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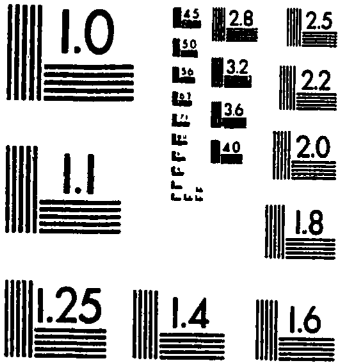

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CHARACTERIZATION OF POLYOLEFINS BY TEMPERATURE RISING ELUTION FRACTIONATION
(TREF)

BY

Jayant Chakravarty

A THESIS

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

DEPERTMENT OF CHEMICAL ENGINEERING

EDMONTON, ALBERTA
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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 **Characterization of Polyolefins by Temperature Rising Elution Fractionation (TREF)** submitted by **Jayant Chakravarty** in partial fulfillment of the requirement for the degree of **Master of Science in Chemical Engineering**.

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Date : 1 October, 1993

ABSTRACT

A Temperature Rising Elution Fractionation (TREF) apparatus was constructed and procedures were developed for determining short chain branching distributions in polyolefins. The off-column method of preparing polyolefin specimen for TREF analysis was used since it offers several advantages over the commonly used on-column method. An air bath was used for the temperature programmed elution; the elutions were usually carried out by linearly increasing the temperature from -10 to 130°C at a rate of 2°C/min. The same air bath, or a liquid bath containing diethylene glycol, was used for off-column crystallization for the polyolefin samples.

Commercial and laboratory prepared samples of various grades of polyethylene, as well as laboratory-prepared samples of polypropylene and propylene-ethylene copolymers were examined by TREF. Comparisons of TREF results obtained with the apparatus and procedure developed in this study with TREF results from other laboratories showed that the developed procedure and equipment produced reliable results. Analytical TREF (5 mg sample) and preparative TREF (20 mg sample) experiments were done. Fractions with different elution temperature ranges were collected during preparative TREF, and the molar mass distribution of the polyolefins in each fraction was determined by size exclusion chromatography (SEC). The combined TREF-SEC characterization (cross fractionation) provided information on the distribution of short chain branching as a function of molar mass.

Analysis of laboratory-prepared samples of propylene-ethylene copolymers provided valuable insight into the effect of reactor operating procedures on the degree of copolymer incorporation. The TREF capabilities developed in this project will be a valuable tool in the ongoing copolymerization studies in the Department of Chemical Engineering at the University of Alberta.

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I express sincere gratitude to my wife, Kusum, who silently withstood two months of neglect and supported me while this thesis was being written. Thanks are due to my colleague and good friends Ramesh Sadhankar and Robert Spaans who made my work at office enjoyable.

Above all, I express my gratitude to my parents whose love and support have been the driving force behind all my accomplishments.

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NOMENCLATURE

ASTM	American Society of Testing and Materials
A-TREF	Analytical Temperature Rising Elution Fractionation
ASCII	American Standard Code of Information Interchange
C_P	Specific heat (J/kg.°C)
CFD	Continuous Fractionation Device
DSC	Differential Scanning Calorimetry
DCB	Dichlorobenzene
EBA	Ethylene-butyl Acrylate
EEA	Ethylene-ethyl Acrylate
EMA	Ethylene Methacrylate
EPR	Ethylene-Propylene Rubber
EVA	Ethylene Vinyl Acetate
ESCR	Environmental Stress Crack Resistance
FTIR	Fourier Transform Infrared (spectrometry)
GPC	Gel Permeation Chromatography
HDPE	High Density Polyethylene
HMW	High Molecular Weight
HPLC	High Performance Liquid Chromatography
IR	Infrared
LCB	Long Chain Branching
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
MI	Melt Index
MMD	Molar Mass Distribution
MW_n	Number average molar mass

MW_w	Mass average molar mass
MSDS	Materials Safety Data Sheet
NMR	Nuclear Magnetic Resonance
o-DCB	Ortho dichlorobenzene or 1,2-dichlorobenzene
OSHA	Occupational Safety and Health Administration
P_L	Pressure in the transfer lines in bar
PC	Personal Computer
PE	Polyethylene
PP	Polypropylene
P-TREF	Preparative Temperature Rising Elution Fractionation
RI	Refractive Index
SAXD	Small Angle X-ray Diffraction
SCB	Short Chain Branches
SCBD	Short Chain Branching Distribution
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
SSF	Successive Sample Fractionator
T_g	Glass Transition Temperature (°C)
T_i	T=Temperature (°C); i= location
TCB	2,4,6 trichlorobenzene
TEM	Transmission Electron Microscopy
TREF	Temperature Rising Elution Fractionation
UHMW	Ultra High Molecular Weight
ULDPE	Ultra Low Density Polyethylene
V_e	Volume of eluted solution (ml)

1.0 INTRODUCTION

Temperature Rising Elution Fractionation (TREF) is an instrumental method that has found application in characterization of semi-crystalline polymers. Among semi-crystalline polymers, polyolefins are a dominating constituent and over the years TREF has come to be known as a strong characterization tool for polyolefins. Keeping this in view, a description on this family of polymers is provided.

1.1 HISTORY OF POLYOLEFINS

Polyolefins, the world's most widely used polymers, are the product of modern polymer science research. At a production rate of over 15 million tons annually in the United States, more polyolefins are produced than all metals combined. Polyolefin is a generic term applied to represent polymers of ethylene, propylene and other α-olefins. It is actually a misnomer as the polymer molecule is not really a multiple of olefin molecules. The genesis of such nomenclature is perhaps based on the fact that these polymers have the corresponding olefin as the main reactant. Simple polyolefins are in fact multiple of units, i.e. mers, which are saturated in their structure, thus they are polyalkanes with an empirical formula of $H(CH_2)_nH$. An excellent description of the chronological developments in the field of polyolefins is provided by Seymour (1987). Polyethylene, the first polyolefin, was produced in laboratory scale in 1932 by the researchers of Imperial Chemical Industries (ICI) in the United Kingdom; this polyethylene later became known as low density polyethylene (LDPE). Industrial production of LDPE started in 1940. It is produced by free radical polymerization at very high pressures ranging from 1000 to 3000 bar and temperature of 150 to 260°C. Though its market is shrinking, it is still significantly used in wire and cable coating, co-extrusion, extrusion coating, extruded film and in blow and injection molding. In 1991, 3.5×10^9 kg of LDPE grade polyethylene were produced in the United States (Mills, 1991).

In 1950, Hogan and Banks of Phillips Company, using a supported chromium oxide catalyst produced high molecular weight linear polyethylenes, which became known as high density polyethylene (HDPE). In 1960, Karl Ziegler obtained patent for the production of narrow molecular mass distribution HDPEs using a catalyst system of titanium tetrachloride and triethyl aluminum. This catalyst system, one of the family of Ziegler-Natta catalysts, ushered in revolutionary improvements in the polyolefins industry both in terms of production volumes and process safety. The Ziegler processes for HDPE production required much lower pressures and temperatures (around 7 bar and less than 100^oC) than the earlier high pressure polyethylene manufacturing processes. HDPE sales in the United States were 3.6×10^9 kg in 1991 (Wolfe, 1991). HDPE finds wide acceptance in extrusion, sheet and thermoforming, blow, injection and rotation type molding and film making. A very important factor to the HDPE market in the future is its compatibility with recycling and reprocessing with minimum degradation.

In 1958, a new kind of polyolefin i.e., linear low density polyethylene (LLDPE), described as "HDPE with reduced density" was produced by copolymerization of ethylene with 1-hexene. By the late 1980s Union Carbide and Dow Chemicals produced LLDPE by copolymerization of ethylene with α-C_4 to α-C_8 olefins, using different processes and efficient Ziegler-Natta catalysts. Improved puncture resistance along with superior tensile, impact and tear properties have made LLDPE an ideal film making material. By penetrating the LDPE market, it has now a wide utility in pipe and sheet extrusion and all kinds of molding. The production figure for LLDPE category stood at 5.2×10^9 kg in 1991 in the United States (Taylor, 1991).

In order to circumvent the market penetration by other resins, the LDPE producers have developed a new family of specialty copolymers were the comonomer is ionic in nature. The most common examples of such polyolefins are ethyl vinyl acetate (EVA), ethylene-methacrylate (EMA), ethylene-ethyl/butyl acrylate (EEA or EBA) and also their corresponding acid acrylates. These resins cater to the specialty resins market of adhesive coatings, wire and cable coatings, specific high performance food wrappings, injection and blow molding to name a few. Total production of these branched polyethylenes was 6.4×10^8 kg in 1991 in the United States (Kaus, 1991). The preceding polyethylenes can be classified on the basis of their structure and density as outlined in Figure 1.1.

In 1955, Natta obtained crystalline propylene (PP) and subsequently Montedison was awarded a patent for the process. Since then, polypropylene production has experienced the highest level of growth of all the polyolefins, with a total annual production rate of about 3.6×10^9 kg in 1991 in the United States (Miller, 1991). This is attributed to the fact that polypropylene has replaced HDPE, and other polymers in many market segments. Polypropylene differs from polyethylenes in the sense that every alternate carbon chain atom has a methyl group attached. This stiffens the chain and renders desirable toughness to the polymer. Unless the methyl groups are in an ordered position with respect to the chain, the polymer does not crystallize; hence, in the initial studies only soft and sticky atactic polypropylene were produced. Crystallinity is responsible for the stiffness and solvent resistance of current commercial resins. Polypropylene is widely used in the form of isotactic homopolymer in which all of the methyl groups are lined up on the same side of the polymer chain. It has found very broad application in the thermoplastic industry particularly for fibers, filaments, film extrusion and injection molding. The market for polypropylene is growing at a rate of 13% per year (Blair, 1991). The stiffness of polypropylene chains can be reduced by inserting ethylene at intervals along the chain; thus, rendering the chain less regular and

