13}C NMR, (Nuclear Magnetic Resonance using carbon 13). Polydispersity values were determined by the ratio of M_w / M_n.

The solvents used were purchased from Fisher Scientific and used without further purification. They were 1-hexene, 1-octene, benzene, cyclohexane, n-hexane, n-dodecane, n-heptane, n-nonane, n-pentadecane, n-pentane, n-octane, toluene, xylene. Methane was used as the marker for the determination of the net retention time of the other solvents.

Table 4: Average Molecular Weights, Polydispersity, Melt Index and Branch Content of the Polyethylenes Used.

Polymer	M_n	M_w	**Polydispersity**	**Melt Index**	**Branch content**
A-1	20,500	102,500	5.0	1.02	12.9
A-2	17,300	105,530	6.1	1.02	35.0
A-3	18,800	122,200	6.5	0.40	11.9
A-4	26,400	116,160	4.4	0.65	12.7
A-5	20,800	116,480	5.6	0.60	15.6
A-6	25,500	112,200	4.4	0.70	15.3
M-1	38,700	77,400	2.0	2.6	11.4
M-2	25,700	69,390	2.7	3.2	30.4
M-3	15,300	47,430	3.1	14.7	27.7
M-4	10,500	99,750	9.5	0.72	19.6
M-5	34,800	104,400	3.0	0.68	11.3
S-216	17,000	94,000	5.5	-	20-22

To date, most IGC studies used from 11-14 solvents [1]. In this work, the choice of the above 13 non-polar solvents were used based on previous work done on comparable blend systems where these solvents had shown good miscibility with the samples – in the great majority of the cases, $\chi_{12} < \chi_{12,crit}$. According to the $\chi_{12,crit}$ concept (with the solvent molar volume as a reference) explained in Chapter 2, any value of χ_{12} below 0.5 would make the solvent miscible with the polymer under infinite dilution conditions. And using the other approach where the ethylene molar volume is used as a reference, the χ_{12} values should be no greater than the values obtained by equation (17).

In order to verify that polar solvents are not suitable to characterize the blends, two very polar solvents, methanol and ethanol, were injected in one of the columns (LLDPE, M-4). Their χ_{12} results are summarized in Table 5:

Table 5: Measured χ_{12} Values between Methanol and Ethanol and LLDPE (M-4) Using the Ethylene Molar Volume as a Reference.

Solvent	**T= 170°C**	**T=190°C**	**T=210°C**	**T=230°C**
methanol	23.1	22.3	21.8	21.5
ethanol	15.9	15.4	15.1	14.8

The values for χ_{12} observed for these solvents are significantly higher than the values obtained for the non-polar solvents as such data will be seen in Chapter 4, which indicates that these solvents are most probably not suitable for our studies.

Table 6 summarizes the $\chi_{12,crit}$, using ethylene molar volume as a reference at each temperature. As depicted from Tables 5 and 6, $\chi_{12} >> \chi_{12,crit}$ which confirmed the suspicion that very polar solvents such as methanol and ethanol are not suitable for the characterization of polyethylene blends. And, as a result, the polar solvents were not considered for this study. However, as the non-polar solvents showed better thermodynamic miscibility with the polymers under study, they were the only ones used in our analysis.

Table 6: Calculated $\chi_{12,crit}$ Values for Methanol and Ethanol and LLDPE (M-4) Using the Ethylene Molar Volume as a Reference.

Solvent	**T= 170^{0}C**	**T=190^{0}C**	**T=210^{0}C**	**T=230^{0}C**
methanol	0.28	0.37	0.35	0.36
ethanol	0.20	0.25	0.24	0.26

CHAPTER 4

4 RESULTS & DISCUSSION

Figures 1 to 12 depict the χ_{12} values between the selected solvents and the twelve pure polyethylenes calculated based upon the measured V_g^0 values and the molar volume of an ethylene repeat unit. The errors associated with the χ_{12}, not shown here for clarity, are rather small and usually within 5%. Some of error sources are the measured mass of the polymer, carrier gas flow rates and net retention times. It is evident from the plots that LDPE S-216 and all A-series LLDPEs except for A-6 (i.e., Figures 1- 5 and 12), have χ_{12} values that are rather insensitive to the temperature for the chosen temperature range. This implies that the conformation of the polyethylene molecules may have changed to a more closely packed structure into which the solvents had difficulty penetrating. However, for the M-series LLDPEs and A-6 (i.e., Figures 6-11) we observed an almost 1/T relation over the temperature range of 170 to 200°C. This is what is expected from the Flory-Huggins lattice theory. One possible explanation for this is that the molecular architectures of these polyethylenes allow the molecules to become less closely packed at higher temperatures. It was also observed that both dodecane and pentadecane consistently give lower χ_{12} values (i.e., higher miscibility with the polymers) than other solvents which are aromatic in nature such as toluene and benzene. These results are expected as the aliphatic compounds have similar structures to polyethylene molecules and similar structure leads to higher miscibility. In addition, for certain solvents, such as benzene and cyclohexane, the χ_{12} value increases with increasing temperature. This is probably due to large differences in their thermal expansion coefficients. However, we cannot rule out other possible explanations since most of these resins are commercial and only basic information about their characteristics is given. Therefore, we cannot speculate more about these results.

The temperature dependence of χ_{12} for the A series is very different from the temperature dependence of χ_{12} for the M series. This is probably attributed to the fact that Ziegler-Natta and single-site based catalysts give polyethylene with different structures. It is well-known that Ziegler-Natta catalysts give molecules with randomly distributed branches, while by single-site catalysts, uniformly distributed branches along the backbone are formed. These structural differences may be responsible for the way the molecules pack in the liquid state which will ultimately determine the miscibility of the polymer with any solvent (i.e., a more closely packed liquid morphology will not allow much solvent to get in than one that is less packed and with more available space for the solvent to penetrate). However, this method cannot be used to determine the type of packing.

The A-series LLDPEs showed χ_{12} values ranging from 0.0 to 0.6 while the M-series a broader interval ranging from –0.1 to 0.7. It is worth noting that our extrapolated χ_{12} values at lower temperatures are in good agreement with values for comparable systems obtained by other authors (e.g. 140°C) [1].

Here it is important to point out that because in this work only branched polymers were used, the "real" $\chi_{12,crit}$ for these systems should be smaller than the values found by equation (17). This is because branches should reduce the number of ways the polymer molecules arrange themselves in the lattice which in turn decreases the mixing entropy. However, it is not clear to us by how much χ_{crit} will be smaller.

The same reasoning can be applied for the χ_{12} where equations (32) and (33) may overestimate its value. It is known that if the "real" combinatorial entropy does not conform to the Flory-Huggins lattice theory, different values for χ_{12} will be obtained. Once again, at this point we are not able to quantify by how much χ_{12} is being overestimated.

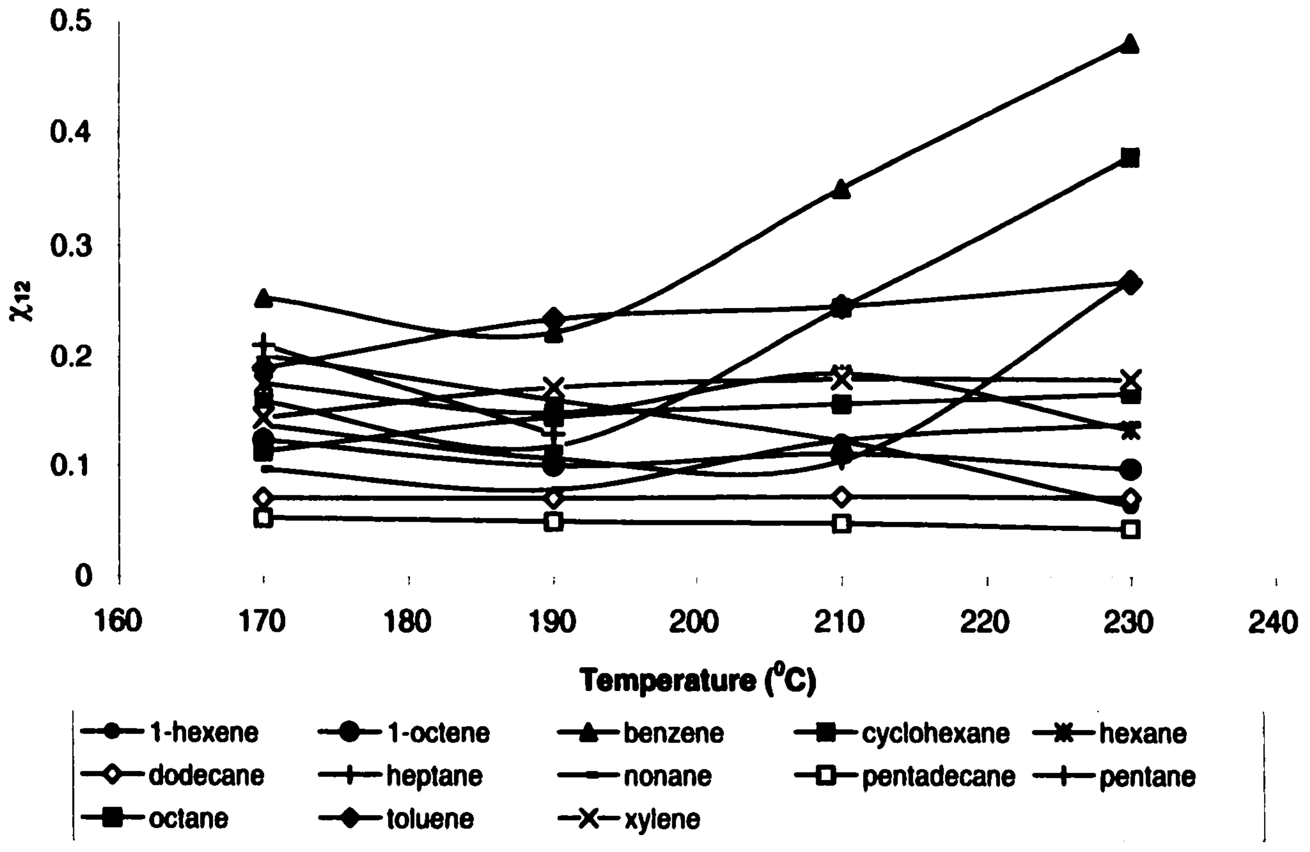

Figure 1: Interaction parameters χ_{12} *between the selected organic solvents with A-1 (LLDPE)*

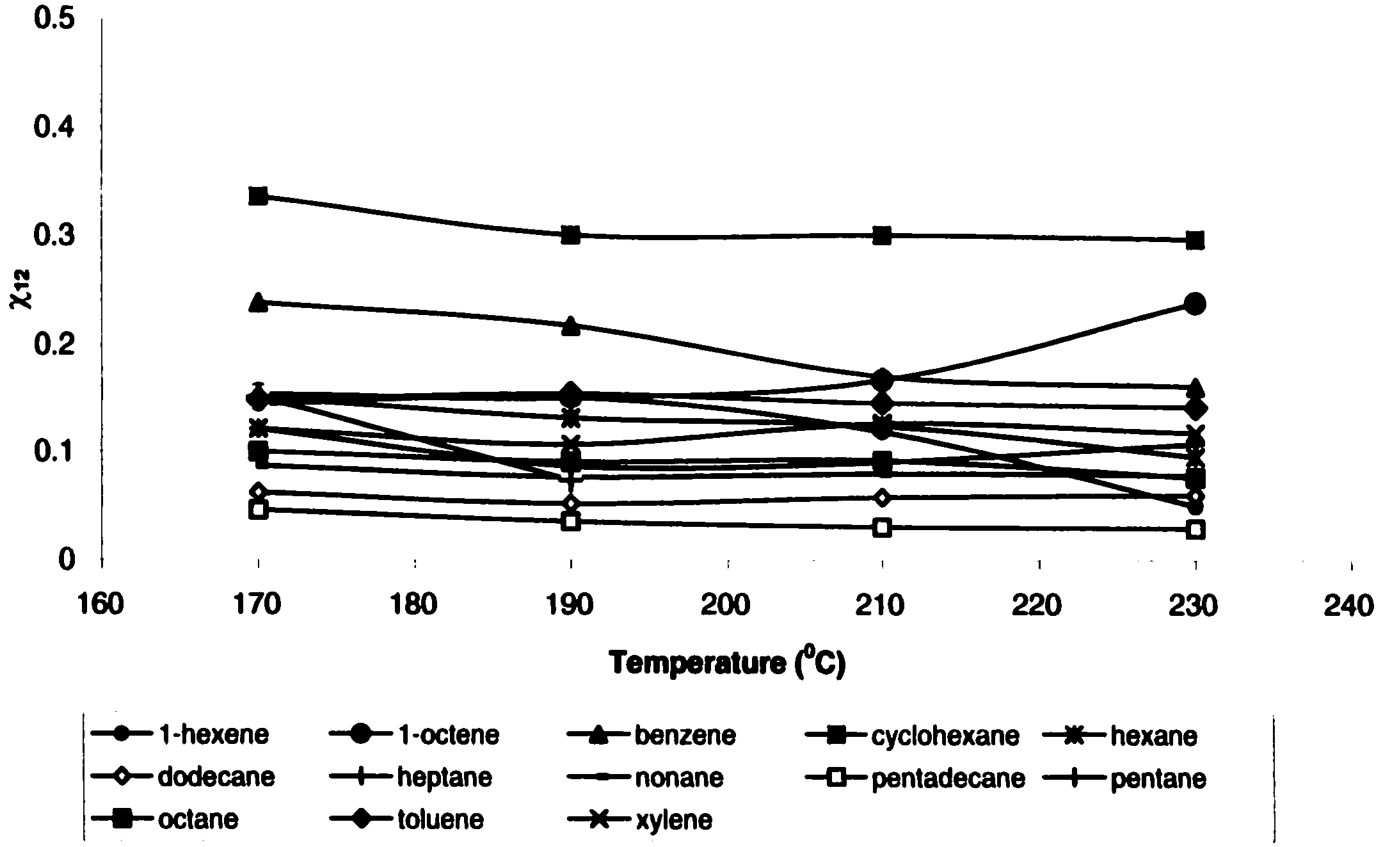

Figure 2: Interaction parameters χ_{12} between the selected organic solvents with A-2 (LLDPE)

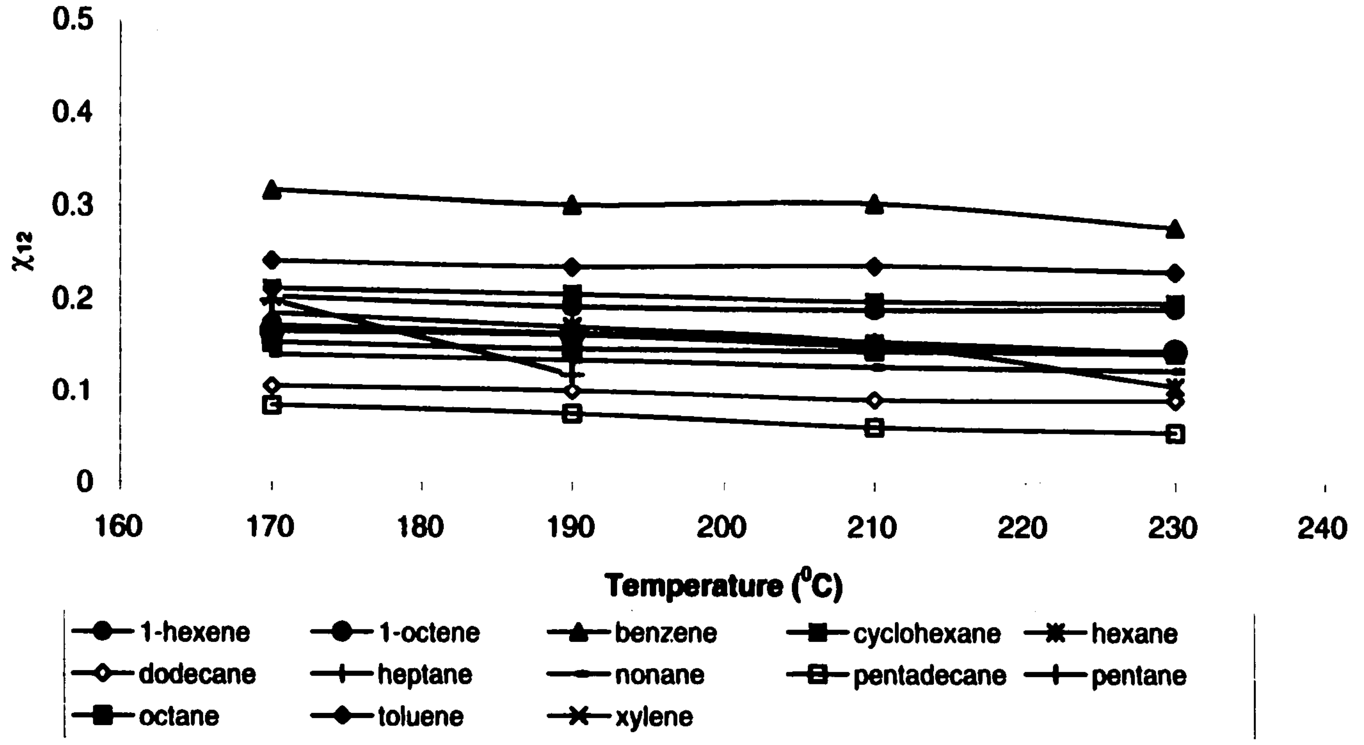

Figure 3: Interaction parameters χ_{12} between the selected organic solvents with A-3 (LLDPE)