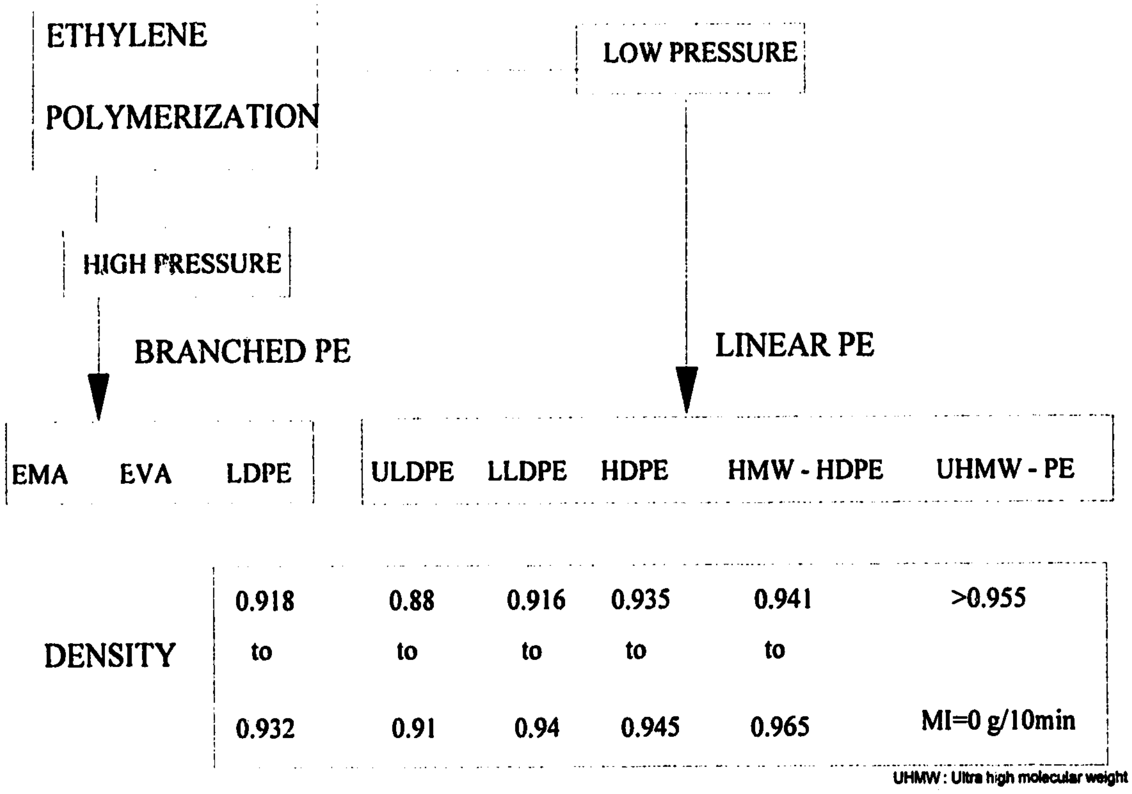


Figure 1.1 : Classification of polyethylenes.

more flexible. This in turn reduces crystallinity, melting point and the sharpness of melting point. Such random copolymers are known as ethylene-propylene rubber (EPR) and were initially introduced by Exxon in 1960. Apart from retaining most of the properties of polypropylene, EPR exhibits improved optical properties and impact resistance properties along with enhanced flexibility and reduced heat sealing temperature. High clarity injection molding, films and sealing layers in co-extruded film structures are the primary fields of its application (Walsh,1991).

Another important variant in polypropylenes are impact copolymers. These polymers are produced by polymerizing EPR and sometimes PE, in-situ, in a homo polypropylene matrix. The EPR forms a separate phase from the matrix, giving it a hazy, translucent appearance. The rubber phase distributed throughout the semi-crystalline homopolymer matrix provides stress concentration points at the interface, resulting in local deformation on impact instead of allowing the propagation of cracks. These materials are not true block copolymers as the EPR portion can be extracted by solvents. Polypropylene impact copolymers are mainly used in injection molding of articles requiring impact resistance, low density, colorability and easy processability. The impact PP copolymer market is growing at a rate of about 15% per year (Vernon, 1991).

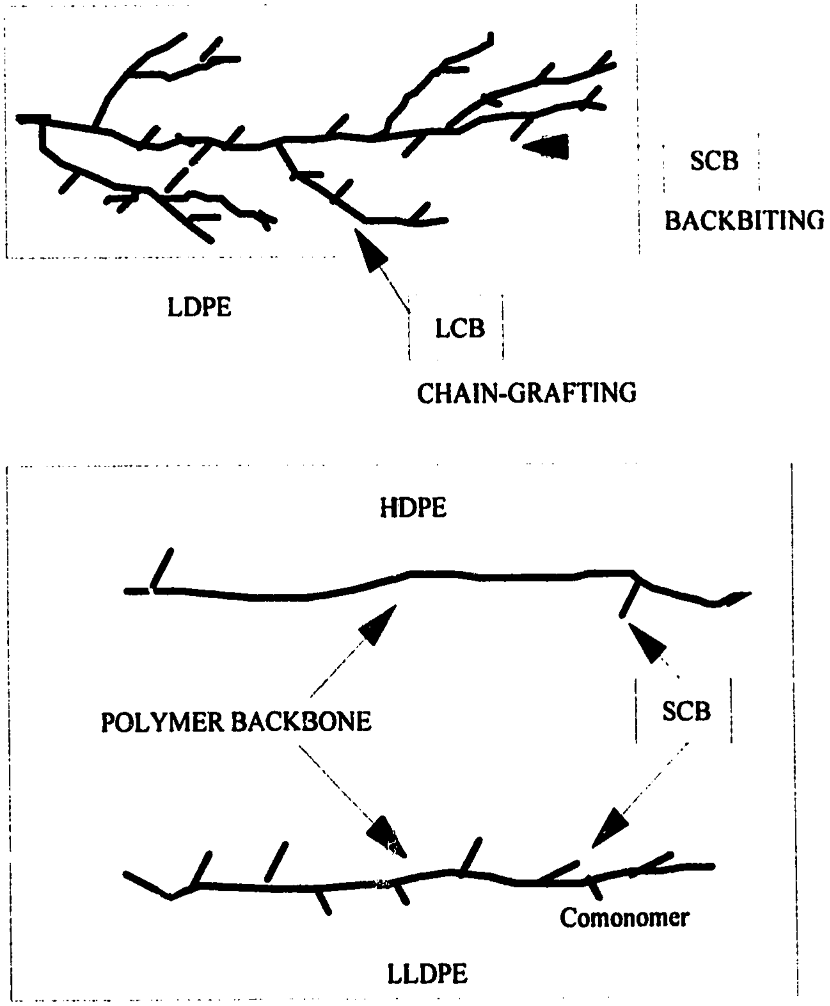
The polyolefin industry is dominated by large companies and it is a fiercely competitive technology-intensive field. New technologies are frequently introduced resulting in newer and more versatile kind of resins. Examples of this are Confined Geometry Catalytic Technology (CGCT) for polyethylenes announced by Dow Chemical Company (Miller, 1992) and Single Site Catalyst Technology of Exxon for production of LLDPE (Schut, 1991); Catalloy technology of Himont for the production of heterophasic polypropylene copolymers (Schut, 1993a, 1993b). These technologies are aimed at tailoring the products to customers specific needs; hence, reducing the requirement of further blending and processing of resins. With narrower molar mass and short chain branching distribution along with uniform comonomer incorporation these new resins are about to provide a combination of properties that was inconceivable even a few years ago.

1.2 STRUCTURE OF POLYOLEFINS

The wide range of properties of polyolefins can be related to the micro and molecular structure of the polyolefins. For this reason, the molecular structure of polyolefins is one of the most widely studied subjects in polyolefins research. Polyolefins are classified according to their density. Density of a polyolefin is directly, but not uniquely, related to its molecular structure. Most of the polyolefins are partially crystalline, i.e. they have a portion which is crystalline and the rest is amorphous. The degree of crystallinity depends on the molecular structure of the polymer. The molecular structures of LDPE, LLDPE and HDPE are shown in Figure 1.2.

1.2.1 LOW DENSITY POLYETHYLENE (LDPE)

The molecules of LDPE are highly branched and these branches are of two kinds: 1) long chain branches (LCB) and 2) short chain branches (SCB). When examined closely, one can see that even the long chains have short chain branches on them. Long chain branching on the main carbon chain of the molecule is induced by chain-grafting reactions occurring during the polymerization. Long chain branching (LCB) greatly affects the dimension of the polymer molecule and the level of LCB gradually becomes higher with higher molecular weights (Usami, 1989). The relative level of branching can be changed by altering the process parameters such as temperature, pressure and reactor configuration (Bergstrom and Avela, 1979).



SCB : Short Chain Branching

LCB : Long Chain branching

Figure 1.2 : Structure of common polyethylenes.

As discussed earlier, LDPE also has short chain branches (SCB) distributed all along the molecule. The distribution of SCB is heterogeneous both on an intermolecular and an intramolecular basis, i.e., the level of side chain branching varies among different molecular chains and also at different zones on a single molecular chain. The size of these small chain branches varies from two to six carbon atoms. The short chain branches are mainly formed by intramolecular hydrogen atom abstraction, called the backbiting mechanism from a cyclic intermediate (Roedel, 1953). Sometimes, SCB can be introduced because of copolymerization with α-olefins which are employed to control the molecular weight of the high pressure LDPEs. Because of the highly branched structure, the degree of crystallinity of LDPE is only 30 to 40%. This low crystallinity provides the lower density, flexibility, optical clarity, sealability and ease of processing along with a few disadvantages such as having low stiffness, low chemical resistance, poor barrier properties, low tensile strength and low heat resistance (Mills, 1991).

1.2.2 LINEAR LOW DENSITY POLYETHYLENE (LLDPE)

The molecules of LLDPE are different from those of LDPE in that they are devoid of LCB. LLDPE is produced with Ziegler-Natta catalyst systems using solution, slurry or gas-phase polymerization. Apart from ethylene, a comonomer is employed for the production of short chain branches. The length of such branches are two carbon atoms less than the parent 1-alkene comonomer. Most commonly used comonomers are 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene. LLDPE can be described as a blend of molecules with both intermolecular and intramolecular heterogeneity of comonomer with respect to molar mass (Mathot et al., 1986). The total number of branches is determined by the amount of comonomer used and the distribution of the short chains. The short chain branching distribution (SCBD) is a function of the catalyst system and process parameters employed (Cady, 1987). The short chain branches affect the stacking capability of the main carbon chains, which in turn, affects the crystallinity of the polymer. Thus, the higher the comonomer concentration, the lower the density of the resin. The use of comonomer molecules, i.e., using octene or hexene instead of butene, results in stiffer resins having better impact and tear properties. Apart from being correspondingly stiffer, other advantages of LLDPE compared to LDPE are better tensile strength, puncture resistance, tear properties, increased elongation and higher melting points. Some disadvantages, due to the higher crystallinity which affects the film surface roughness, are poor haze and gloss characteristics. Coupled with the side chain branching distribution, the molar mass distribution of the resin, controlled by the polymerization catalyst system and reaction conditions, also affects the rheological (melt flow) properties. These rheological properties are very important as far as processing of the resin is concerned.

Compared to LDPE, LLDPE is less shear sensitive because of its SCBD and narrow MMD. During shearing processes, such as extrusion, LLDPE is more viscous and therefore harder to process than LDPE with a comparable melt index. The lower shear sensitivity allows faster stress relaxation, thus during LLDPE processing, such as blow molding, its physical properties are less likely to change. LLDPE also does not show the dramatic strain hardening of LDPE, which is detrimental in film applications. This is because the long chain branches in LDPE results in severe entanglement of chains which causes a rise in viscosity under deformation. In LLDPE, these long side chains are absent and the main polymer chains "slide by" one another upon elongation without getting entangled. The structure-property relationships for LLDPE are summarized in Table 1.1 (Taylor, 1991).

Table 1.1 : Physical effect of density, molar mass and molar mass distribution on linear polyethylenes (LLDPE and HDPE).

Property	Density	Molar Mass	Molar mass distribution
Chemical resistance	I	I	-
Permeability	D	d	-
ESCR	D	I	-
Tensile strength	I	I	-
Stiffness	I	i	d
Toughness	D	I	D
Melt Strength	-	I	I

Legend : I = increase in property as parameter increases. i = slight increase in property as parameter increases. D = decrease in property as parameter increases. d = slight decrease in property as parameter increases. - = no effect; ESCR = Environmental stress crack resistance.

1.2.3 HIGH DENSITY POLYETHYLENE (HDPE)

High density polyethylene (HDPE), as seen from its molecular structure in Figure 1.2, has very few side chain branches on the main carbon chain. This regularity of the molecular structure of HDPE results in high crystallinity. HDPE is produced as homopolymers having very high crystallinity and copolymers having slightly lower density. The comonomer quantity is, however, much less in HDPE than in LLDPE. High densities in polyethylene provide excellent mechanical strength properties such as tensile strength, stiffness and hardness, thermal properties such as high softening points and heat distortion temperatures, and good barrier properties such as gas transmission and water vapor transmission. High densities also result in poor environment stress crack resistance (ESCR), impact strength and optical properties. Small amounts of comonomer are used to improve these properties. Though primarily affected by comonomer incorporation, density is also slightly reduced by higher molar mass. An optimal average molar mass has to be achieved in order to offset the problems of inferior processability (i.e., high viscosity) linked with high molar masses. Molar mass distribution (MMD), controlled by the process and catalyst system used, also affects the resin properties. A simple measure of MMD is the polydispersity. Narrow MMD (low polydispersity), results in better impact strength and low warpage. Higher polydispersity results in improved melt strength and resistance to creep (Wolfe, 1991). The structure-property relationships in Table 1.1 are also applicable to HDPE.

1.3 CHARACTERIZATION TECHNIQUES FOR POLYOLEFINS

According to Barth and Mays (1991), polymer characterization can be defined as a tool to study the kinetic and thermodynamic interactions of a polymer with its environment. Because of the complexity of polyolefin materials in terms of compositional and microstructural heterogeneity, characterization offers unique challenges and subsequent solutions to our quest for better understanding of these materials. As already discussed, short chain branching, molar mass and their distributions are among the most important parameters responsible for the physical properties of the polyolefins. Thus the characterization techniques are aimed at analyzing these parameters in ever increasing detail. The characterization techniques can be on-line or off-line. On-line techniques are relatively easy to carry out and short in duration, some examples being the measurement of melt index, dart strength, impact strength, tensile strength and tear strength. The results from these methods are empirically correlated with the weight average molar mass (MW_w), molar mass distribution (MMD) and the heterogeneity in the SCBD. Melt flow index is by far the most popular technique in the industry to obtain an indication of the MW_w. Dart, impact and tensile strength measurements are similar in a sense that samples are subjected to standard weights and the response is calibrated against standardized materials. Off-line techniques are generally more involved in nature and often require more time and data analysis before any meaningful information is obtained. This discussion will be limited to off-line methods which are important for polyolefins. The characterization methods which will be discussed in the following sections are size exclusion chromatography (SEC), carbon-13 nuclear magnetic resonance (C^{13}-NMR), infrared spectroscopy (IR), differential scanning calorimetry (DSC) and temperature rising elution fractionation (TREF). The discussion of these techniques will be limited to their application to polyolefins.

1.3.1 SIZE EXCLUSION CHROMATOGRAPHY

Size exclusion chromatography (SEC) is one of the most reliable means of determination of molar mass averages and molar mass distribution in polymers. Through the use of an on-line microprocessor-based data handling system it is possible to calculate the molar mass averages (MW_n and MW_w) from the size distribution chromatograms. SEC analysis is carried out by dissolving a small polymer samples dissolved in a solvent at high temperatures (≈140°C) which is then injected into a flowing stream of carrier solvent which passes through packed columns. The SEC columns are filled with a microporous packing or a cross-linked gel. The column packing material has particle sizes in the range 5-10 μm and typically contains pores with a size range of 0.5 to 10^5 nm; this range corresponds to the effective size range of most polymer molecules. The smaller polymer molecules in the sample diffuse into and out of more of the pore volume in the packing than do the larger molecules and thus exit later (Balke, 1991). The fractionation is based on the molecular size in the solution, with the largest molecules leaving the column first and the smallest ones last. The elution time, or the volume of elution (V_e), varies inversely with the molecular size. On leaving the column, the sample molecules enter one or more sequentially attached detectors that provide continuous quantitative data on the concentration of solute molecules in the eluted stream. Initially differential refractometers were used but owing to their high sensitivity to temperature and pressure fluctuations (resulting in an unstable base line), newer kinds of detectors such as ultraviolet-visible spectrophotometers have been developed.

SEC separates molecules according to their molecular size, with the result being presented as a size distribution curve, i.e. the technique does not give absolute values of molar mass. Calibrations with polymer standards of known molar mass are needed to convert the size distribution to molar mass distribution. Monodisperse or polydisperse polymeric materials of known molar mass and molar mass distributions are used as standards. Another method of linking the molecular weight and retention volume (i.e. time) is through the use of a universal calibration curve (Campbell and White, 1989).

1.3.2 CARBON 13 - NUCLEAR MAGNETIC RESONANCE (C^{13}-NMR)

This method, used since 1970, is a very useful characterization tool for polyolefins and is widely used. A salient feature of NMR studies is that it is absolute in its nature. C^{13}-NMR studies can provide detailed information on the three dimensional atomic conformation in a molecule; for polymers it has the ability to provide information on the polymer microstructure (Cheng, 1991). Some of the specific applications of C^{13} NMR to polyolefin characterization include:

(a) Polyolefin Identification: This is simply done by comparing the chemical shifts with the ones available in the spectral libraries or by using empirical chemical shift rules to predict the spectral shifts and thus identifying the components. C^{13}-NMR is particularly employed in detecting the functional groups in ionic branched polyethylenes like EVA, EMA, etc.

(b) Homopolymer tacticity: Different configurations of atoms along a polymer chain can generate different chemical shifts. Thus, in polypropylene the particular kind of arrangement can be identified.

(c) Copolymer sequence distribution: The comonomer incorporation sequence can vary a great deal among polymer samples. Different sequences result in differing chemical neighborhoods and this can be determined by NMR analysis.

(d) Chain branching determination: As already discussed, the chain branches have carbon atoms with different neighborhoods than the main chain carbon atoms. This difference can be detected by NMR.

The shortcoming of the NMR method lies in its inherent complexity which makes it incompatible for routine use. The requirement of operating the NMR probe at high temperature for polyolefins can also present problems.

1.3.3 INFRARED SPECTROSCOPY (IR)

Infrared spectroscopy can be used to determine the structural properties of polyethylenes (Campbell and White, 1989). For the study of SCBD of polyolefins the methyl symmetrical deformation band near 1378 cm^{-1}, the methyl rocking band ranging from 880 to 940 cm^{-1} and methylene rocking band ranging from 720 to 770 cm^{-1} are of interest for qualitative and quantitative analysis (Usami, 1989). However, there are difficulties in quantifying conventional IR spectra due to the uncertainties in the extinction coefficient. This problem has been overcome by the use of Fourier transform infrared (FTIR). Apart from not having the above mentioned shortcoming, FTIR gives excellent reproducibility and the difference spectrum can easily be calculated (Usami and Takayama, 1984). The polymer to be tested is generally pressed into a very thin film (1 to 50 μm) by compression molding or solvent casting before being inserting into the infrared beam.

1.3.4 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The DSC characterization method comes under the general category of thermal analysis and is designed to measure transition temperatures. At the transition temperature, the thermal behavior of the sample changes abruptly in comparison to the surrounding. In a DSC the energy that is required to keep the polymer sample and the reference at temperatures as close as possible to the programmed one is plotted against the programmed temperature. The most important parameters that can be ascertained from DSC are glass transition temperature (T_g), heat capacities (C_p), and melting and crystallization ranges. Both exotherms and endotherms are plotted for the scanned temperatures. The glass transition temperature is a very important parameter for ascertaining thermal effects on product performance. DSC analysis also provides a wealth of information on the copolymer content and glass transition temperatures of blends, the change in transition temperature and melting ranges of materials due to fabrication and aging, the crystal melting behavior and determination of the degree of crystallinity (Campbell and White, 1989).

1.3.5 TEMPERATURE RISING ELUTION FRACTIONATION (TREF)

Temperature rising elusion fractionation (TREF) is a method for analyzing semi-crystalline polymers by separating the molecular species according to their crystallizabilities (Wild, 1991). Many polyolefins are semi-crystalline in nature and their crystallinity is directly related to the molecular structure of the species. Thus, TREF can be used to investigate the molecular structure of the polyolefins. The molecular structure of common polyolefins, shown in Figure 1.2, contains a distribution of short chain branches and long chain branches along the main carbon atom backbone of the polymer molecule. Branching, particularly short chain branching, and other irregularities in the molecular architecture reduce the crystallizability of the polymer. For example, in Figure 1.2, LDPE is the least crystalline and HDPE is the most crystalline polyolefin with LLDPE having an intermediate level of crystallinity. Diminished crystallinity, apart from reducing the density of the polymer also reduces its temperature of dissolution into a solvent. During TREF analysis, a small sample of the polymer is eluted with a solvent at rising temperatures. The relation between molecular structure, crystallinity and the dissolution temperature are the basis of TREF, which is an efficient method for the evaluation of side chain branching distribution in polyolefins (Glockner, 1990). The effect of molecular weight on this kind of fractionation has been found to be very small (Wild and Ryle, 1977).