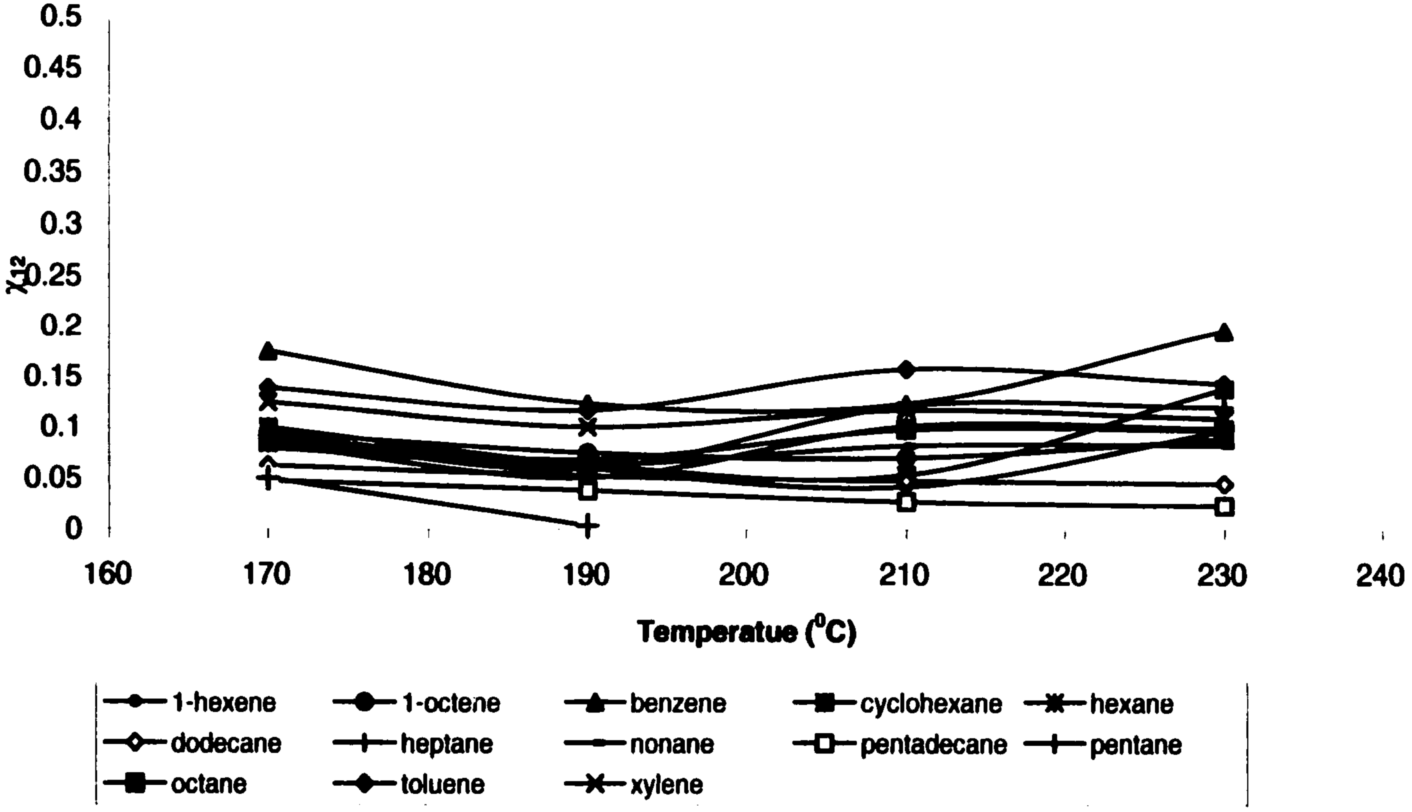

Figure 4: Interaction parameters χ_{12} between the selected organic solvents with A-4 (LLDPE)

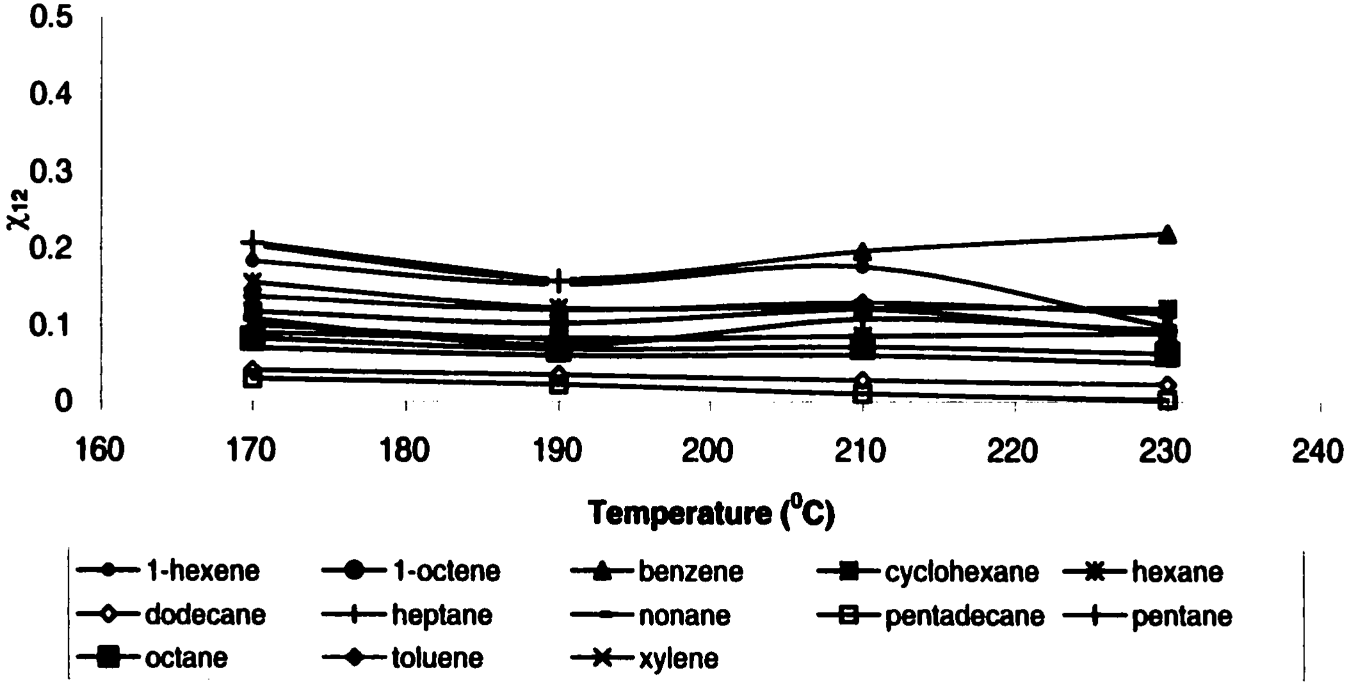

Figure 5: Interaction parameters χ_{12} *between the selected organic solvents with A-5 (LLDPE)*

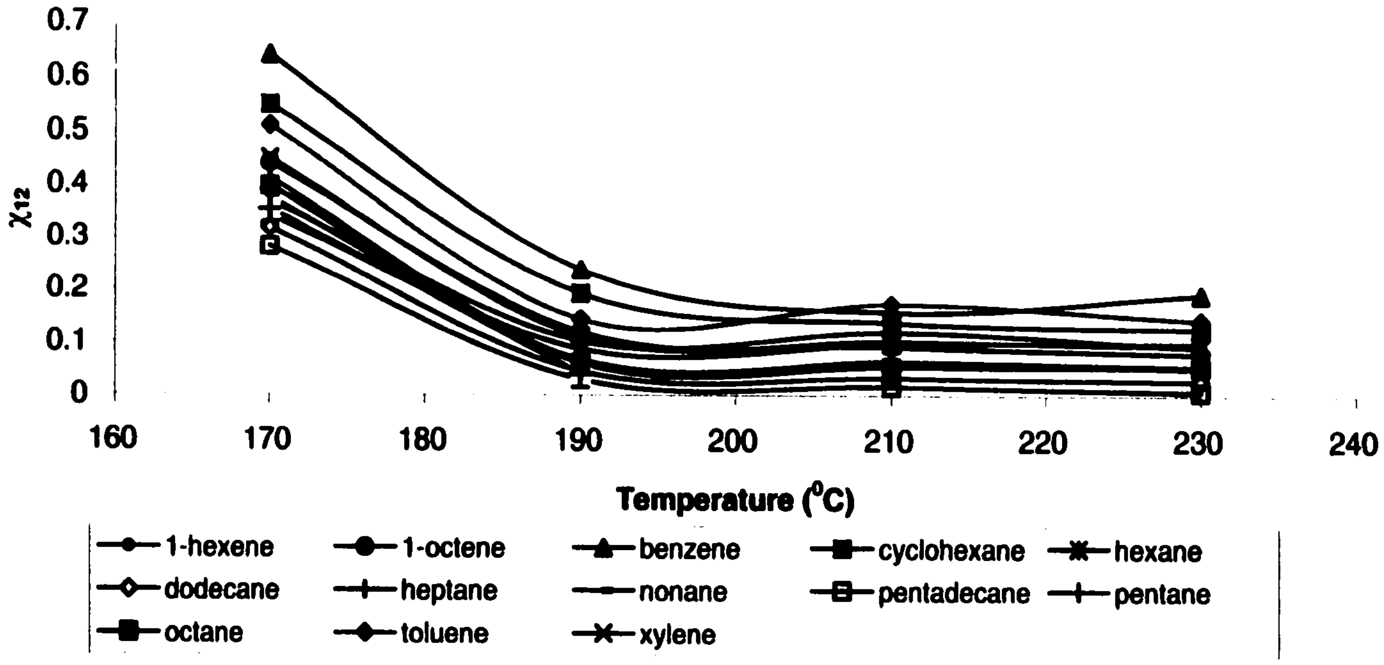

Figure 6: Interaction parameters χ_{12} betweenthe selected organic solvents with A-6 (LLDPE)

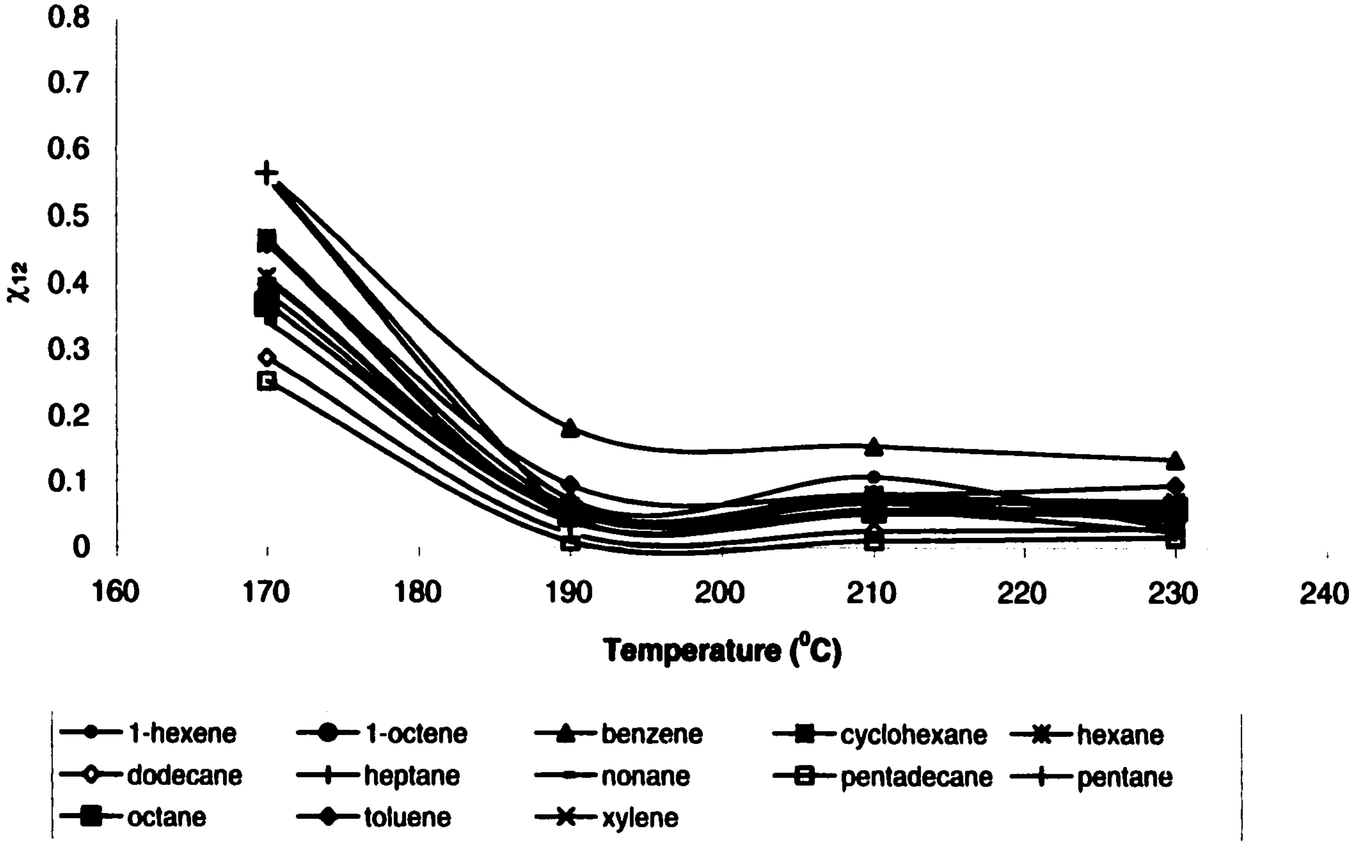

Figure 7: Interaction parameters χ_{12} between the selected organic solvents with M-1 (LLDPE)

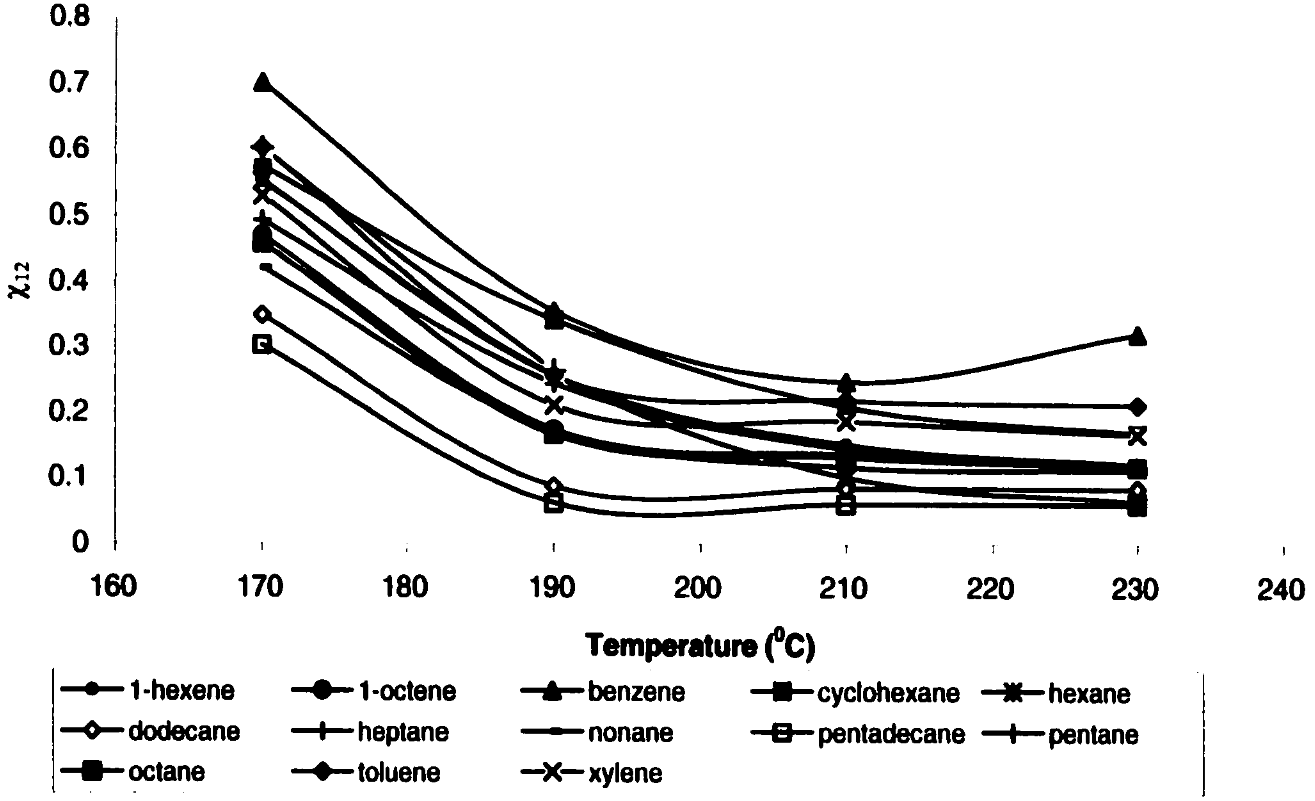

Figure 8: Interaction parameters χ_{12} between the selected organic solvents with M-2 (LLDPE)