TREF is performed in different ways as shown in Figure 1.3. Analytical TREF (A-TREF) is performed for the determination of the short chain branching distribution

(SCBD) of the polymer. However, to obtain the SCBD, a calibration curve between the branching frequency and elution temperature is required. This calibration curve is obtained using FTIR or C^{13}-NMR analysis of preparative TREF (to be discussed later) fractions. The SCBD is represented as a plot of the polymer concentration in the eluted stream versus the corresponding branching frequency. Preparative TREF (P-TREF) is a mode of preparing fractions that are separated on the basis of branching frequency for further analysis. These fractions are subsequently subjected to IR spectroscopy, NMR, SEC or DSC analysis. Normally the sample sizes required for P-TREF are four to five times larger than those for A-TREF. The heating procedure that is employed for fraction collection is often different such as the stop flow procedure for better resolution between fractions (Kelusky et al., 1987). The combined analysis by P-TREF followed by subsequent analysis of TREF fractions by another method such as SEC, is referred to as cross fractionation.

A-TREF and P-TREF can also be performed differently on the basis of how the polymer is placed in the column i.e., off-column or on-column basis. Off-column means crystallization and separation of polymer sample from solvent takes place outside the column and the pure sample is loaded into a packed column for elution. In the on-column procedure the crystallization takes place in the packed column only. Although procedural convenience is evident in the on-column method, the interaction of column packing material with the polymer solution is still unexplained (Kumar, 1989) and the effects of surface chemistry and surface particle geometry has been listed as possible factors affecting TREF (Baker et al., 1989). Furthermore, off-column TREF has some operational advantages such as preparation of multiple samples, improved resolution of profile, reduced sample zone in the column and larger scale fractionation (Wild, 1989).

Although the off-column procedure has advantages over the on-column procedure, it also requires more efficient handling of polymer precipitates. A review on

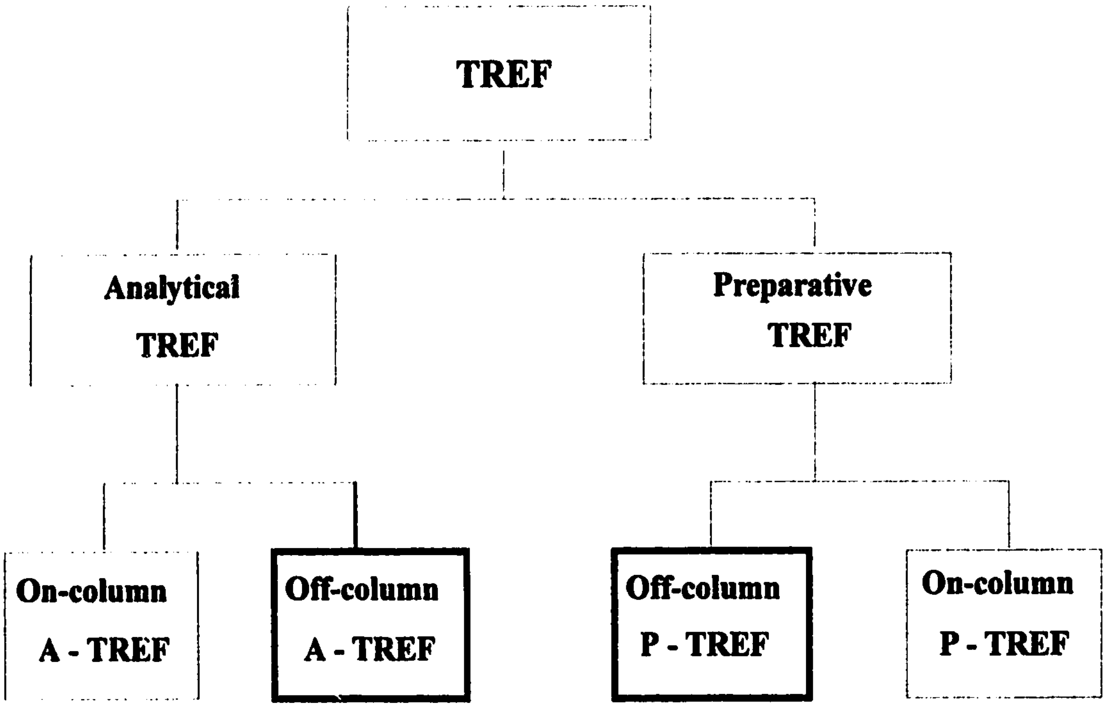


Figure 1.3 : Different methods of performing TREF

TREF related literature is provided in Chapter 2; TREF procedures are discussed in Chapter 3 and results of TREF analysis on selected polyolefin samples are provided in Chapter 4.

1.3.6 OTHER CHARACTERIZATION METHODS

In addition to the above mentioned characterization techniques, there are other characterization techniques used for polyolefins such as (a) X-ray diffraction which provides information on molecular orientation and fractional crystallinity; (b) transmission electron microscopy (TEM) and scanning electron microscopy (SEM) which provide detailed morphological information, (c) Raman spectroscopy which is used for measuring lamellar thickness and (d) small angle light scattering (SALS) and small angle X-ray diffraction (SAXD) used for determination of average spherullite size (Campbell and White, 1989). The list of applicable characterization techniques for polyolefins is expanding as a result of advances in instrumentation and data handling techniques.

2.0 LITERATURE SURVEY OF TREF

The aim of this chapter is to provide a review of the literature related to TREF. While underlining the chronological development in the procedures and analytical efficiency of this particular characterization technique, information is also provided on the general topics which were investigated using TREF as one of the tools for characterization of polyolefins. After the literature review on development of TREF, a brief discussion is provided on methods used to determine methyl group concentrations in polyolefins.

2.1 REVIEW OF THE DEVELOPMENT OF TREF

Desreux and Spiegels (1950) recognized the potential of using elution at differing temperatures to obtain fractionation of polyethylene on the basis of crystallizability. They were studying ways to fractionate polyolefins by solubility for structural evaluation. It was stated that separation on the basis of molar mass and crystallinity would occur when the polymer is eluted by solvents whose concentrations and temperatures are changed. Another procedural development reported by Schneider (1965) was the adoption of packed column elution instead of stepwise crystallization. This resulted in improved experimental convenience, faster fractionation and cost savings as smaller amounts of solvent were necessary.

Further studies, based on the work of Desreux and Spiegels using high density polyethylene, was performed by Hawkins and Smith (1958). They concluded that the solubility of polymers is also dependent on the crystallinity of the particular fraction, i.e., the branching level in the fraction, thus confirming the earlier results of the study of Desreux and Spiegel (1950). Wijga et al. (1960) performed TREF on 1 g samples of polypropylene with kerosene as a solvent using a glass apparatus and fire brick as a column packing. The temperature of the column was raised from 30 to 150^{o}C in 13 intervals by means of a circulating hot oil. Details of fractionation efficiency were not provided; however, it was shown that gradient elution fractionation (at 150^{o}C) resulted in a molar mass based fractionation whereas TREF separated the polymer according to crystallinity, i.e., the stereo-regularity of polypropylene. This was the first application of TREF described in the literature.

Shirayama et al. (1965) first coined the term "Temperature Rising Elution Fractionation (TREF)" for the method they used to fractionate LDPE on the basis of its short chain branching (SCB). The experimental apparatus they used for the fractionation was simple, but it inspired subsequent research activities. A 70 mm I.D. and 380 mm long glass column was filled with 1400 g of sea sand coated with 4 g of polymer. The eluting solvent was xylene and a stepwise temperature ramp was employed in the range of 50 to 80^{o}C by an oil bath. The ten fractions that were collected were subjected to IR measurements for SCB determination. Gradient elution was performed using the same equipment for fractionation on the basis of molar mass. They concluded in this early study that low molar mass fractions of LDPE contained higher degrees of branching and that the distribution arises purely from statistical reasons and not from polymerization conditions. They also noticed a fairly broad distribution of SCB in all the fractions, particularly in the lower temperature ones.

From these early studies one would have expected TREF to become a common tool for polyolefin characterization but this did not happen as most of the effort in polyolefin characterization shifted to size exclusion chromatography (SEC), a technique developed for polymer characterization in the 1960s. SEC is also frequently referred to as gel permeation chromatography (GPC). For the next decade, i.e., from the late sixties to the late seventies, SEC related studies were dominant but they only provided data on the molar mass distribution (MMD) and MMD alone could not account for the wide range of properties of the newer kinds of semi-crystalline resins like HDPE, LLDPE and various ethyl copolymers. Thus, it was thought that the structural and compositional details must have considerable influence over the resin properties; hence, researchers again shifted their attention to the crystallinity-based fractionation. After the study by Shirayama (1965) on polymer fractionation by TREF, no major studies in TREF occurred until the late 1970s. The loss of a decade in the development of TREF was not entirely detrimental though, as the advances made in high performance liquid chromatography (HPLC) for SEC were quickly transferred to TREF. Components developed for HPLC such as column systems, detectors, valves, fittings and pumps were used resulting in large scale and robust TREF systems.

The first description of analytical TREF was provided by Wild and Ryle (1977) and important improvements in TREF procedures were reported in this publication. The P-TREF and A-TREF apparatus described in this publication were the first ones constructed from metal. Secondly, the crystallization of the polymer sample, i.e., the cooling of the polymer solution, did not receive much attention as the polymer was deposited on the column packing by rapid precipitation or natural cooling of the hot polymer solution. It was already known that molecular separation takes place during the cooling step; hence, for a good, reproducible separation on the basis of crystallizability, it was important that the crystallization step be controlled. Therefore, Wild and Ryle (1977) resorted to a slow programmed cooling of the hot polymer solution in the polymer deposition step. It was further reported that a cooling rate of 2°C/h results in an optimal level of molecular separation on the basis of the crystallizabilities. It was further mentioned that at these cooling rates a single linear relationship exists between the elution temperature and the methyl content of the fractions for a wide variety of polyethylenes. Thus, the need to determine the methyl content for each resin was eliminated and the experimental effort was reduced.

Improvements in TREF techniques aimed at making the procedure less time consuming and more efficient were also reported by Wild and Ryle (1977). Efficient time management resulted from the simultaneous use of two controlled temperature baths, one for the crystallization of a number of samples and the other for elution purposes. The TREF apparatus contained the pump, differential refractometer, solvent reservoir and solvent degasser from a SEC system. The temperature gradients were provided by the aforementioned controlled temperature baths. Smaller sample sizes and columns were used during analytical TREF aimed at increasing the resolution of the TREF profiles. Analytical TREF was performed on an on-column basis as the polymer solution was cooled on the column packing material inside the column. Another procedural change to make A-TREF feasible was the selection of 1,2,4-trichlorobenzene as a solvent after it was discovered that xylene, which was used as a solvent in the case of P-TREF, and polyethylene have similar refractive indices. This had resulted in the non-detection of polyethylene in the on-line refractive index detector of the A-TREF apparatus during preliminary runs.

HDPE, LDPE and a four-part blend of various LDPEs were analyzed by Wild and Ryle (1977) and the differences in the A-TREF profiles arising out of the different crystallizabilities were highlighted. The differences in SCBD shown by differing A-TREF profiles of similar resins produced by different production processes were also shown. The authors concluded by forecasting an accelerated development of TREF due to the existence of a relationship between the SCBD and some important commercial properties of the resin.

Bergstrom and Avela (1979) also described a preparative TREF procedure while studying the methods of ascertaining the side chain branching distribution in various LDPE samples. The equipment was very similar to the P-TREF equipment of Wild and Ryle (1977). It was shown that the methyl content in the P-TREF fractions of various LDPE grades were not linearly related to the elution temperature of the fractions as reported previously (Wild and Ryle, 1977). The reason was attributed to formation of composite molecules that were generated because of chain transfer reactions taking place in different thermal zones of the reactor. Nakano and Goto (1981) described an automated TREF combined with SEC for auto-cross fractionation studies. The TREF system they developed was referred to as crystallizability fractionation device (CFD), in an attempt to differentiate it from the less automated TREF equipment. Most of the procedural aspects were done with the help of valves controlled by logic controllers. Cross fractionation of various LDPEs and physical mixtures of LDPE and HDPE were performed and it was shown that molar mass and crystallizability data, when shown together, can give an overall picture of the resin structure. The concept of a universal calibration curve proposed by Wild and Ryle (1977) was once again contested since the methyl group concentration in the fraction was not a linear function of the elution temperature. The automated cross fractionation system, however, did not find much application owing to its experimental difficulties and inferior separation during TREF (Wild, 1991).

In the 1970s LLDPE had been introduced in the market and Wild et al.(1982a) were the first to characterize 1-butene LLDPE by analytical TREF. A wide variety of resins such as LDPE, HDPE and ethylene copolymers of vinyl acetate and ethyl acrylate were also examined by analytical TREF. The column dimensions were further reduced from those reported in the previous publication (Wild and Ryle, 1977). The smaller size of column was chosen for better resolution of the profiles as the physical dimensions of big columns made it difficult to avoid channeling, "dead" spots, and longitudinal and axial temperature gradients in the column. Smaller sample sizes and on-line detectors for analytical TREF were used to improve the operating efficiency and the quality of fractionation. It was further mentioned that calibration with suitable standards allowed the direct calculation of the meaningful branching distribution. This eliminated the need for the analysis of individual fractions of a particular resin, thus reducing the experimental work. In the conclusion it was stated that the analytical TREF system allowed a schedule of two fractionations per day which was an improvement from the two or three runs a week experienced with the original P-TREF system. Wild et al. (1982b) in a subsequent communication used P-TREF and SEC to determine SCBD and MMD of TREF fractions, i.e., cross fractionation. They presented their results on three dimensional plots which showed the polymer concentration as a function of molar mass and SCB. The three dimensional plots showed that the lower molar mass fractions contained more SCB. These 3D plots were also used to show the subtle structural differences among the three similar LLDPE resins manufactured with different processes.

Usami et al. (1986) described a TREF system with a temperature programmed air oven instead of the oil baths or jacketed columns which were the norm until then. The advantages of an air oven over liquid baths, while using columns of small dimensions, is the ease of operation and shorter turn-around time between two TREF analyses (Wild, 1990). The aim of this paper was to discuss the mechanism of SCB generation in LLDPEs. They performed preparative and analytical TREF on six different LLDPEs, manufactured by four different processes such as slurry, solution and gas-phase polymerization processes, and a high pressure LDPE sample. A sample size of 2 mg in a 1,2 dichlorobenzene (ortho-DCB) solution of 0.4% concentration was stepwise eluted at a solvent flow of 1 ml/min. A bigger sample of 2.5 g was taken for P-TREF and further investigations using NMR, DSC and FTIR analysis were performed on the P-TREF fractions taken at 40, 64, 74, 84, 91 and 97°C. The authors first showed that LLDPEs indeed have a bimodal branching distribution unlike the unimodal distribution found in high pressure LDPEs. It was proposed that this was a result of multiple types of catalytic sites on the Ziegler-type catalysts.

Cady (1987) made a detailed study of the relation between LLDPE properties and their branched structure. Details regarding TREF procedures were not provided but an excellent comparison of A-TREF data for "fingerprinting" of resins was presented. He pointed out that due to the catalyst system and the process, intramolecular and intermolecular distribution of branches existed in the LLDPE macromolecules. He also stated that the heterogeneous character of LLDPE is due to the combined effect of these two kinds of distributions and careful control of catalyst and process parameters is necessary for the achievement of desired uniformity in branching distribution. A comparison of LLDPE having various α-olefins (1-alkenes) in the range of C_4 to C_8 was performed and it was found that the length of short branches strongly influences resin properties; e.g., larger comonomer resulted in increased stiffness of the chain.

Kelusky et al. (1987) used TREF for analysis of polyethylene blends. LDPE and LLDPE blends are used in processing to take advantage of their individual properties that are suitable for a particular application. Implicit in such studies is the ability to analyze competing resins which are often blends of patent-protected constituents. The authors studied 50-50 and 10-90 blends of LDPE and LLDPE and found that the TREF profile for blends was the same as the summation of normalized TREF profiles for the resins from which the blends were made. The subtle differences were attributed to co-crystallization and overlapping of comparable molecules of the resins during crystallization. Studies were also done for EVA-LLDPE blends and similar results were reported. Thus, blend analysis was shown to be a very useful TREF application. The advantages over the NMR study of blends is that although NMR can easily identify LDPE, TREF can also give an accurate determination of blend ratios.

Schouterden et al. (1987) characterized 1-octene LLDPE using A-TREF along with DSC analysis of the whole polymer and P-TREF fractions. The fractions were extracted using a particular device called a successive solution fractionator (SSF) which worked on the theory of successive thermal extraction. This study concluded that LLDPE as a whole and all its TREF fractions, except those below 45°C, have a broad bimodal SCBD. The polydispersity was found to decrease with increasing temperatures for the below 45°C fractions, remained constant for the 45 to 80°C fractions and increased with increasing temperature for the 80 to 100°C fractions.

Mirabella and Ford (1987) used TREF for the characterization of LLDPE along with other characterization methods like SEC, NMR and X-ray diffraction. They found that more than 50% of the comonomer was contained in the low temperature TREF fractions. A peculiarity noted in this study was the tri-modal SCBD encountered in 1-butene LLDPE as only bimodal distribution has been reported previously. In another study Mirabella et al. (1988) examined 1-butene LLDPEs and other grades of polyethylenes from BP Chemicals to find a morphological explanation for the extraordinary fracture toughness of LLDPEs. TREF along with scanning electron microscopy (SEM) were the characterization tools used. Extremely broad and bimodal A-TREF profiles of LLDPE suggested extreme heterogeneity in branching distribution. It was found that the high SCB, low crystallinity ends of chains formed a discrete phase embedded as small particles in a continuous semi-crystalline matrix of polyethylene copolymers. This low crystalline second phase, similar to what is found in other toughened plastics such as ABS and polystyrene, was detected by the SEM study of etched samples. The excellent impact strength of LLDPE was attributed to this phase separation.

Dohrer (1988) discussed the effect of SCBD on industrial ultra low density polyethylene (ULDPE) used by the food industry. ULDPE is a special case of LLDPE having a density < 0.915 g/cc. The general conclusions of this study was that narrow SCBD provide better impact and tensile strengths as well as better optical properties. Lower extractables and better heat sealing qualities were additional benefits of narrow SCBD. Thus, Dohrer (1988) clearly showed the importance of SCBD on product properties. Lee et al. (1988) also used TREF to demonstrate that SCBD affects the shear induced crystallization properties of terpolymers (LLDPEs with two kinds of comonomer). Kakugo et al. (1988) demonstrated that TREF can be used for the fractionation of other copolymers such as ethylene-propylene (EP) and 1-butene propylene copolymers (BP). It was stated that the elution fractionation at various temperature intervals could fractionate the copolymers according to their crystallinity which depended on the molecular tacticity.

Hosoda (1988), while studying the SCBD of LLDPE and LDPE, represented the cross fractionation data in a novel and easily understandable form. He presented the cross fractionation data in contour maps instead of the three dimensional plots mentioned previously. These contour mappings easily show the breadth of SCB distribution along with the molecular weight distribution. It was also shown that although the calibration curves for LLDPEs of different comonomer types were linear, the slopes were different for each variety of LLDPE. Consistent trends were noticed indicating that LLDPEs with bulkier comonomers had correspondingly lower crystallinity and melting temperatures.

Bibee and Dohrer (1988) used A-TREF to evaluate the side chain branching distribution while studying the blown film properties of LLDPE. Instead of using qualitative terms for the SCBD like heterogeneous and homogeneous, they devised a rough method to calculate the "percentage high density" portions in LLDPE from their A-TREF profiles. Higher percentage high density resins were considered heterogeneous and the lower ones homogeneous. The authors concluded that blown film properties of LLDPE can be improved by reducing the high density fraction.

In late 1989, owing to the increasing use of TREF in industrial and academic research, a TREF workshop was held at the Pennsylvania State University (College Station, PA, USA). At this meeting the effects of variations in equipment design and operating procedures on TREF profiles were discussed (Baker et al. 1989). New results on TREF characterization were also reported, for example Karoglanian (1989) reported that the thickness of lamallae increased with decreasing methyl group content of the LLDPEs. However, the most important contribution of the workshop was the description of the off-column method for the preparation of TREF specimen by Wild (1989). In the off-column method the crystallization of the dissolved polymer during the controlled cooling occurs in a vial; in the previously used on-column method the crystallization was done in the TREF column. The off-column method has some significant advantages over the on-column method, these include the ability to prepare multiple sample, improved resolution, reduced sample zone in the column and larger scale fractionation.