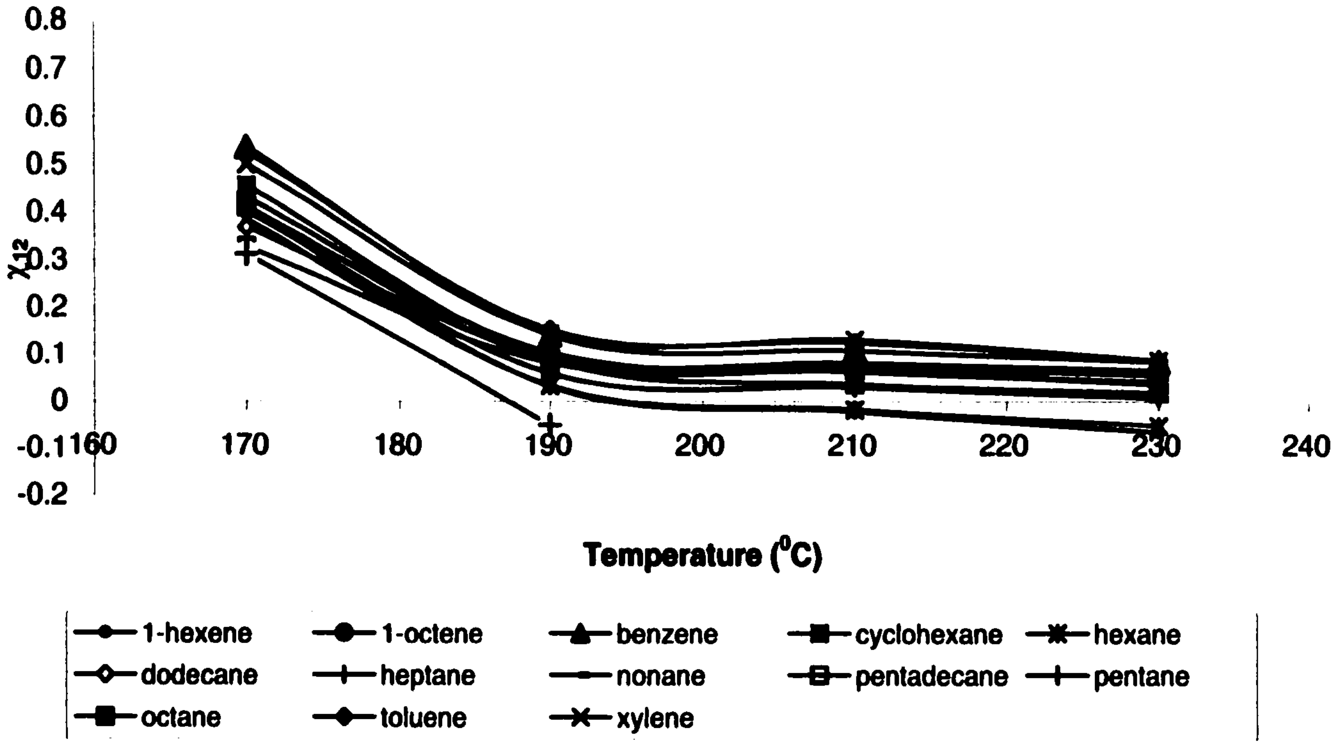

Figure 9: Interaction parameters χ_{12} between the selected organic solvents with M-3 (LLDPE)

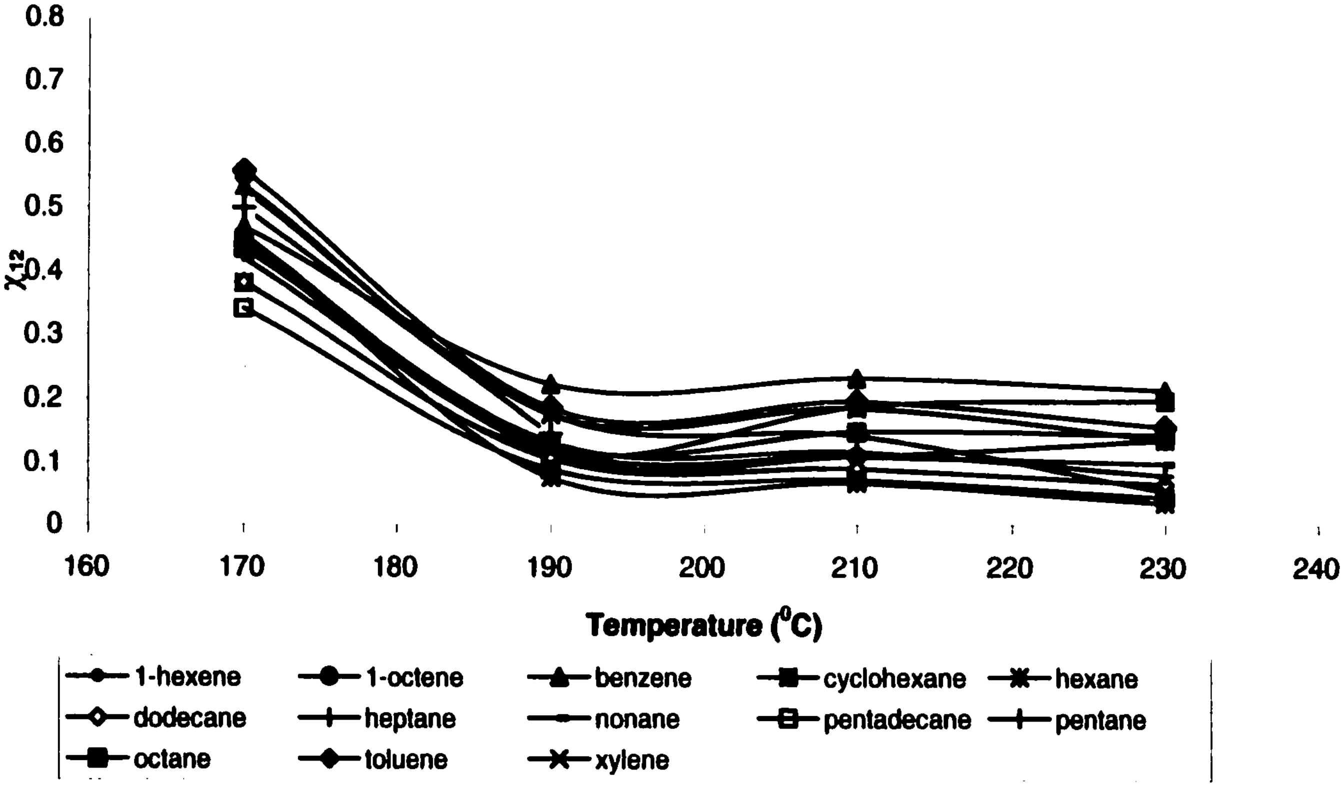

Figure 10: Interaction parameters χ_{12} *between the selected organic solvents with M-4 (LLDPE)*

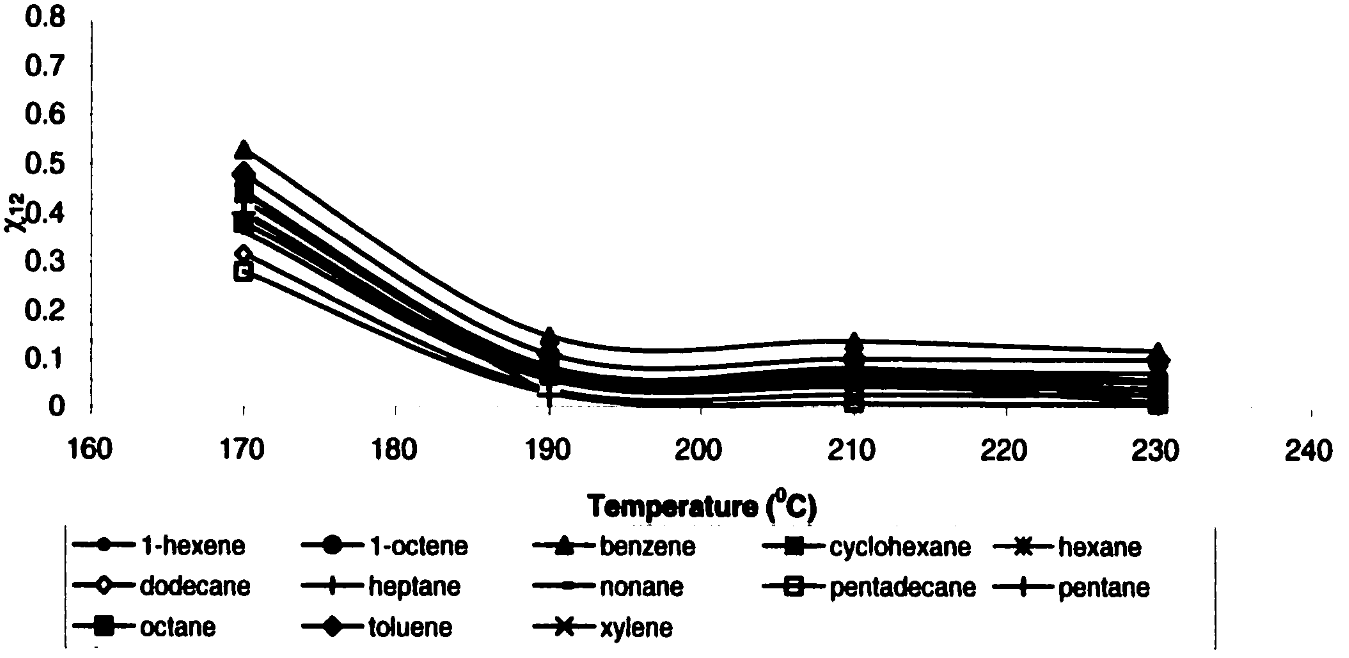

Figure 11: Interaction parameters χ_{12} *between the selected organic solvents with M-5 (LLDPE)*

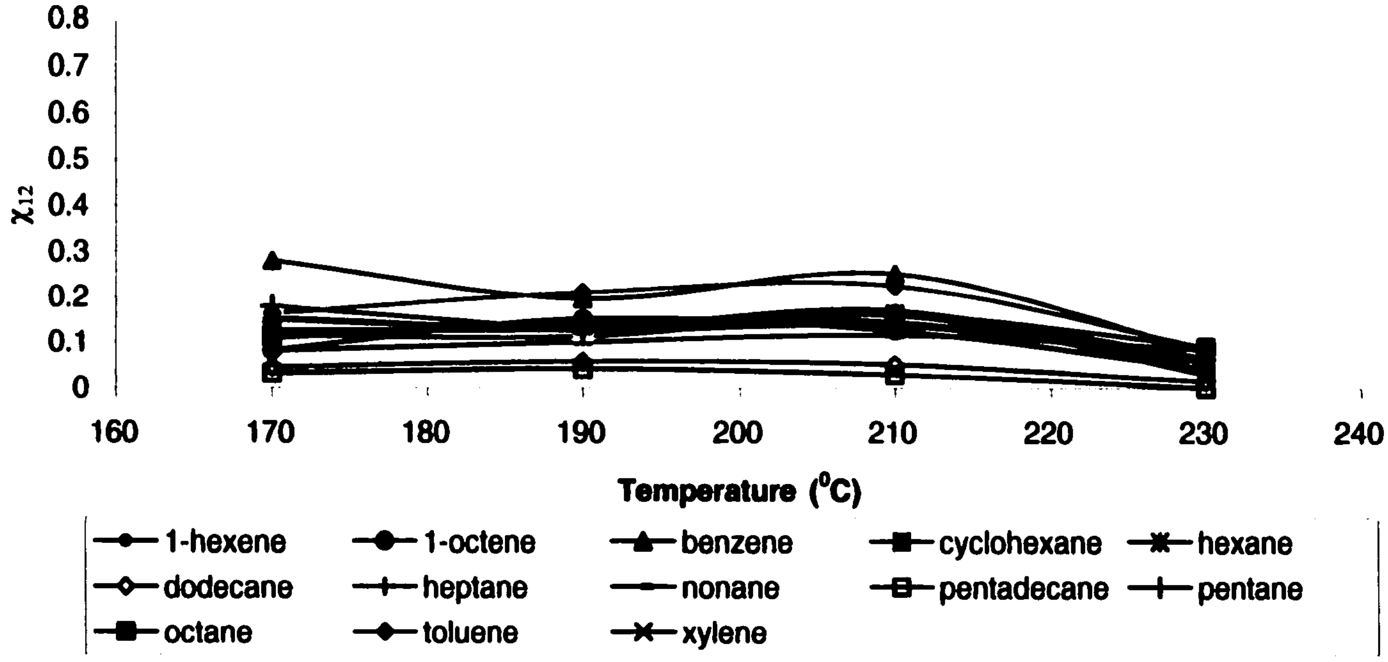

Figure 12: Interaction parameters χ_{12} between the selected organic solvents with S-216 (LDPE)

Using the procedures described in Chapter 2, we summarize the values for δ_2 by the two different approaches in Tables 7 and 8. The first is referred to as the average method and the second as the plot method.

Table 7: Measured Solubility Parameters of LLDPE (A series and M series) and LDPE (S-216) at the Experimental Temperatures Using the Average Method.

Polymer	T= 170°C	T= 190°C	T= 210°C	T= 230°C
LLDPE – A1	13.5 ± 0.3	12.3 ± 0.4	12.0 ± 0.6	10.4 ± 0.7
LLDPE – A2	13.5 ± 0.5	12.1 ± 0.8	11.9 ± 0.8	11.2 ± 0.7
LLDPE – A3	12.5 ± 0.8	12.2 ± 0.7	11.5 ± 0.9	10.6 ± 0.5
LLDPE – A4	12.6 ± 0.8	11.8 ± 1.1	11.8 ± 0.9	11.8 ± 0.4
LLDPE – A5	13.3 ± 0.4	11.8 ± 0.7	12.2 ± 0.4	11.6 ± 0.5
LLDPE – A6	12.2 ± 1.1	11.6 ± 1.5	12.0 ± 0.6	11.4 ± 0.7
LLDPE – M1	13.1 ± 0.4	11.7 ± 0.6	11.8 ± 0.5	10.6 ± 0.7
LLDPE – M2	12.7 ± 0.4	11.8 ± 0.6	11.5 ± 0.5	10.6 ± 0.7
LLDPE – M3	11.1 ± 0.8	10.8 ± 0.8	11.0 ± 0.6	10.3 ± 0.7
LLDPE – M4	13.1 ± 0.4	11.7 ± 0.6	11.8 ± 0.5	10.6 ± 0.7
LLDPE – M5	12.5 ± 0.5	11.7 ± 0.6	11.5 ± 0.5	10.6 ± 0.7
LDPE – S-216	13.5 ± 0.3	13.0 ± 0.2	12.7 ± 0.3	10.6 ± 1.4

Table 8: *Measured Solubility Parameters of LLDPE (A series and M series) and LDPE (S-216) at the Experimental Temperatures Using the Plot Method.*

Polymer	T= 170°C	T= 190°C	T= 210°C	T= 230°C
LLDPE – A1	12.2	11.2	11.1	9.5
LLDPE – A2	12.2	11.1	11.1	9.6
LLDPE – A3	12.2	11.1	11.1	9.6
LLDPE – A4	12.2	11.2	11.1	9.6
LLDPE – A5	12.2	11.1	11.1	9.5
LLDPE – A6	12.2	11.1	11.1	9.6
LLDPE – M1	12.2	11.2	11.1	9.6
LLDPE – M2	12.2	11.1	11.1	9.6
LLDPE – M3	12.2	11.1	11.1	9.5
LLDPE – M4	12.2	11.2	11.1	9.6
LLDPE – M5	12.2	11.1	11.1	9.6
LDPE – S-216	12.2	11.1	11.1	9.6

As can be seen in Tables 7 and 8, at each temperature, the plot method gives the same δ_2 value, regardless of the polymer used. Consequently, these results lead to zero χ_{23} values for all pairs of polyethylene, which is physically unreasonable. This is due to the fact that the only term in equation (39) that varies from one polymer to another is χ_{12}^{∞} / V_1. And as the measured χ_{12} values were rather small and almost identical to each other, similar δ_2 were obtained. In our view, this method is more suitable to systems of which polymers of interest exhibit significantly different χ_{12} values with the solvents used. However, with the use of the average method, individual numbers were obtained at each temperature for each polymer, which allowed the calculation of χ_{23}. It should be pointed out that the δ values obtained by the average method extrapolated to lower temperatures are in agreement with the results previously obtained by other IGC researchers [1,2] where the measured solubility parameters range from 10 to 13 $[\mathrm{MPa}]^{1/2}$.