By 1990, enough work had been done in TREF for interested researchers to compile reviews on TREF. Review articles by Glockner (1990) and Wild (1991) provided a detailed description of TREF, its application and potential advances in this field. Since these reviews were written, improvements in TREF equipment and procedures, and additional TREF-based insight into the structures of polyolefins have been reported. Hazlitt (1990) described another automated TREF system which is claimed to be able to perform 56 A-TREF analysis per week. It was also proposed to heat the polymer solutions to 160°C before the crystallization step to ensure homogeneity.

Karbashewsky et al. (1991) used TREF to determine the SCBD of 1-octene LLDPEs having similar MMD to determine the effect of polymer structure on the processabilities of the LLDPEs. It was found that the percentage high density polyethylene in the whole polymer, and the breadth of SCBD in the polymer, both derived from TREF profiles, affect the processability of the resin; higher fractions of

HDPE and broader SCBD yield resins which are difficult to process. Karbashewsky et al. (1992) characterized LLDPEs by TREF, NMR, DSC and SEC. They concluded that the advantage of TREF over the other techniques was that it provided mass distribution for the levels of branching. For various LLDPEs examined it was shown that important physical properties, such as density and enthalpy of melting, can be accurately ranked according to the breadth of SCBDs.

In a recent publication Kuroda et al. (1992) used TREF to ascertain the branching sequence and distribution of 1-butene LLDPE, prepared over vanadium catalysts. They showed that unlike titanium-based Ziegler catalysts, vanadium-based Ziegler catalysts produced resins of unimodal SCBD. This unimodal distribution, together with NMR studies led to the conclusion that soluble vanadium catalysts have only one kind of catalytic site.

Wild and Blatz (1992) reported the development of a "high performance" TREF system with improved operational convenience and separation efficiency. Dual columns were used during elution to allow monitoring of actual separation temperatures. The crystallized polymer was loaded into the column by slurrying with the column packing which allowed increased column loading without sacrificing the separation efficiency. Furthermore, increased column loading allowed the IR detector sensitivity to be lowered and as a combined effect an improved detector response without any loss of resolution was reported. In a departure from previous publications (Wild et al., 1977 and 1982a, b) a new calibration curve for 1-butene LLDPE, which showed a linear relationship between the ethyl side chain content of fractions and the elution temperature, was constructed and it was recognized that LLDPEs of different comonomer would require separate calibration curves due to the possible effect of branch sizes. Examples of TREF application in the analysis of blends with crystalline and non-crystalline components were provided. The authors concluded by highlighting the recent advances in TREF which has established it as a routine analysis tool for polyolefin characterization.

Defoor et al. (1993) used P-TREF to fractionate 1-octene LLDPEs and analyzed the fractions for their thermal behavior and morphology. It was again shown that the branching level is higher in lower temperature fractions than in high temperature fractions. Also, the lower temperature fractions had lower molar masses and the polydispersity decreased for the fractions with increasing elution temperature. Different blends were prepared by mixing fractions of widely different branching at varying ratios. It was seen that these blends of diverse constituents crystallized into two different lamellar populations, which exhibited a mutual influence and determined the spherulite morphology.

2.2 METHODS FOR MEASURING METHYL GROUP (CH_3) CONCENTRATION

The methyl group concentration of the chains of polyolefin macromolecules is a parameter directly related to the branching in polyolefins. Infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) analysis are the common methods for ascertaining the methyl group concentration in polyolefins. IR spectroscopy is easier to use routinely than NMR analysis. A brief description of the IR and NMR methods is given below.

Fox and Martin (1940) first showed that the infrared (IR) spectrum of polyethylene had a band at 2960 cm^{-1} which indicated the presence of methyl groups; however, the band intensity could not be quantitatively related to the number of chain ends (methyl groups). Since this early study, much development has occurred in this field, and this has resulted in increased understanding of the ethylene polymerization and branching mechanisms (Roedel, 1953). Cross et al. (1950) determined the methyl group concentration in polyethylene by measurement of the 1378 cm^{-1} IR band (this is the symmetrical methyl deformation band).

This method, and variants thereof, have been used since then to determine the methyl group concentration in polyethylenes. The methylene doublet bands at 1350 and 1367 cm^{-1} cause some interference with the 1378 cm^{-1}, but Willbourne (1959) devised a compensation method which corrects for this interference. The interference can largely be removed by placing a HDPE wedge (having less than 3 methyl groups per 1000 carbon atoms) in the reference beam. The ASTM method (ASTM/D/2238-68, 1986) is also based on this procedure. Rueda et al. (1978 and 1979) discussed IR methods for determining methyl group concentrations in polyethylenes using a computer method based on difference spectra for Fourier transform interferograms.

The preparation of the polyethylene film for which methyl group concentration is to be determined, is a crucial step in the analysis. The ASTM/D/2238-68 (1986) publication provides the details for the preparation of the specimen film. The ASTM procedure make routine determination of methyl group concentrations, usually expressed as methyl groups per 1000 carbon atoms, possible.

Carbon^{13} NMR can be used to determine the methyl group concentrations, as well as other structural information, of polyethylenes. Hsieh and Randall (1982) describe the C^{13} NMR method for characterization of LLDPEs. One of the disadvantages of the NMR method for characterization is the requirement that the polyethylene be dissolved; hence, the sample has to be heated in a solvent at 120 to 130^{o}C during NMR scans. Analysis of NMR data is more complex than analysis of IR data. Hence, the IR method is used more commonly for the determination of methyl group concentration than the NMR method.

3.0 EQUIPMENT AND PROCEDURE

The objective of this thesis project was the construction of a TREF facility and the development of procedures for obtaining reproducible TREF profiles for polyolefins. These aspects of the project are discussed in this chapter. The overall aim was to construct a reliable, robust and economical apparatus, and develop simple and reliable operational procedures.

3.1 THE TREF EQUIPMENT

As mentioned in the Section 2.1 of the literature review, TREF equipment and procedures have undergone continuous refinements over the years. At the time this project was started, no commercial TREF apparatus was available and one of the main objective of this project was the assembly of a TREF apparatus. A Japanese manufacturer is currently marketing an automatic TREF set-up, but the general trend is still to custom-built TREF apparatus. A detailed description of the TREF system that was constructed is presented in this chapter. The main components of the TREF equipment that was constructed are the solvent system, the heating and cooling system, the TREF column, the detection system, the fraction collection system and the data acquisition system. A general schematic diagram of the TREF apparatus is shown in Figure 3.1. Each of the components of TREF system is discussed below. All the TREF equipment was housed in a special enclosure which was continuously vented into the building exhaust system. The precaution taken to prevent accidental spillage of the o-DCB into the laboratory (see Appendix B for additional safety information).

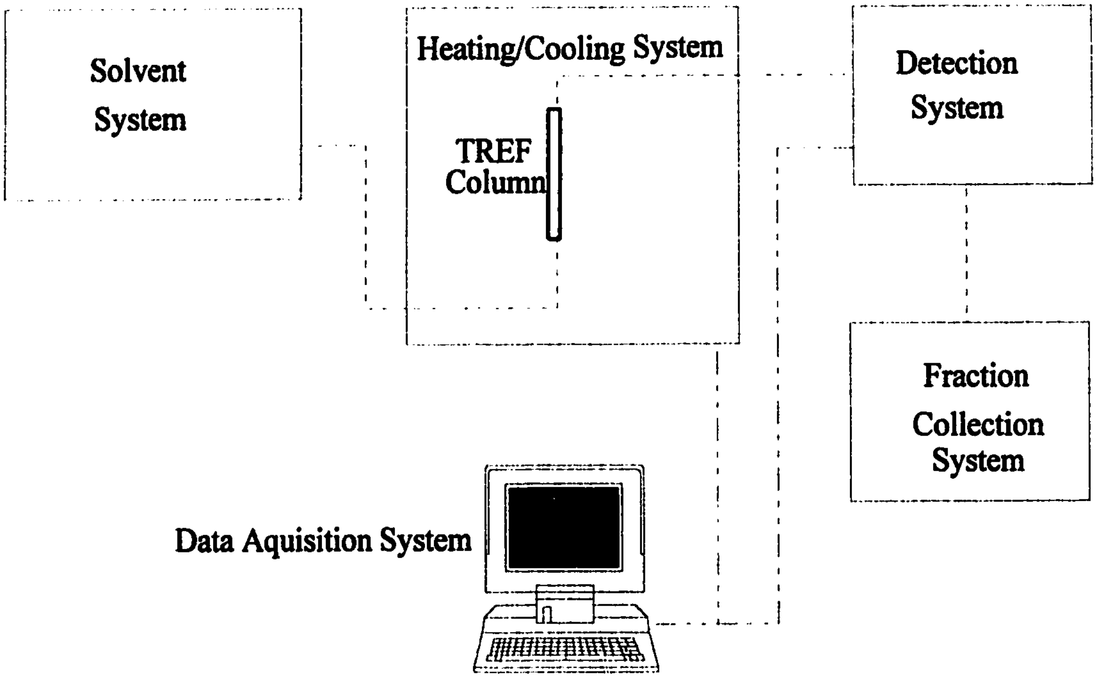


Figure 3.1 : Schematic diagram of TREF system.

3.1.1 THE SOLVENT SYSTEM

This part of the equipment contains the mobile phase, i.e., the solvent storage and transportation system. The solvent used was HPLC grade 1,2-dichloro-ortho-benzene (o-DCB) and it was stored in a glass bottle coated with soft plastic to avoid spillage in case of breakage. The choice of solvent was based upon the solubility of polymer in the solvent, its melting and boiling point, and the absence of methyl groups in the solvent. For example, the melting point of 1-2-4-trichlorobenzene (TCB), which is a frequently used solvent for SEC, is 17^{o}C. Thus, the solvent would freeze at the subzero temperatures that are encountered during crystallization. Hence, the use of TCB was discarded in favor of o-DCB which has a melting point of -17^{o}C. Anti-oxidant (2,6-di-tert-butyl-4-methyl-phenol) was added to the o-DCB at 0.25 g/L, to prevent oxidation of the polymer at high temperatures. The reservoir was connected to an HPLC pump for fluid transportation through the 1.6 mm (1/16") stainless steel lines.

The pump used was an HPLC pump from DuPont Instruments (Model 860). The pump was a reciprocating, two piston pump to minimize pulses in the flow. The pump had a flow range of 0.1 to 10 ml/min. A pressure transducer was located at the exit of the pump to measure the exit pressure. The exit pressure was a very useful diagnostic tool for identifying anomalies in TREF profiles. The o-DCB solvent flows from the pump to the column inlet inside the oven. Once inside the oven, the solvent passes through a preheating coil which provides the necessary residence time for the solvent to achieve the temperature of the oven chamber.