Here, it is important to point out that Sperling *et al.* [3], based upon PVT (Pressure - Volume - Temperature) measurements of a series of polyolefins over a temperature range of 30°C to 220°C, obtained Hildebrand solubility parameter values which are significantly higher than those reported here. For instance, at 166°C, Sperling *et al.* reported δ values for comparable polyethylene systems, between 16.2-18.2 $(\mathrm{MPa})^{1/2}$ which are essentially in the range of the δ values of polyethylene at 25°C [4]. As one can see, there is a clear paradox here: how can one obtain values for the Hildebrand solubility parameters at 166°C that are within the same range as the ones reported in the literature at 25°C if it is well known that the Hildebrand solubility parameter decreases with increasing temperature?

If values obtained from the PVT measurements at elevated temperatures are reliable, the Hildebrand solubility parameters of these materials at 25°C need to be reexamined. One possible explanation for the above described paradox is that the concept of the Hildebrand solubility parameter is only valid for amorphous polymers and as this concept is extended to semi-crystalline polymers in the solid state, the crystallinity present in such polymers is not properly accounted for.

With the use of the measured δ values and equation (40), χ_{23} values for the LDPE/LLDPE and LLDPE/LLDPE blends were calculated and are summarized in Figures 13-30. For clarity, the data points at the experimental temperatures 170, 190, 210, 230°C were shifted horizontally to the right. As depicted in these figures, χ_{23} does not exhibit an inverse temperature dependence. This is unexpected according to the Flory-Huggins lattice theory but not very surprising since various researchers have reported such observations for other polyolefin blends [5-7].

Even though the values of $\chi_{23,crit}$ can only be used as an ad hoc reference, it is the only available means to determine miscibility of these blends. Therefore, the $\chi_{23,crit}$ value of each pair of the blends was determined and are summarized in Table 9. By comparing the information in Table 9 to the curves from Figures 13-30, one can infer that at some temperatures the blends are relatively more miscible than others. For instance, in Figure 13, the calculated χ_{23} for the blend of S-216 and A-1 at T=170, 190, 210, 230°C are 0.0, 0.0005, 0.00045, 0.0001, respectively, and the corresponding $\chi_{23,crit}$ for this blend is 0.00030 (Table 9).

Table 9: Calculated $\chi_{23,crit}$ for the Blends Based upon the Molar Volume of the Ethylene Repeat Unit

	$\chi_{23,crit}$ x 10^4										
Polymer	A-1	A-2	A-3	A-4	A-5	A-6	S-216	M-1	M-2	M-3	M-4
A-2	3.0	-	-	-	-	-	-	-	-	-	-
A-3	2.8	3.1	-	-	-	-	-	-	-	-	-
A-4	2.4	2.6	2.5	-	-	-	-	-	-	-	-
A-5	2.7	3.0	2.8	2.4	-	-	-	-	-	-	-
A-6	2.5	2.7	2.6	2.2	2.4	-	-	-	-	-	-
S-216	3.0	3.2	3.1	2.7	3.0	2.7	-	-	-	-	-
M-1	2.0	2.2	2.1	1.8	2.0	1.8	2.3	-	-	-	-
M-2	2.4	2.7	2.6	2.2	2.4	2.2	2.7	1.8	-	-	-
M-3	3.2	3.4	3.3	2.8	3.2	2.9	3.5	2.4	2.9	-	-
M-4	3.9	4.2	4.1	3.5	3.9	3.6	4.2	3.1	3.6	4.5	-
M-5	2.1	2.4	2.2	1.8	2.1	1.9	2.4	1.5	1.9	2.5	3.2

This leads to the conclusion that this blend is probably immiscible at 190°C and 210°C and miscible at 170°C and 230°C. However, most of the blends showed extremely small χ_{23} values indicating that they are miscible over the temperature range of interest.

The calculated χ_{23} values observed between the A series LLDPEs and S-216 LDPE (0.0-0.0018), are significantly lower than the ones obtained for the M series LLDPEs and S-216 (0.0-0.0057). However, both A and M series blends have similar

$\chi_{23,crit}$ values (0.0002-0.0004). The great majority of the χ_{23} values obtained were below the $\chi_{23,crit}$ values for the corresponding blends indicating that they form homogeneous mixtures at elevated temperatures.

The χ_{23} values calculated between the various LLDPEs within the A series polymers ranged from 0.0-0.0018 and the great majority of these results were below the $\chi_{23,crit}$ values for the corresponding blends. The same was observed for the χ_{23} values calculated between various LLDPEs within the M series polymers, ranging from 0.0-0.004. These results suggest that M series LLDPEs are less miscible than the A series LLDPEs.

The χ_{23} values calculated between the A series and M series LLDPEs ranged from 0.0-0.0012 with the exception of the blends composed of M-3 and A-series LLDPEs that exhibited a broader range of 0.0-0.0058 (Figure 28). Once again, the blends of M-3 and A-series LLDPEs, the great majority of the χ_{23} values were below the corresponding $\chi_{23,crit}$ values.

It is worth noting that the blends in which M-3 was one of the components, higher χ_{23} values were observed. This may be due to the lower M_w or higher melt index of M-3 (Table 4) comparing to the other polymers. It is well-known that miscibility of polymer blends is controlled by the chain lengths of the components. As can be seen from Table 4, M-3 has a M_w that is significantly smaller than those of other polymers which may explain the higher χ_{23} values found. In the case of A-6, only based on the information given by Nova Chemicals Corporation we cannot explain why its behavior is so different from the other members of the A series.

It is important to point out that as the $\chi_{12,crit}$ values were overestimated (because of the branches) the same will happen to $\chi_{23,crit}$. So, in reality the $\chi_{23,crit}$ should be even smaller than the values found by equation (19). Once again, it is not clear to us the magnitudes of the overestimation. In terms of χ_{23}, we cannot really tell if it is overestimated or not because it will depend on the values of the δ for the individual components.

The large uncertainties associated with the χ_{23} values are mainly caused by equation (40) where, in order to calculate χ_{23}, one has to use δ. The problem arises when the standard deviations for δ are large because δ is squared in equation (40) and the error propagates into the calculation of the standard deviation of χ_{23}, which results in even larger uncertainty values.

It is very difficult to compare the results given by IGC to another technique such as SANS. We tend to believe that SANS results [10] are more reliable as in such cases, the determination of χ_{23} does not rely on the use of solvents. However, it is important to point out that in the case of SANS, the reliability of the measured χ_{23} depends critically on the sample preparation procedure. However, the sample preparation information is usually not given in detail.

As can be seen from the thesis, even though there is still some room for improvement of the IGC approach, it is a valuable technique that can give fast and inexpensive information about solubility and miscibility of the polymers over a wide range of temperatures. Therefore, the theories pertinent to IGC should be further refined to enhance its applicability as a means of studying thermodynamics of polymer solutions and blends.

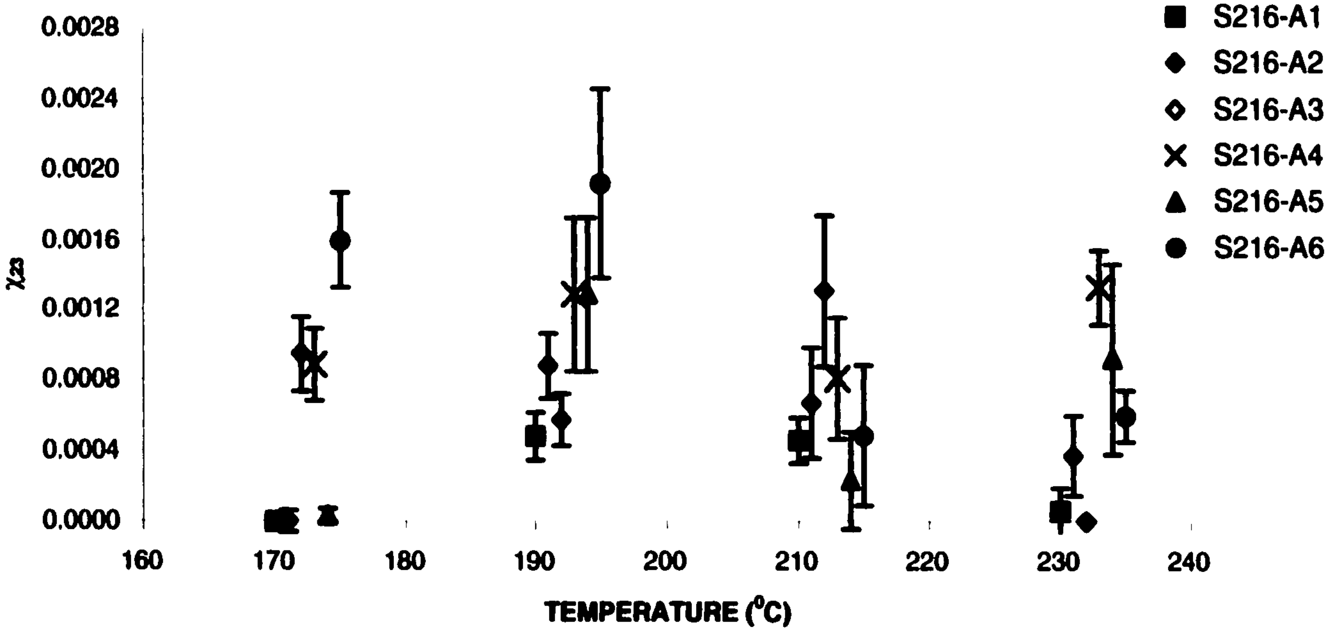

Figure 13: Interaction parameters between the LLDPEs (A-1 to A-6) and the LDPE (S-216) The data points and the corresponding standard deviations are shifted horizontally for clarity.

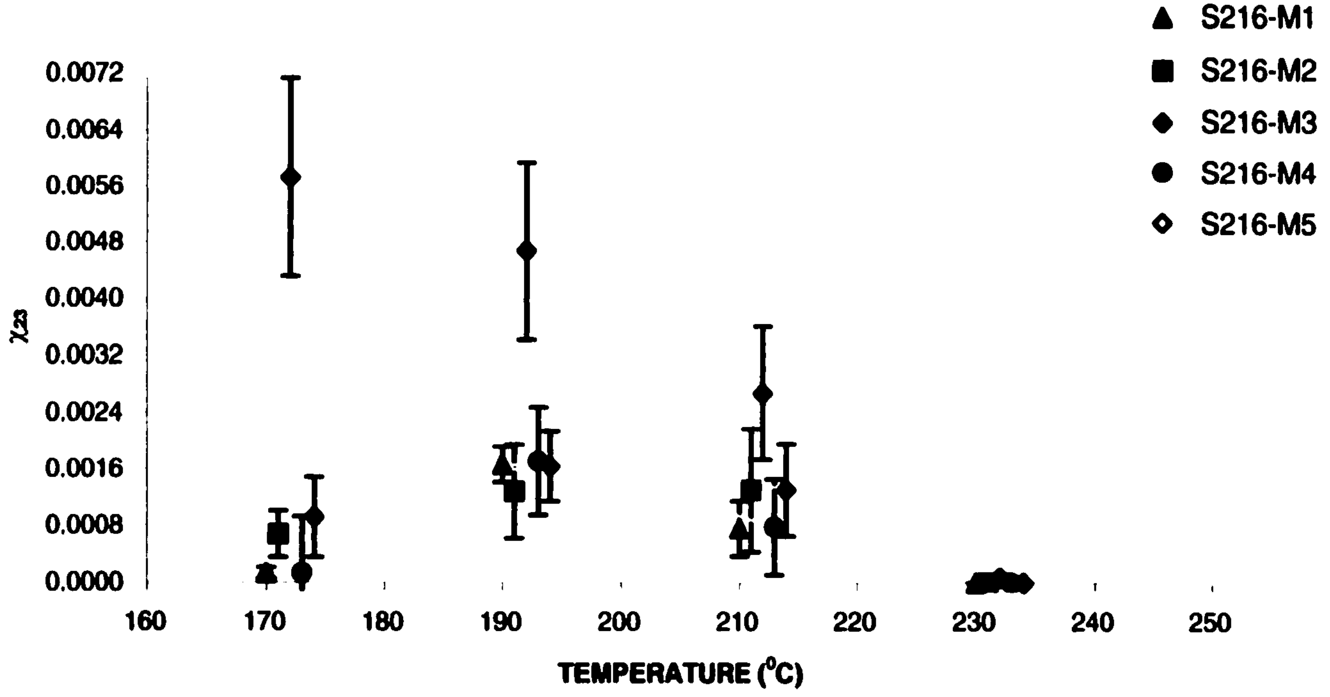

Figure14: Interaction parameters between the LLDPEs (M-1 to M-5) and the LDPE (S-216) The data points and the corresponding standard deviations are shifted horizontally for clarity.

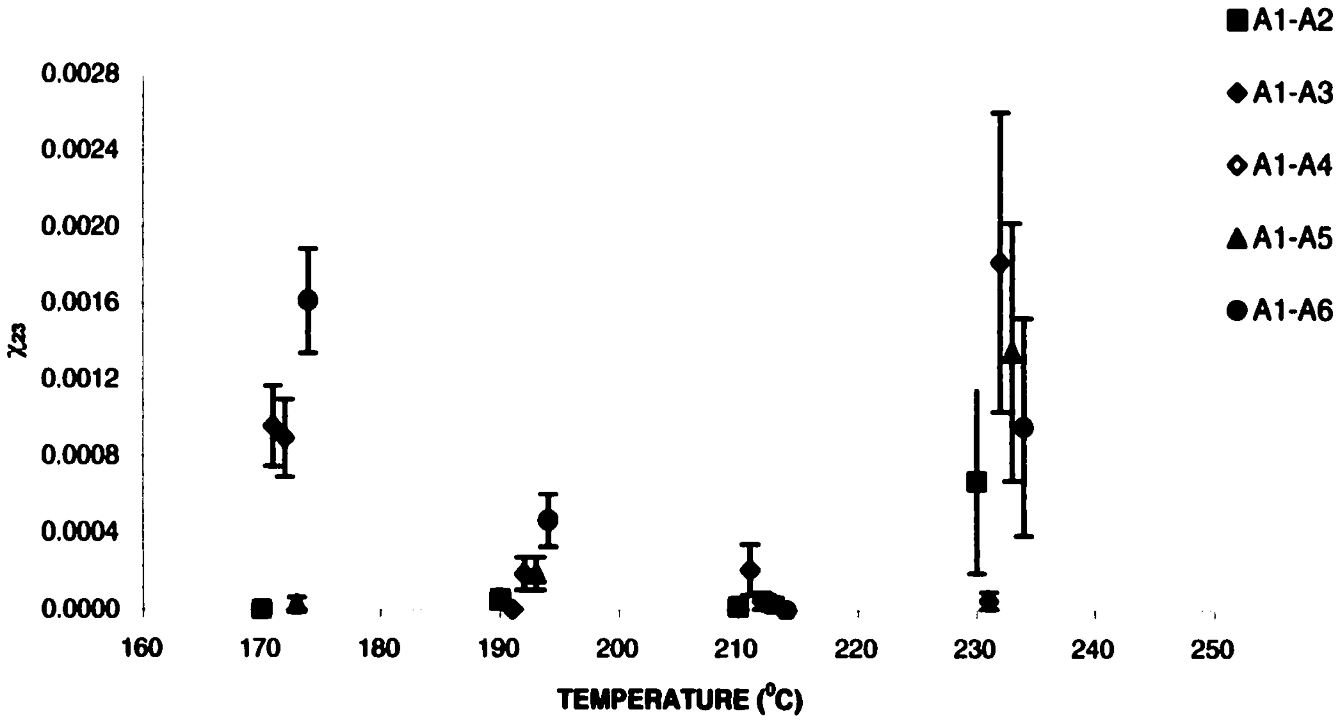

Figure 15: Interaction parameters between the LLDPEs (A-series and A-1)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

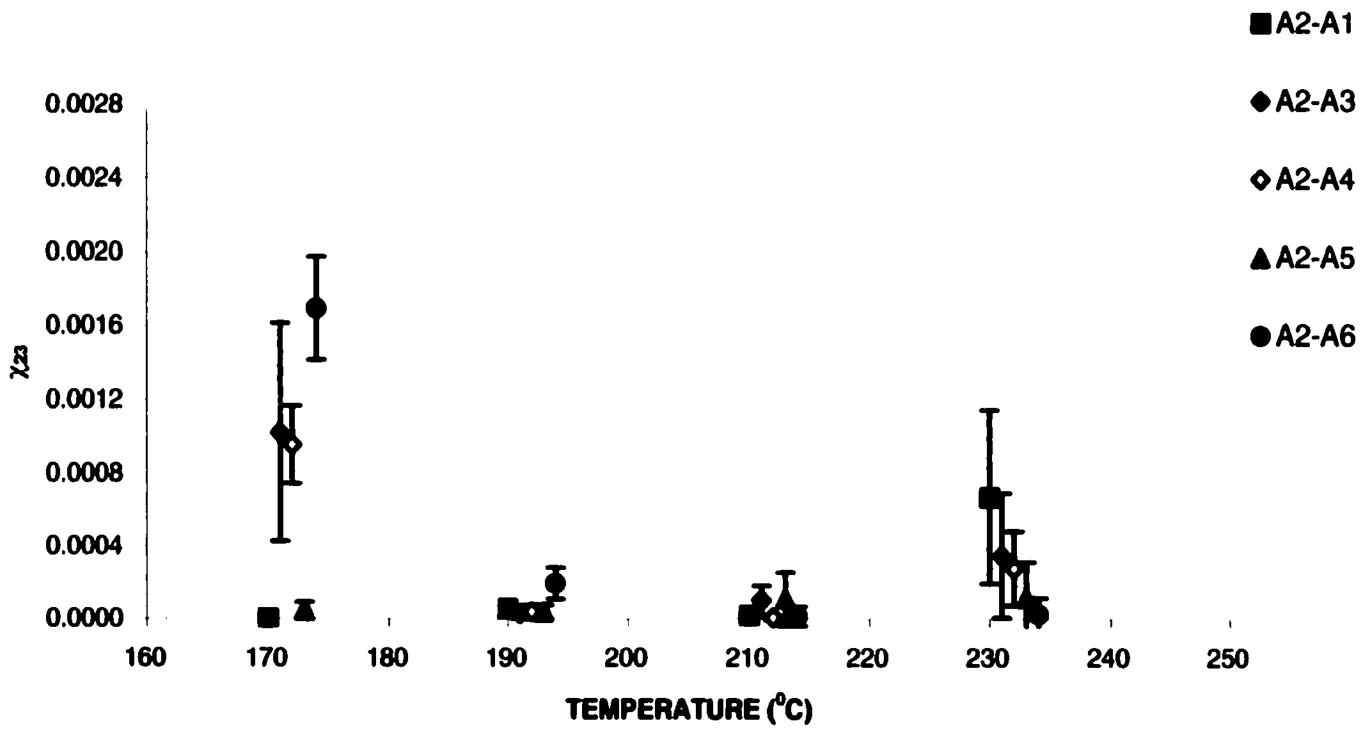

Figure 16: Interaction parameters between the LLDPEs (A-series and A-2)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

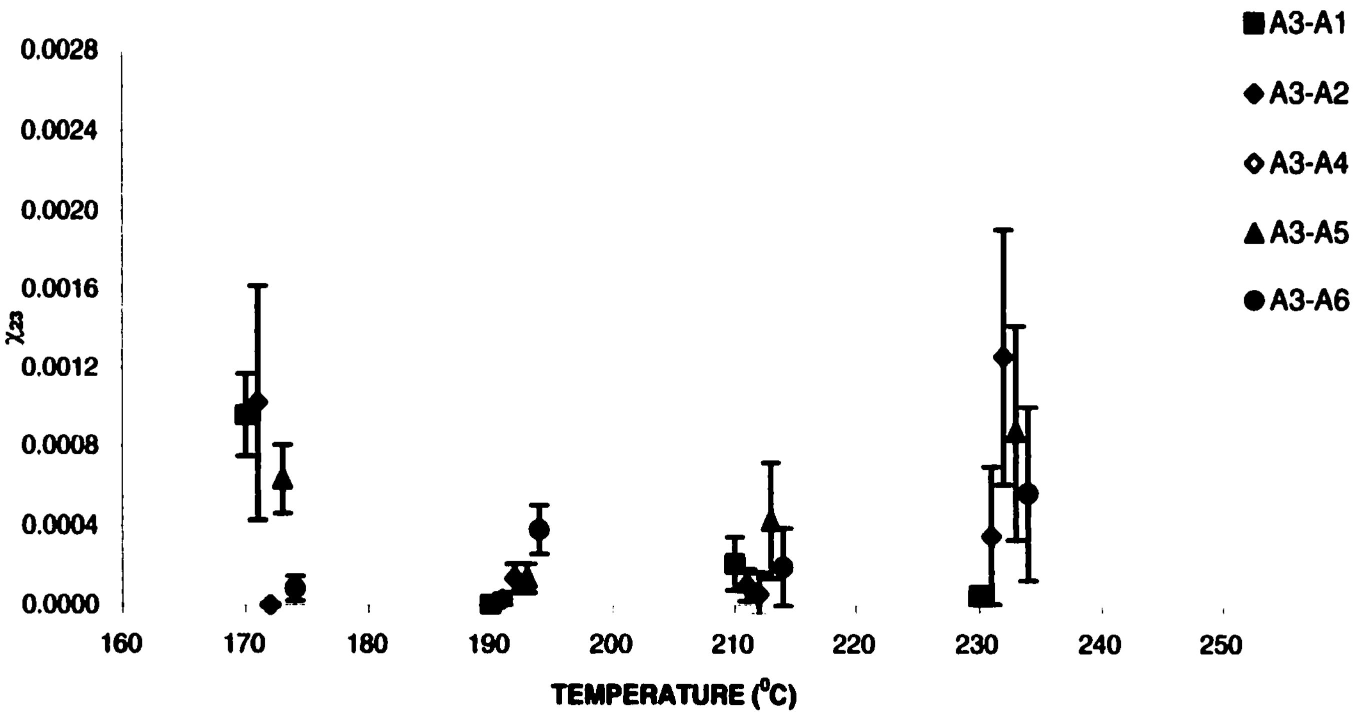

Figure 17: Interaction parameters between the LLDPEs (A-series and A-3)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

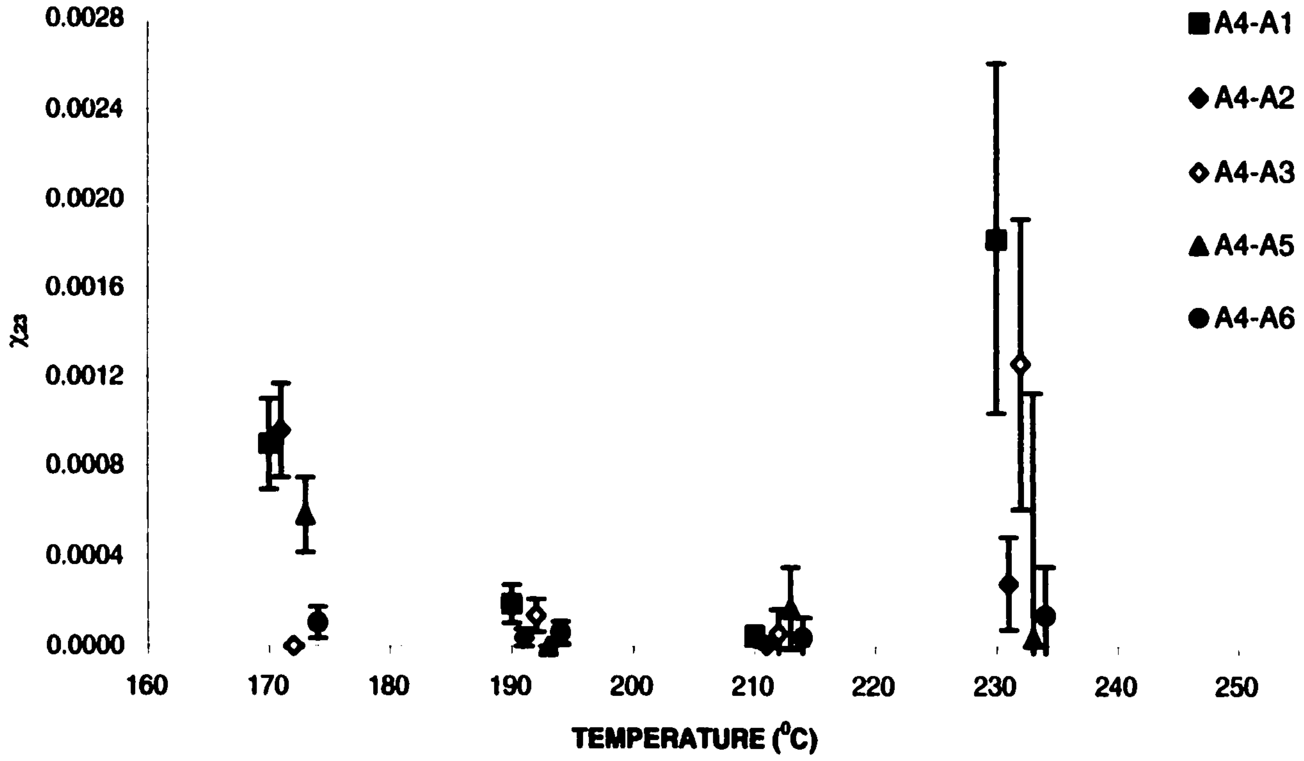

Figure 18: Interaction parameters between the LLDPEs (A-series and A-4)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

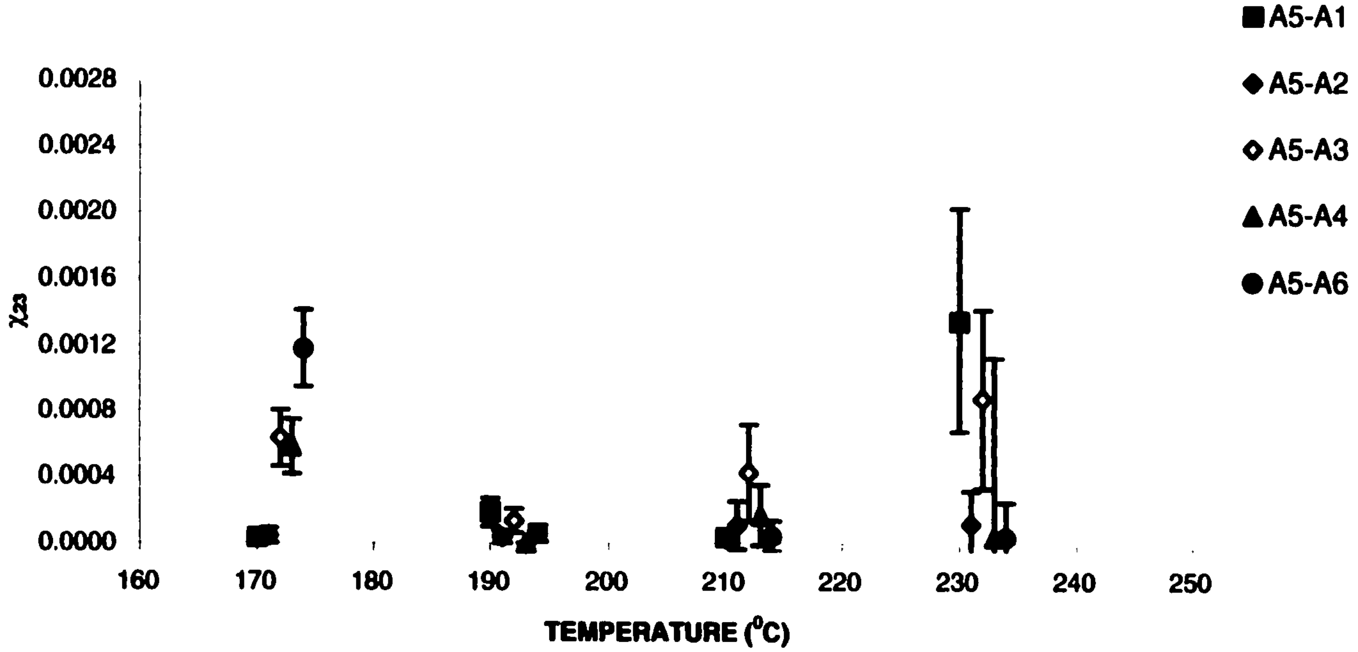

Figure 19: Interaction parameters between the LLDPEs (A-series and A-5)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

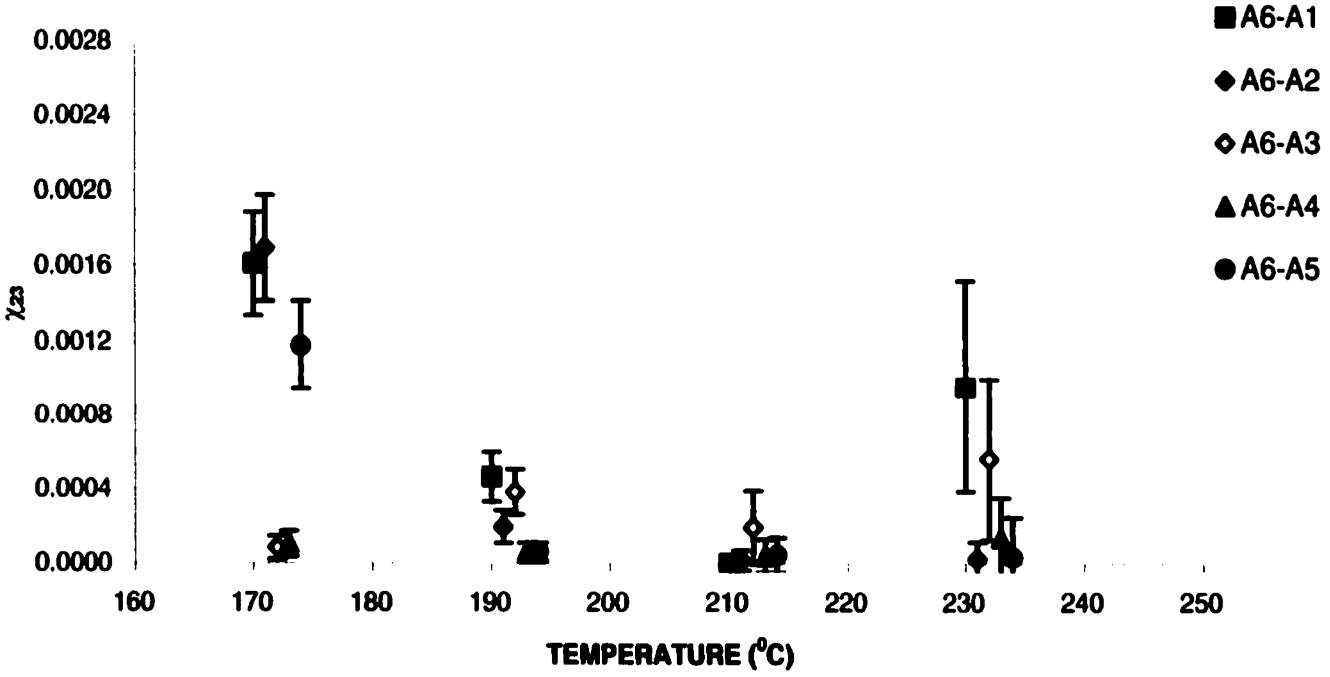

Figure 20: Interaction parameters between the LLDPEs (A-series and A-6)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