3.1.2 HEATING AND COOLING SYSTEM

One of the most vital components of the TREF apparatus is the heating and cooling system. Usually a temperature controlled liquid or air baths is used for cooling and heating of the TREF samples. In our case, both an air oven and a liquid bath were used in order to be able to do heating and cooling independently. The crystallization process (cooling) takes about 100 h, but several samples can be cooled at the same time. Hence, the liquid bath was used for the crystallization processes for some of the samples while the air oven was used for all elution processes. Only one sample at a time can be eluted (heating), but the elution process only takes 1 to 2 hours. During the crystallization process the sample temperature is decreased linearly from about 140°C to -10°C at a rate of 1.5°C/h, while during the elution process the temperature is increased linearly from -10 to about 130°C at a rate of 0.5 to 2°C/min.

Accurate temperature ramping is required in order to obtain reproducible TREF profiles. The precision of the air and liquid baths used met the requirements for TREF. The air bath was a Thermotron Model S5.5C environmental chamber with a temperature range of -87 to 190°C. A microprocessor-based programmable temperature controller was part of the oven, and the precision (temperature control tolerance) of the temperature was ±1.1°C. The liquid bath was a Neslab Model RTE-220 programmable temperature bath with a controllable temperature range of -26 to 130°C. The liquid in the bath was diethylene glycol.

Increasing as well as decreasing temperature can be achieved with both the air and the liquid baths. The temperature-time data were stored in a microcomputer; the data acquisition system is described in detail in section 3.1.6 .

3.1.3 THE TREF COLUMN

The column in TREF analysis contains the crystallized polymer and packing material. A schematic diagram of the TREF column used is shown in Figure 3.2. The columns used were fabricated from SEC columns manufactured by DuPont Instruments. This ensured an excellent finishing of the internal surface of the columns which is important for elution purposes.

The stainless steel (SS316) columns were cut into lengths of 45 mm and had an O.D. and I.D. of 10 and 6 mm, respectively. The inlet and exit tubing was 1.6 mm (1/16") stainless steel tubing. The tubing was connected to the column by Swagelok reducers. Filters (7 micron, Swagelok) were placed into the reducers at each end of the column. The column was placed into a vertical position in the oven, and the solvent entered the bottom of the column.

Two thermocouples were used to measure the temperatures of the solvent at the inlet and the exit of the column. A third thermocouple was used to measure the air temperature in close vicinity to the outside of the column at the middle of the column. The initial column used had a length of 61 mm; this length of column resulted in a maximum temperature difference of 6.5^{o}C between the inlet and the exit solvent. The column length was reduced to 45 mm, and this reduced the difference between inlet and exit temperatures to a maximum of 2.8^{o}C (encountered in the range of -10 to 0^{o}C), and typically was less than 1^{o}C during higher oven temperatures. The loading of the column with the packing material and the crystallized polymer is described in section 3.2.2 .

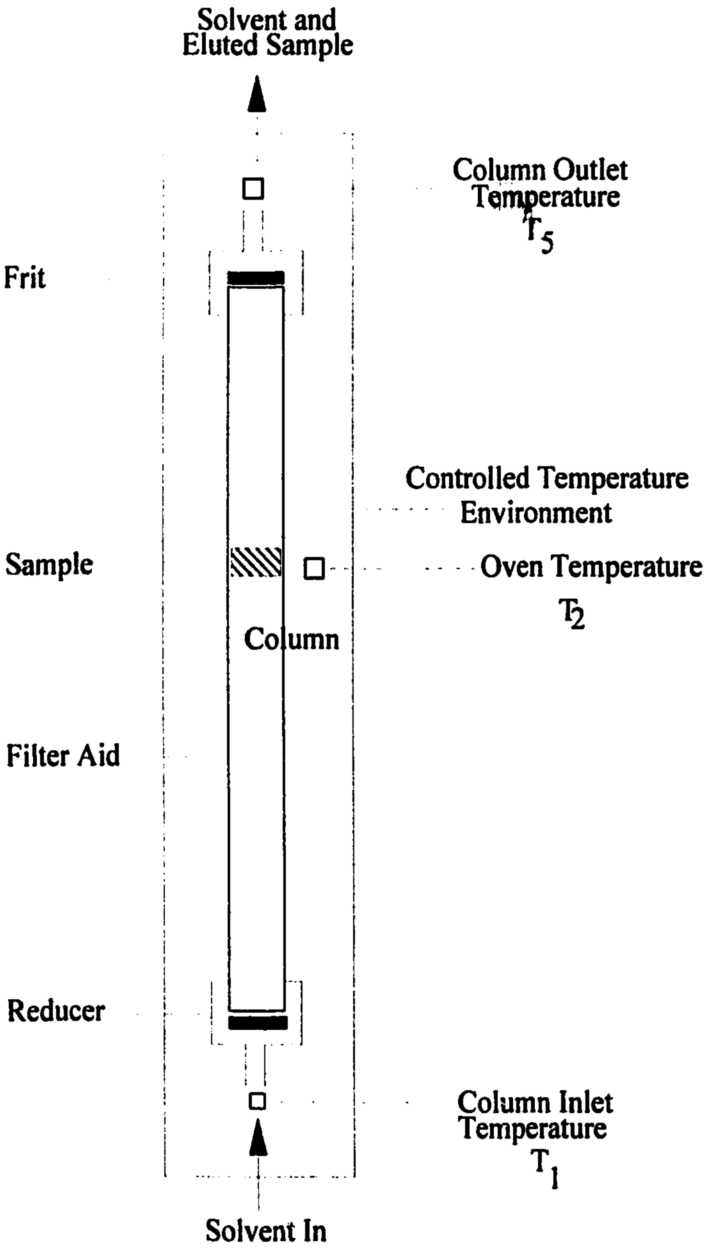


Fig. 3.2 : Schematic diagram of the TREF column

3.1.4 INFRARED CELL AND DETECTOR

The exit from the TREF column was connected to an infrared (IR) detector for measuring the polymer concentration in the solvent. The tubing connecting the column to the detector was heated to 130°C with heating tape in order to prevent crystallization of the polymer in the lines. The IR cell into which the solvent flowed was also kept at 130°C. The temperature of the solvent entering the IR cell should be approximately equal to the temperature of the cell since temperature differences can cause the windows on the IR to crack. The IR cell was a sandwich type cell in which a lead gasket was located between two calcium fluoride windows; diagrams of the IR window are shown in Figure 3.3. A lead gasket with a thickness of 1 mm was used for runs done before January 29, 1993 and a lead gasket with a thickness of 0.5 mm was used for subsequent runs. The size of the windows was 38.5 mm by 19.5 mm and they had a thickness of 4 mm. Great care has to be taken when assembling the cell and when heating the cell. The cell should be kept at 130°C at all times once leak-free operation has been attained. Cooling and heating the cell can result in leaks and breakage of windows.

The detector was a DuPont Instruments (Model 830085, Serial No. 099) infrared detector for liquid chromatography. The IR wave length was fixed at 3.41μm (asymmetric stretch of CH_2 group). The pathlength was equal to the thickness of the lead gasket, and the slit width was set at 1 mm. With this mode of operation, the voltage output of the detector was proportional to the CH_2 concentration in the solvent passing through the IR window.

3.1.5 FRACTION COLLECTION SYSTEM

After the solvent laden with polyethylene had passed through the IR detector it was either discarded when performing A-TREF or it was collected as fractions when P-TREF was being performed. During P-TREF operations, the output transfer line was

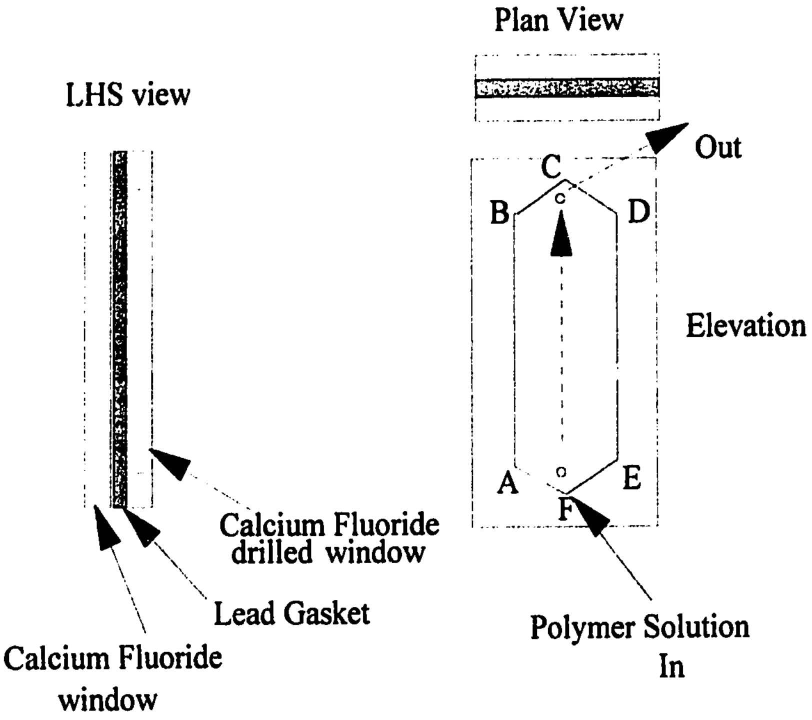


Figure 3.3 : Schematic diagram of infrared detector cell sandwich

directed into 4 ml vials (WATERS auto sampler receptacles) for a fixed range of elution temperatures. Subsequent molar mass analysis was done on the fractions using a Waters 150C ALC/GPC. The output solution was collected manually in the vials over various elution temperature intervals. The samples were arranged in order of increasing temperature ranges in the SEC carousal.

3.1.6 DATA COLLECTION AND PROCESSING

An OPTO22 system and a 486 minicomputer were used for data acquisition from the TREF apparatus. Thermocouples were used to measure temperatures at various locations (shown in Figure 3.4 and 3.5); a pressure transducer was used to measure the pressure at the exit of the pump and polymer concentration in the solvent was measured by the IR detector. All these analog outputs were converted to digital signals by the OPTO22 system. The following data were stored in an ASCII data file.