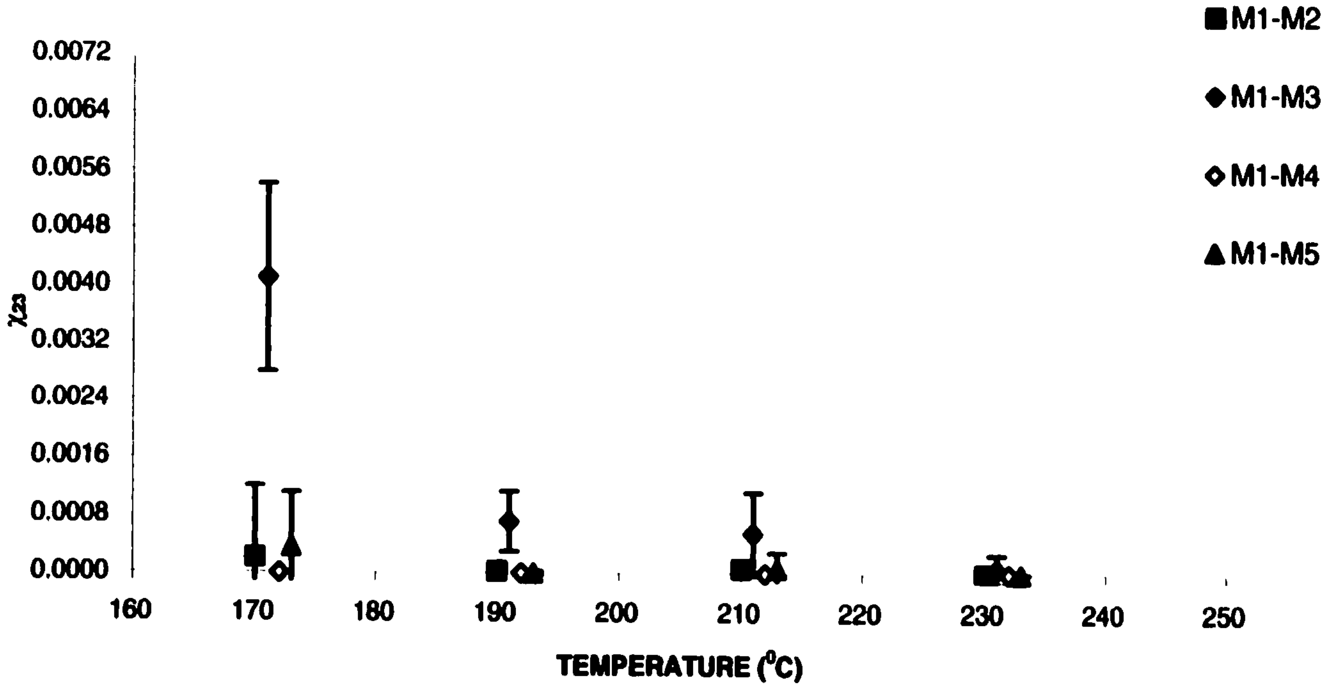

Figure 21: Interaction parameters between the LLDPEs (M-series and M-1)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

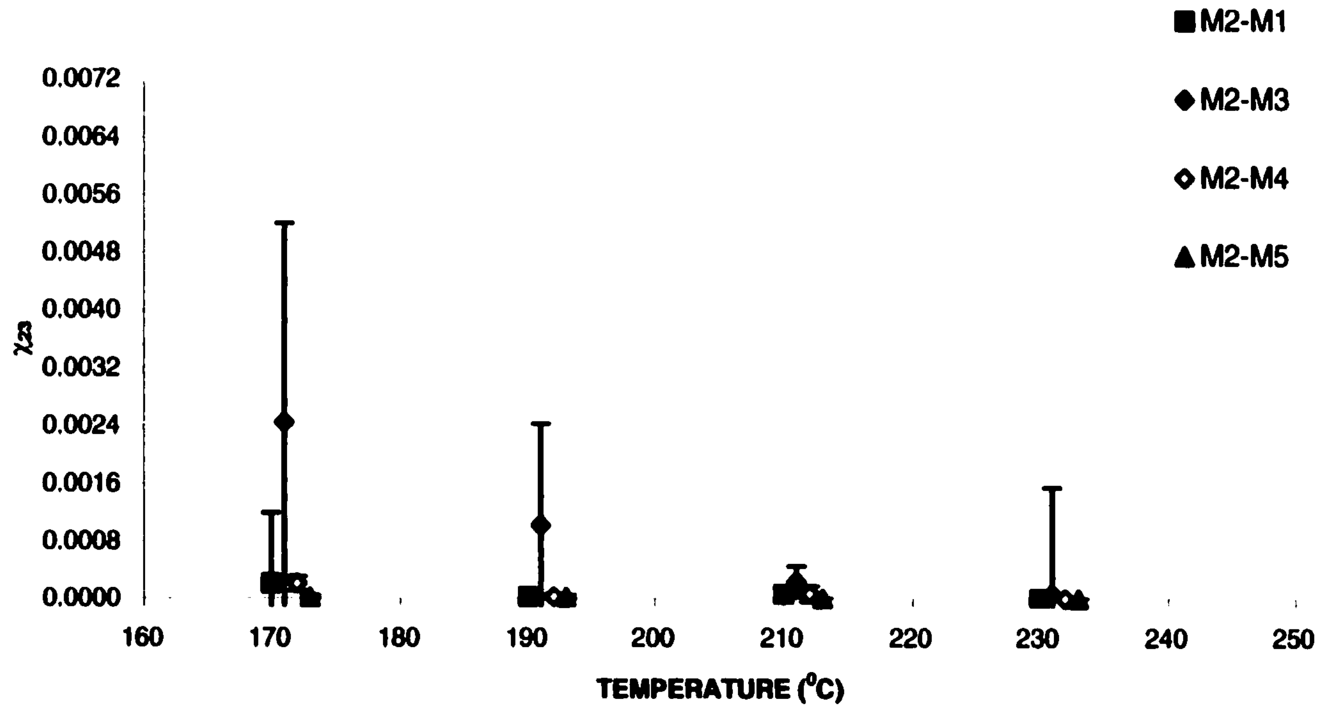

Figure 22: Interaction parameters between the LLDPEs (M-series and M-2)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

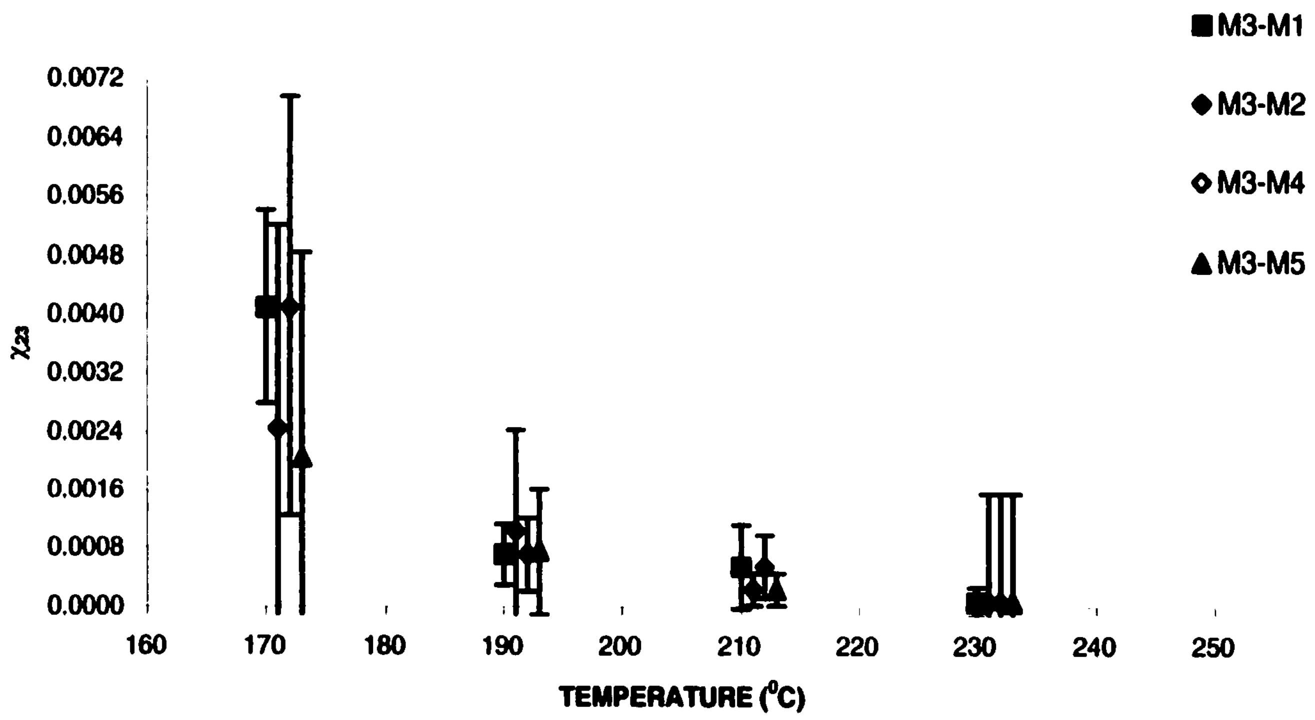

Figure 23: Interaction parameters between the LLDPEs (M-series and M-3)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

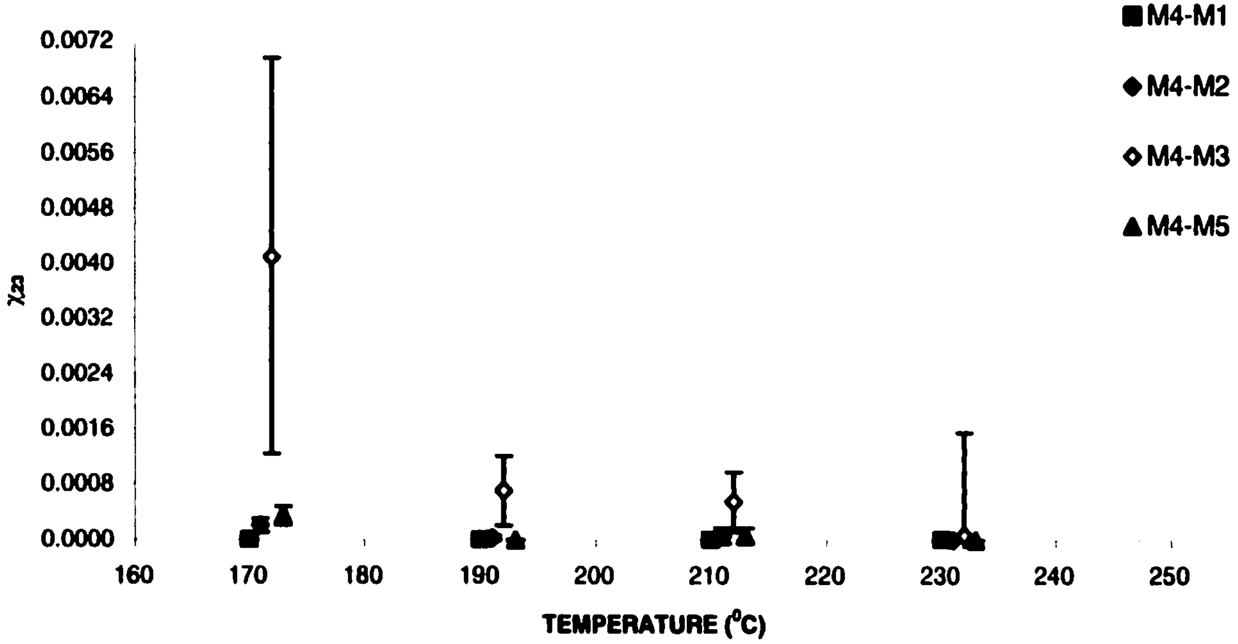

Figure 24: Interaction parameters between the LLDPEs (M-series and M-4)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

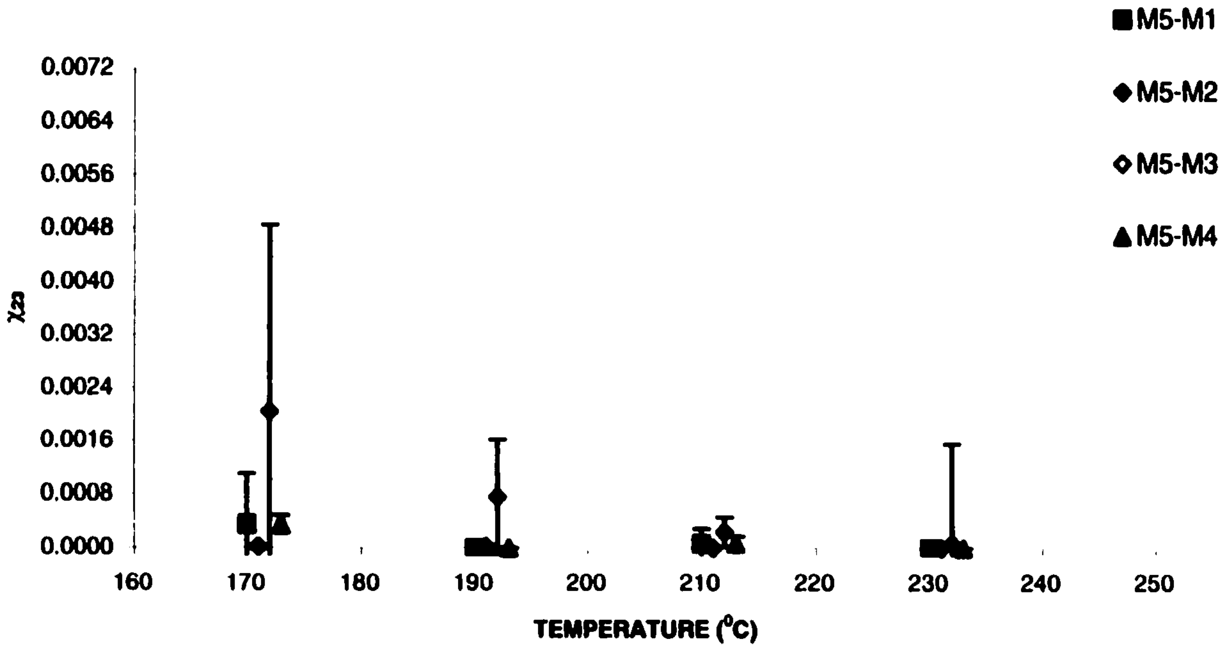

Figure 25: Interaction parameters between the LLDPEs (M-series and M-5)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

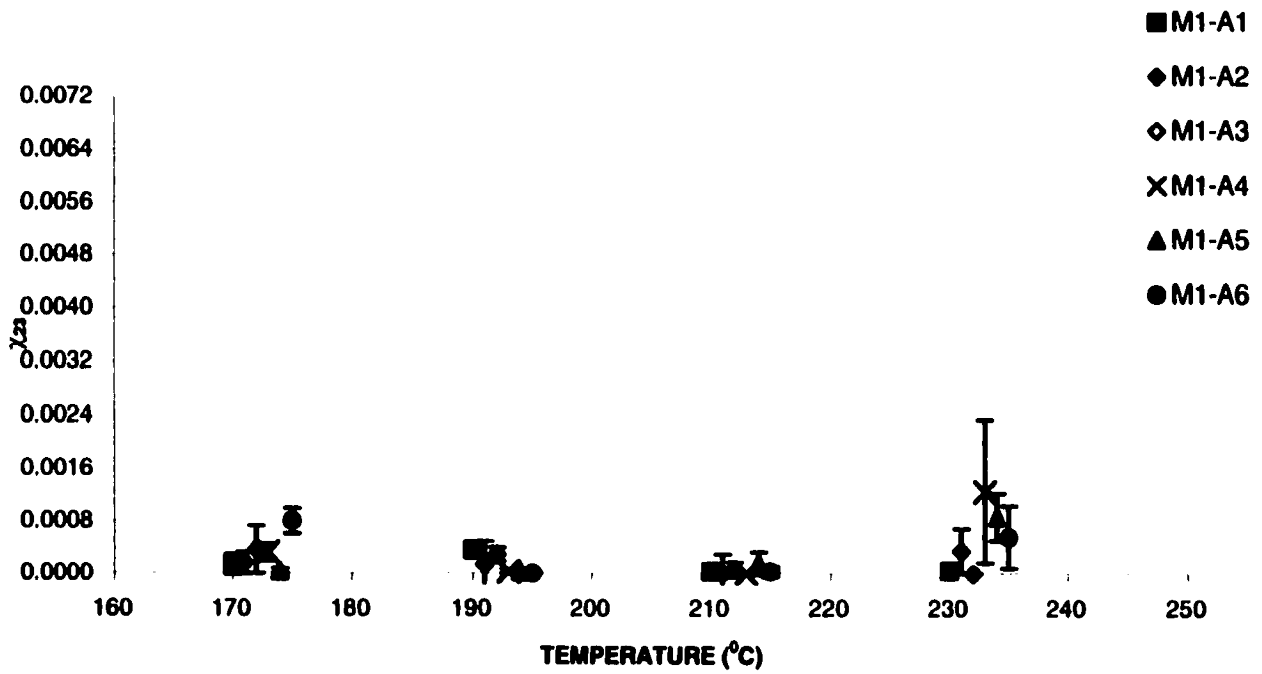

Figure 26: Interaction parameters between the LLDPEs (A-series and M-1)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

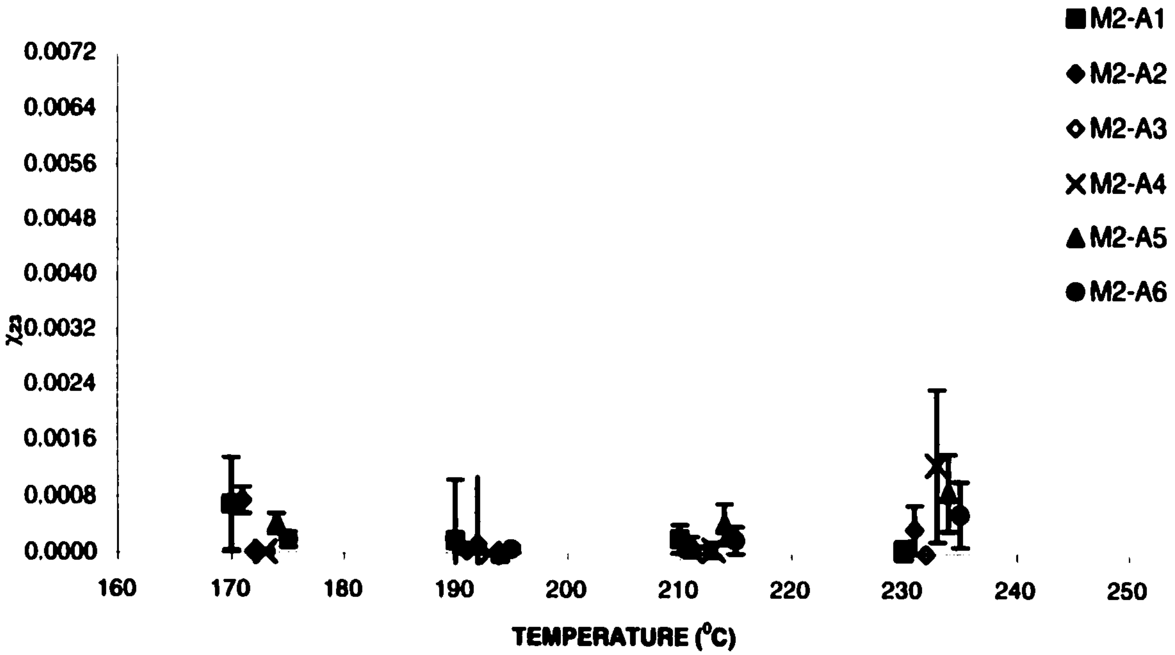

Figure 27: Interaction parameters between the LLDPEs (A-series and M-2)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

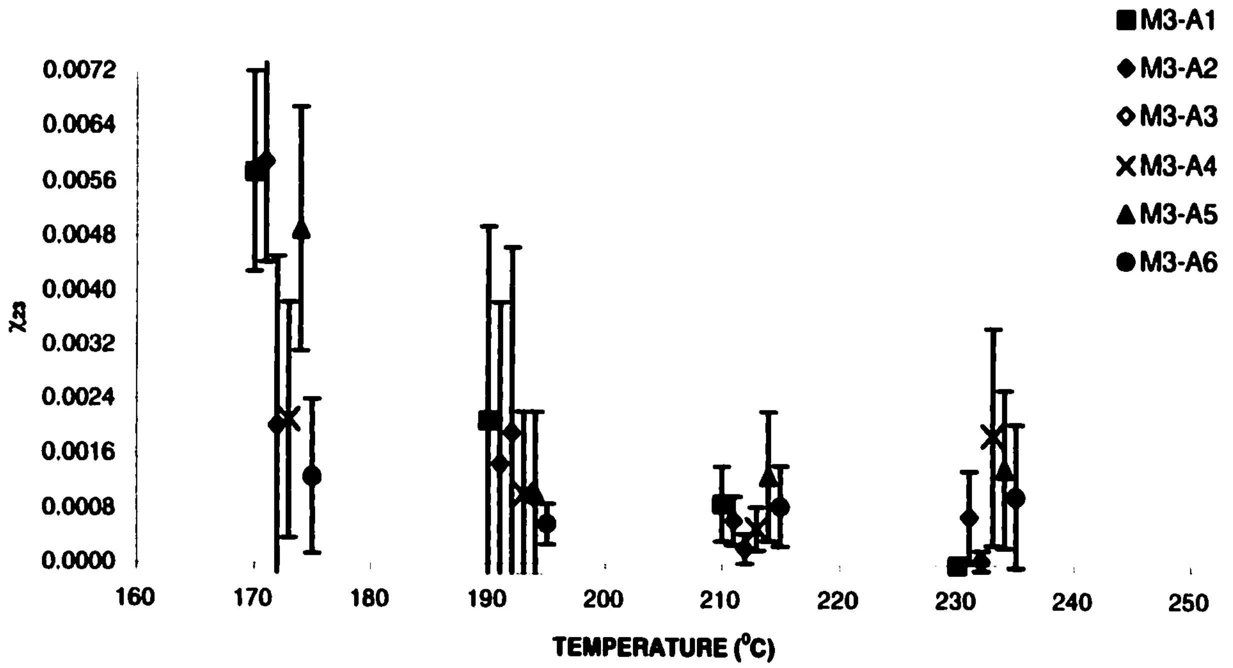

Figure 28: Interaction parameters between the LLDPEs (A-series and M-3)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

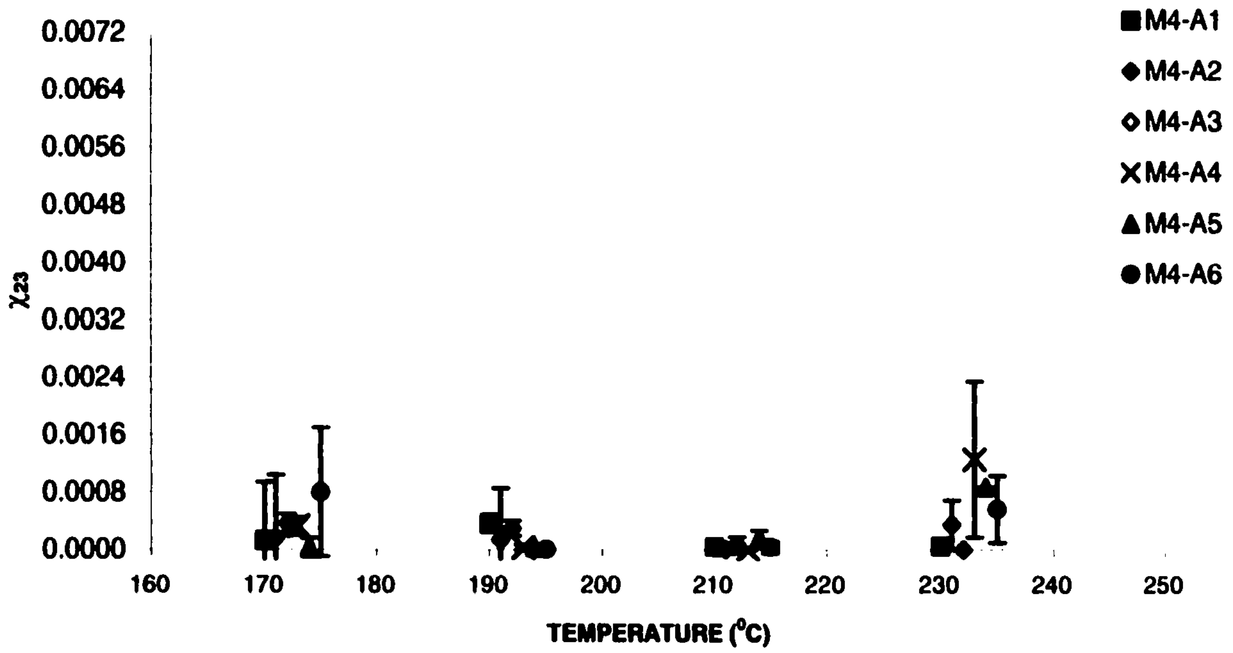

Figure 29: Interaction parameters between the LLDPEs (A-series and M-4)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

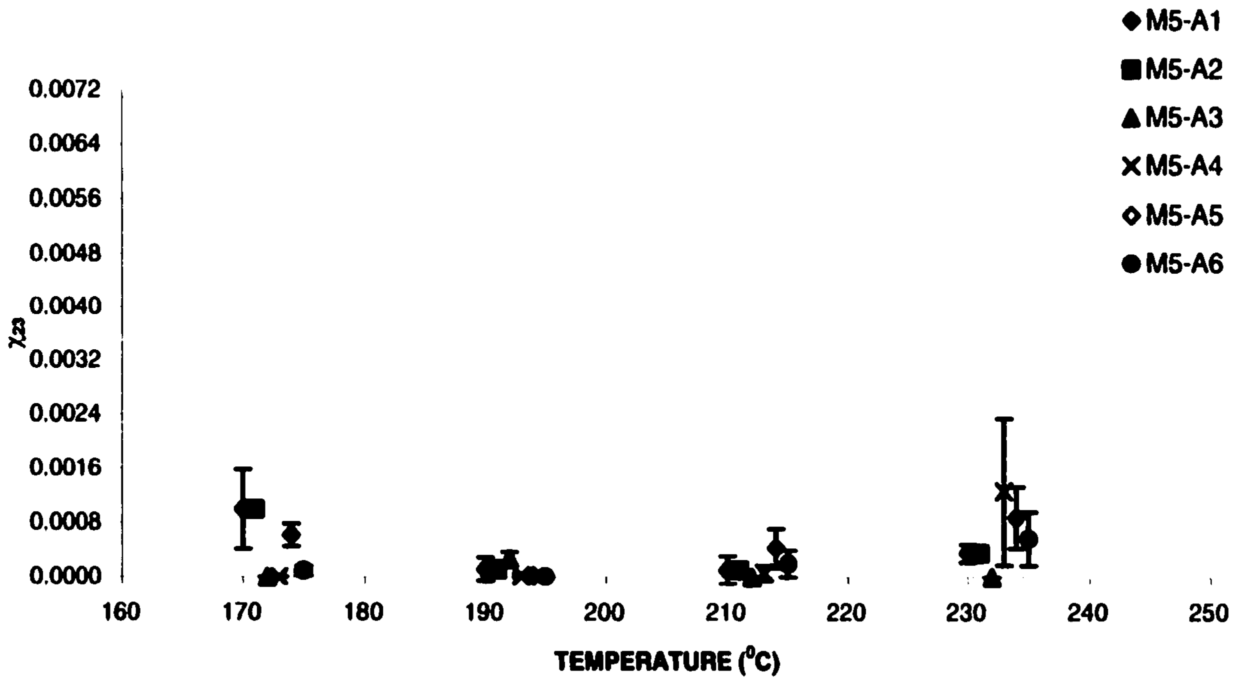

Figure 30: Interaction parameters between the LLDPEs (A-series and M-5)
The data points and the corresponding standard deviations are shifted horizontally for clarity.

4.1 References

1. Lloyd DR, Ward TC, Schreiber HP, Pizana CC, ACS Symposium Series, Inverse Gas Chromatography, Characterization of Polymers and other Materials, American Chemical Society, Toronto (1988)
2. Lipson JEG, Guillet JE, *J. Polym. Sci., Part B*, 19, 1199 (1981)
3. Sperling LH, Han SJ, Lohse DJ, Condo PD, *J. Polym. Sci., Part B*, 37, 2835 (1999)
4. Barton FM, *CRC Handbook of Solubility Parameters and other Cohesion Parameters*, 123-133,303-308, CRC Press (1991)
5. Graessley WW, Krishnamoorti R, Balsara NP, Fetters LJ, Lohse DJ, Schulz D, Sissano, *Macromolecules*, 27, 2574-2579, 3073-3081, 3896-3901 (1994)
6. Graessley WW, Krishnamoorti R, Reichart GC, Balsara NP, Fetters LJ, Lohse D, *Macromolecules*, 28, 1260 (1995)
7. Graessley WW, Krishnamoorti R, Garner RJ, Fetters LJ, Lohse D, *Macromolecules*, 28, 1252 (1995)
8. Zhao L, Choi P, *Polymer*, 42, 1075 (2000)
9. Fan J, Williams M.C, Choi P, submitted to *J. Polym. Sci.*, Part B (2000)
10. Balsara NP, Fetters LJ, Hadjichristidis H, Lohse DJ, *Macromolecules*, 25, 6137 (1992)

CHAPTER 5

5.0 CONCLUSIONS AND FUTURE WORK

The measured δ_2 values obtained by the average and plot methods were compared and the latter gave the same δ_2 regardless of the polymer used, leading to zero χ_{23}, which is physically unreasonable (δ depends on the structure of the polymer and since there are twelve polymers used have distinct structures, it is reasonable to assume that each one should have its unique δ) . The average method, on the other hand, gave individual δ_2 results (10-13 (MPa)$^{1/2}$) that allowed us to calculate the χ_{23}. And the δ_2 values obtained by the average method extrapolated to lower temperatures are in accord with the results obtained by the plot method for LDPE done by other IGC researchers. The temperature dependence of the solubility parameter obtained behaved as expected, i.e., the values decreased with increasing temperature.

The calculated χ_{23} values did not exhibit a 1/T relationship as expected from Flory-Huggins lattice theory. The χ_{23} values observed between the A series LLDPEs and S-216 LDPE (0.0-0.0018) are significantly lower than those obtained between the M series LLDPEs and S-216 (0.0-0.0057) even though both A and M series blends have similar $\chi_{23,crit}$ values (0.0002-0.0004). The great majority of the χ_{23} values obtained were below the $\chi_{23,crit}$ values for the corresponding blends indicating that they form homogeneous mixtures at elevated temperatures.

The χ_{23} values calculated between various LLDPEs within the A series polymers ranged from 0.0-0.0018 and the great majority of these values were below the $\chi_{23,crit}$ values for the corresponding blends. And the χ_{23} values calculated between the various LLDPEs within the M series LLDPEs ranged from 0.0-0.004 and again, the great majority of these values were below the $\chi_{23,crit}$ values for the corresponding blends.

The χ_{23} values calculated between the A series and M series LLDPEs ranged from 0.0-0.0012, except for the blends of M-3 (very higher melt index) and A-series polyethylenes that showed a broader range of 0.0-0.0058 (Figure 28). Once again, except for the blends composed of M-3 and A-series LLDPEs, the great majority of the χ_{23} values were below the $\chi_{23,crit}$ values for the corresponding blends.

Since a majority of the calculated χ_{23} values are quite small and below the corresponding $\chi_{23,crit}$ values, there is an indication that both LDPE/LLDPE and LLDPE/LLDPE blends are likely to be miscible at the chosen experimental temperatures, even considering the large uncertainties. This finding is in good agreement with recent molecular dynamics (MD) results reported by other members of our research group [1,2] in which they obtained comparable χ_{23} values, and found that the difference in the branch contents of different polyethylenes is the key factor controlling their miscibility. In particular, if the difference is in the range of 30-40 branches/1,000 carbons (note that the corresponding χ_{23} values for such blends are in the range of 0.01-0.1), the polymers phase separate. In this work, since the differences in the branch contents of LDPE and the eleven LLDPE used (Table 4) are considerably less than the above critical values, it is not surprising to observe that all the blends exhibit favorable interaction parameters.

As the miscibility behavior of the studied blends has been determined, the future work in this area will be focusing on correlating this behavior to the processability and performance of these blends.

5.1 References

1. Choi P, *Polymer*, 41, 8741 (2000)
2. Fan J, Williams M.C, Choi P, submitted to *J. Polym. Sci, Part B* (2000)

APPENDIX A

Sample Calculations

Choosing A-2 LLDPE as the example and dodecane as the solvent, the following, all the calculations involved.

The A-2 column at 170°C = 443.15 K had the following characteristics:

- From Table 1: $W_l = 0.0379$g
- F= 19.35 cm^3/min,
- From Table 2: $P_{i(\text{manometric})}$= 150 KPa and P_0 = 96.23 KPa, $P_{i\ (absolute)}$ = 150+ 96.23 = 246.23 KPa.
- t_R= 0.692 min for the dodecane
- t_0= 0.156 min (marker's retention time)

The net retention time for the dodecane will be given by:

$t_N = t_R - t_0 = 0.536$ min.

Substituting the inlet and outlet pressure values in equation (21), (Chapter 2):

$$J = \frac{3}{2}\left\{\frac{\left[\left[\left(\frac{P_i}{P_0}\right)^2 - 1\right]\right]}{\left[\left[\left(\frac{P_i}{P_0}\right)^3 - 1\right]\right]}\right\}$$

J= 0.5282

And the specific retention volume for the dodecane will be given by equation (21):

$$V_g^{\,0} = \frac{t_N * F * J * 273.15}{W_l * T}$$

$V_g^0 = (0.536*19.35*0.5282*273.15) / (0.0379*443.15) = 89.09\ \text{cm}^3/\text{g}$

The polymer specific volume is calculated by equation (20):

$$v_2 = 1.282 + 9*10^{-4}(T-150)$$

For T=170°C, in this equation T is in °C :

$v_2 =\ 1.3\ \text{cm}^3/\text{g}$

Let's calculate the saturated vapor pressure of the dodecane from equation (27):

$$\log P_1^{\,0} = A - \frac{B}{(T+C)}$$

where A= 6.99795, B= 1639.27, C= 181.84 and T= 170°C

P_1^0= 218.18 mmHg = 0.2871atm

From equation (28), one can calculate B_{11}:

$$B_{11} = \left(f^{(0)} + wf^{(1)}\right)*\frac{RT_c}{P_c}$$

where $f^{(0)}$ and $f^{(1)}$ can be calculated by equations (28a) and (28b):

$$f^{(0)} = 0.1445 - \frac{0.33}{T_r} - \frac{0.1385}{T_r^{2}} - \frac{0.0121}{T_r^{3}} - \frac{0.000607}{T_r^{8}}$$

$$f^{(1)} = 0.0637 + \frac{0.331}{T_r^{2}} - \frac{0.423}{T_r^{3}} - \frac{0.008}{T_r^{8}}$$

For dodecane: w= 0.575, T_c = 658.2 K, P_c= 17.96 atm, T_r = 443.15 /658.2 = 0.6732. Substituting the latter in equations (28a) and (28b):

$f^{(0)} = -0.7052$

$f^{(1)} = -0.7816$

Substituting these values in equation (28) where R = 0.08205 atm*l/(mol*K), one finds:

$B_{11} = -3.4719$

With the necessary data calculated the interaction parameter between A-2 and dodecane can be obtained by equation (32):

$$\chi_{12} = \ln\left(\frac{273.15 * R * v_2}{Vg^0 * P_1^0 * V_1}\right) - 1 - P_1^0 * \frac{(B_{11} - V_1)}{R * T}$$

The molar volume of the solvent was determined by:

First the density has to be calculated and from the literature:

$$\rho = dA\left[dB^{-(1-Tr)^{2/7}}\right]$$

where for the dodecane: dA= 0.2222, dB= 0.238. Substituting these values in the latter equation:

$\rho = 0.6304$ g/ml = 630.4 g/l

The molar volume will be then calculated using the molecular weight of the dodecane, $M_w = 170.34$,:

$V_1 = M_W / \rho = 170.34 / 630.4 = 0.27$ l/mol

Now, with all the required information calculated, the interaction parameter based on the solvent's molar volume as a reference is:

$\chi_{12} = 0.4701$

Based on this reference, as this number is below the $\chi_{12,crit}=0.5$, dodecane is miscible in A-2.

Let's take a look in the value of χ_{12} based on the ethylene molar volume, V_0= 28*1.3 = 36 ml/mol = 0.036 l/mol, in equation (33):

$$\chi_{12} = \frac{V_0}{V_1}\left[\ln\left(\frac{273.15 R v_2}{V_g{}^0 V_1 P_1{}^0}\right) - 1 - P_1{}^0 * \frac{(B_{11} - V_1))}{RT}\right]$$

$\chi_{12} = 0.0626$

$\chi_{12,crit}$ in this case will be given by:

$$\chi_{12,crit} = \left(\frac{1}{2} * \frac{V_0}{V_1} \right)$$

Substituting the values:

$\chi_{12,crit} = 0.066$

According this calculation which is based on the ethylene molar volume as the reference, $\chi_{12} < \chi_{12,crit} = 0.066$, which means that dodecane is miscible in A-2.

The next step is to calculate the Hildebrand Solubility parameter for the dodecane and this can be done by equation (36):

$$\left(\frac{\delta_{1,T_2}}{\delta_{1,T_1}} \right)^2 = \left(\frac{V_{1,T_1}}{V_{1,T_2}} \right)^{2.27}$$

where $\delta_{1,T_1} = \delta_{1,25^oC} = 16.2\ (\text{MPa})^{1/2}$ taken from the literature, $\rho_{1,25^oC} = 0.744\ \text{g/cm}^3$ (calculated the same way as shown before), $V_{1,T_1} = V_{1,25^oC} = 170.34/\ 0.744 = 0.228$ l/mol and $V_{1,T_2} = V_{1,170^oC} = 0.27$ l/mol. Substituting these values:

$\delta_{1,T_2} = \delta_{1,170^oC} = 13.4\ (\text{MPa})^{1/2}$

The Hildebrand solubility parameter of A-2 (δ_2) can be calculated using the plot or average methods. Let's analyze the results given by the two approaches. First, let's calculate δ_2 by the plot method.

With the information of Table 1, the left-hand side of equation (39) can be plotted against δ_1, giving a linear graph with the δ_2 value obtained from the slope:

$$\left(\frac{\delta_1{}^2}{RT}-\frac{\chi_{12}{}^{\infty}}{V_0}\right)=\left(\frac{2\delta_2}{RT}\right)\delta_1-\left(\frac{\delta_2{}^2}{RT}+\frac{\chi_S{}^{\infty}}{V_0}\right)$$

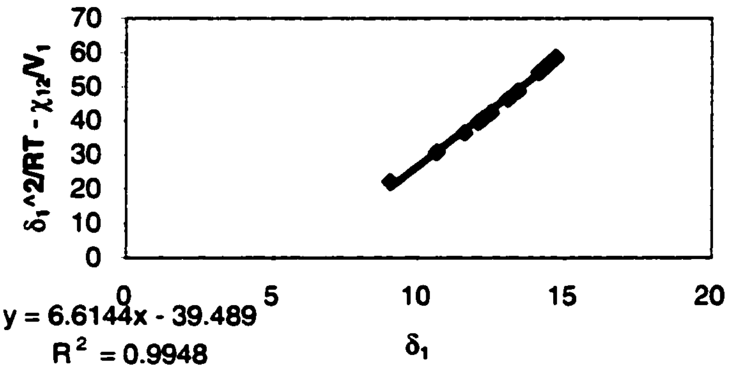

Figure 31: Equation 39 plot for A-2

So,

$$\frac{2\delta_2}{RT}=6.61\leftrightarrow\delta_2=\frac{6.61*0.008313*443.15}{2}=12.2(MPa)^{1/2}$$

Let's now do the same calculation for another polymer, let's say A-4, in order to check if the values for δ_2 using the plot method would be the same. Table 10 summarizes the information needed:

Table 10: χ_{12} and δ_1 Values for A-4 (LLDPE) and Selected Solvents at 170°C.

Solvents	χ_{12}^{*}	$\chi_{12,crit}^{*}$	$\delta_1(\text{MPa})^{1/2}$
1-hexene	0.09	0.10	10.7
1-octene	0.08	0.09	12.3
benzene	0.15	0.16	14.7
cyclohexane	0.10	0.13	13.1
hexane	0.08	0.10	10.7
n-dodecane	0.06	0.07	13.4
n-heptane	0.08	0.09	11.6
n-nonane	0.07	0.09	12.5
n-pentadecane	0.05	0.06	14.1
n-pentane	0.05	0.10	9.0
octane	0.08	0.12	12.2
toluene	0.13	0.17	14.7
xylene	0.12	0.13	14.4

* values calculated with the ethylene repeat unit molar volume as a reference.

Now, substituting the values of Table 10 in equation (39) and plotting its left-hand side versus δ_1, we should find something similar to what was found for A-2:

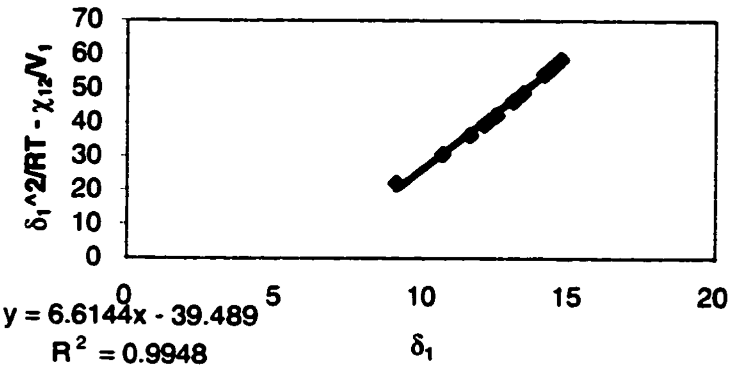

Figure 32: Equation 39 plot for A-4

Following the same procedure done for A-2, δ_2 was estimated to be 12.2 $(\mathrm{MPa})^{1/2}$. One can see now why this method wasn't adopted in this work.

The other method used to determine the Hildebrand Solubility parameter for the polymer is by averaging the δ_1 of the solvents that presented a $\chi_{12} < \chi_{12,crit}$ (the average method). In the case of A-2, xylene, toluene, pentadecane, nonane and octane also satisfied this condition (Table 1). By doing the same development, one reaches the values of δ_1 for all of these other solvents which led to:

$$\delta_2 = 13.5 \pm 0.3\ (\mathrm{MPa})^{1/2}$$

The final step is to determine the Flory-Huggins interaction parameter, χ_{23}, between the different polymers. Let's take the Hildebrand Solubility parameter obtained for A-4 (Table 10), $\delta_3 = 12.6 \pm 0.8\ (\mathrm{MPa})^{1/2}$, by the same technique showed here.

Substituting these values in equation (40):

$$\chi_{23} = \frac{V_0}{R*T}(\delta_2 - \delta_3)^2$$

$$\chi_{23} = 0.001 \pm 0.0002$$

From Table 8, the $\chi_{23,crit}$ = 0.00026 for a blend of A-2 and A-4, which leads to the conclusion that at this temperature the 2 polymers tend to be imiscible.

APPENDIX B

The Flory-Huggins Lattice Theory

The most widely used theory for the thermodynamic properties of polymer solutions and blends is the Flory-Huggins (FH) lattice theory, which was originally formulated in terms of a lattice model. The lattice theory is based on the idea that a liquid can be considered in a solid-like, quasicrystalline state, where the molecules do not translate in a chaotic manner as in the gas state, but where each molecule tends to stay in a small region, a more or less fixed position in space about which it moves back and forth. In this approach, molecules in the liquid state is supposed to sit in a regular position in space, called a *lattice site.* Since the lattice theory of liquids assumes that molecules are confined to the lattice positions, the excess thermodynamic properties cannot be calculated, which is a serious deficiency of the theory.

Molecular considerations suggest that deviations from ideal behaviour in liquids are due primarily to the following factors. The first one is the forces of attraction between unlike molecules which are quantitatively different from those between like molecules and create an enthalpy of mixing that does not vanish. For unlike molecules that differ significantly in size or shape, the molecular arrangement in the mixture may be significantly different from that for the pure liquids, giving rise to a nonideal entropy of mixing. If the forces of attraction in a binary mixture between one of three possible pair interactions are very much stronger or weaker than those of the other two, there are certain preferred orientations of the molecules in the mixture that may lead to thermodynamic instability and demixing.

The FH theory represents a simple mean field approximation to this standard lattice model in which all correlations are ignored in estimating both excluded volume effects and interaction energies. While the classic FH theory successfully explains the fact that long-chain polymers in the liquid state generally tend to be immiscible, it is inadequate in several respects. First of all, it fails to describe the molecular origins of the substantial, temperature-independent (entropic) portion of the small-angle neutron scattering Flory interaction energy parameter χ, and it does not provide a molecular basis for the observed composition dependence of χ and other thermodynamic properties. A brief discussion of the FH lattice theory is shown below.

Let's consider a mixture of liquids 1 and 2. Molecules of the solvent, type 1 liquid, are single spheres. Molecules of the polymer, type 2 liquid, are assumed to behave like flexible chains as if they consist of a large number of mobile segments, each having the same size as that of the type 1 liquid. It is also assumed that each site of the quasilattice is occupied by either a solvent molecule or a polymer segment, i.e., there are no empty sites.

Let's say that there are N_1 molecules of solvent and N_2 molecules of polymer and there are r segments in a polymer molecule. The total number of lattice sites is $(N_1 + rN_2$). Fractions Φ_1^* and Φ_2^* of sites occupied by the solvent and the polymer are given by:

$$\Phi_1{*} = \frac{N_1}{N_1 + rN_2} \qquad \Phi_2{*} = \frac{rN_2}{N_1 + rN_2} \tag{1}$$

Flory and Huggins have shown that if the amorphous polymer and the solvent mix without any energetic effects, the change in Gibbs free energy and entropy of mixing are given by the simple expression:

$$-\frac{\Delta G^C}{RT} = \frac{\Delta S^C}{R} = -(N_1 \ln \Phi_1{}^* + N_2 \ln \Phi_2{}^*) \tag{2}$$

where the subscript C stands for combinatorial.

The entropy change in equation (2) is similar in form to that for the regular solution theory except that segment fractions are used rather than mole fractions.

When r=1, equation (2) reduces to that of the regular solution. However, when r>1, equation (2) always gives a combinatorial entropy larger than the one obtained by the regular solution theory for the same N_1 and N_2. Much discussion has led Hildebrand in 1947 to the conclusion that for non-polar systems, the expression for entropy obtained by the regular solution theory gives a lower limit to the combinatorial entropy of mixing, while equation (2) gives an upper limit. The real combinatorial entropy probably is in between, depending on the size and shape of the molecules.

Some experiments have shown that the combinatorial entropy is strongly affected by the bulkiness of the large molecule. The FH expression depends only on the size ratio r, ignoring the influence of the shape of the polymer molecule. So, for mixtures of the same solvent with different polymers, the FH expression will give always the same result independent of the molecular shape of the polymer.

It should be mentioned here that even though, the simple expression of FH does not always give the presumably correct, quantitative combinatorial entropy of mixing, it qualitatively describes many features of athermal polymer solutions.

The FH expression leads to an equation for the excess entropy that is, per mole of mixture:

$$\frac{s^E}{R} = -x_1 \ln\left[1-\Phi_2^{*}\left(1-\frac{1}{r}\right)\right] - x_2 \ln\left[r-\Phi_2^{*}(r-1)\right] \qquad (3)$$

It can be shown that for all $r>1$, s^E is positive. Therefore, for an athermal solution of components whose molecules differ in size, the FH theory predicts negative deviations from Raoult's law:

$$\frac{g^E}{RT} = \frac{h^E}{RT} - \frac{s^E}{R} = 0 - \frac{s^E}{R} < 0 \qquad (4)$$

For an athermal solution, the activity of the solvent from equation (3) is:

$$\ln a_1 = \ln\left(1-\Phi_2^{*}\right) + \left(1-\frac{1}{r}\right)\Phi_2^{*} \qquad (5)$$

and the activity coefficient is:

$$\ln\gamma_1 = \ln\left[1-\left(1-\frac{1}{r}\right)\Phi_2^*\right]+\left(1-\frac{1}{r}\right)\Phi_2^* \qquad (6)$$

It is common to add the combinatorial part of the Gibbs free energy, (2), in order to apply the theoretical result of FH to real polymer solutions, i.e., if there is no difference in free volumes, the term that is added is given by the enthalpy of mixing. The FH equation for real polymer solutions then becomes:

$$\frac{\Delta G_{mix}}{RT} = \frac{\Delta G^C}{RT}+\frac{G^R}{RT} = N_1\ln\Phi_1^* + N_2\ln\Phi_2^* + \chi\Phi_1^*\Phi_2^*\left(N_1+rN_2\right) \quad (7)$$

This equation can be modified to be shown in terms of the number of moles, volume fraction and FH interaction parameter and its final expression is then given by:

$$\frac{\Delta G_{mix}}{RT} = RT\left(n_1 \ln\phi_1 + n_2 \ln\phi_2 + \chi n_1\phi_2\chi_{12}\right)$$