Column 1 = time in seconds of data collection (t)

Column 2 = Set-point (T_0, not used as the temperature was controlled by the oven itself)

Column 3 = Temperature of solvent at the column entrance (T_1)

Column 4 = Temperature of air at the vicinity of the column midpoint (T_2)

Column 5 = Temperature of the heated transfer line downstream from the column but upstream from the IR cell (T_3)

Column 6 = Temperature of the heated transfer line downstream of the IR cell (T_4)

Column 7 = Temperature of the solvent at the exit point of the column (T_5)

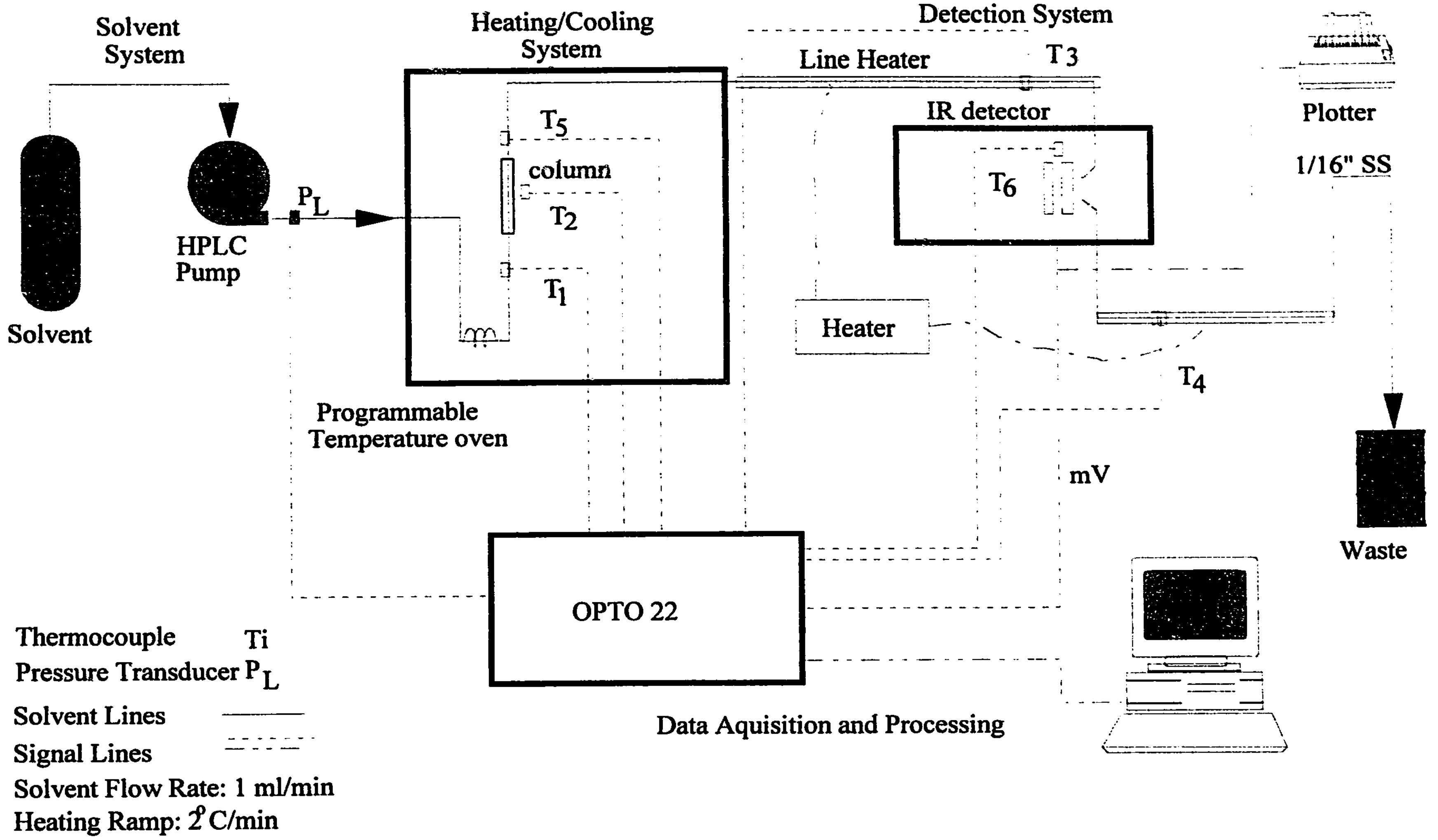


Figure 3.4 : Analytical TREF Schematics

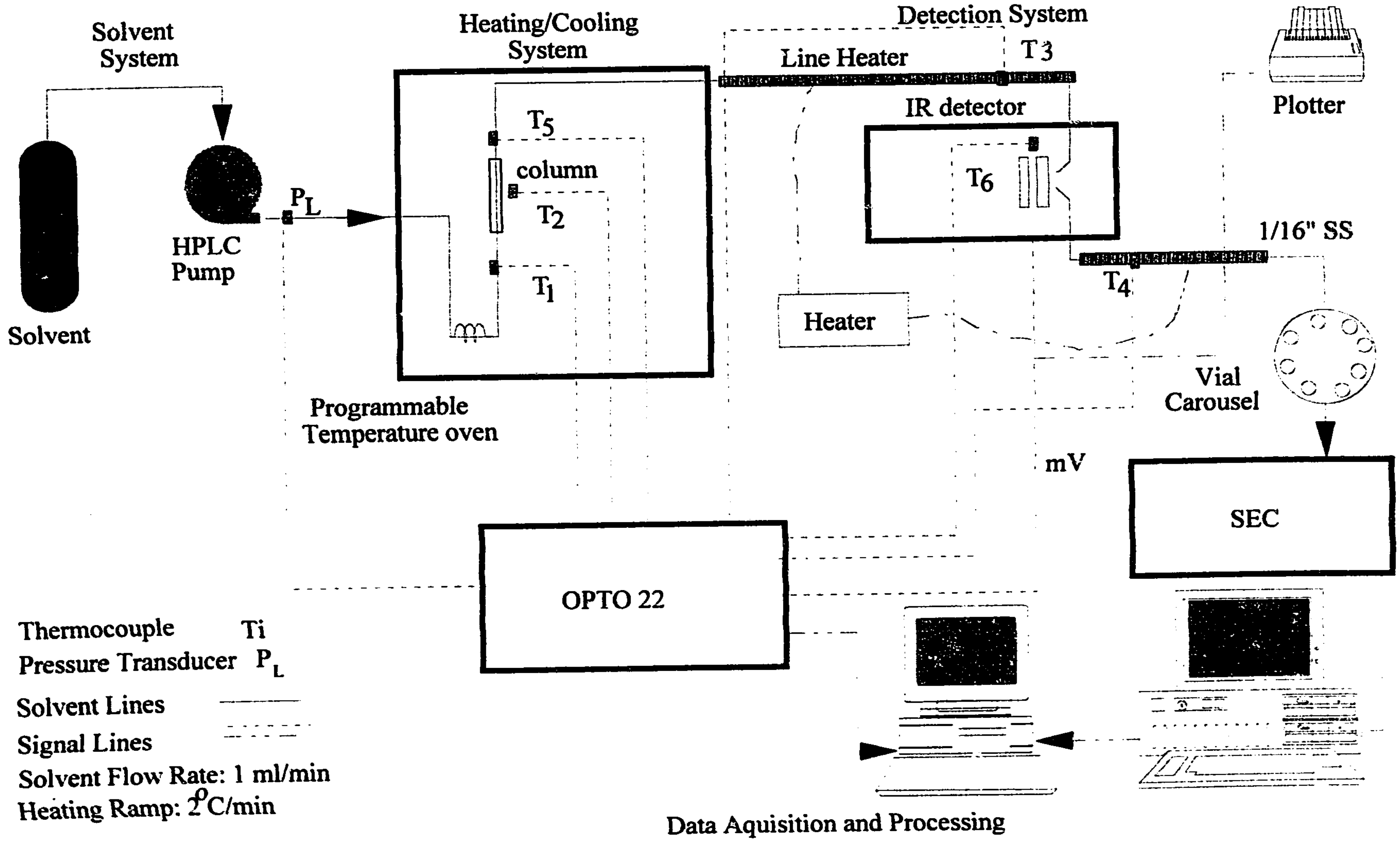


Figure 3.5 : Preparative TREF Schematics

Column 8 = Output signal from IR detector cell in millivolts (V_1)

Column 9 = Temperature in the IR flow through cell sandwich (T_6)

Column 10 = Pressure at the exit of the pump (P_1)

Each run was stored in a separate data file; these data were processed and graphics software (Axum) was used to prepare graphs and plots. The following sections describe the procedural aspects of analytical and preparative TREF.

3.2 DESCRIPTION OF TREF PROCEDURE

Analytical and preparative TREF analysis were performed using the pieces of equipment described in the previous parts of this chapter. Details of the procedures used in the three steps essential to TREF, namely, polymer crystallization, loading of column and the elution of polymer, are described in the following sections.

3.2.1 SAMPLE PREPARATION

Commercial and laboratory prepared polyolefins were used in the TREF studies. The commercial polyethylene samples were received as cylindrical extrudates with a diameter of 4 mm and a length of 4 mm. Each pellet was much larger than the sample size needed for a TREF analysis. The polyethylene and polypropylene samples, produced in our laboratory reactors, were irregularly shaped particles or small spheres varying in size from 0.1 to 3 mm. Some of these particles and globules, particularly of polypropylene, were difficult to dissolve in the 1-2 dichlorobenzene solvent. Secondly, representative sampling was a problem due to the small size of sample required for TREF analysis. Therefore, about 50 g of polymer sample was ground to fine particles <0.5 mm size using a Brinkman Retsch centrifugal grinder (at approximately 10000 rpm). This shredding improved the sample homogeneity. While grinding, liquid nitrogen was continuously added to cool the polymer sample to prevent thermal degradation during the shredding.

A small portion of the shredded polymer sample was weighed with a high precision Mettler HL52 electronic balance having a precision of 10^{-5} grams. For analytical TREF the sample size was 5 mg and for preparative TREF the size was 20 mg. The 1,2-dichlorobenzene (ortho-DCB) was added to the weighed samples (1 ml of solvent per mg of sample). The solvent contained 2,6-di-tert-butyl-4-methyl-phenol antioxidant at a concentration of 0.25 g/L. Clean Teflon coated magnetic stirrers of appropriate dimensions were put in the suspension for subsequent stirring operations. After this, the vials were sealed with Teflon coated seals which were clamped tightly in position by aluminum seal caps. Vials sealed in this fashion were insufficiently sealed when placed into the liquid diethylene glycol bath as some diethylene glycol leaked into the vials. The problem was solved by covering the aluminum vial seals with aluminum foil and tightening it firmly.

The suspensions in the vials were then heated to $160^{o}C$ while stirring. The combined heating and stirring was achieved by placing the vials in a flat bottom container filled with diethylene glycol. This container, in turn, was placed on a hot plate equipped with magnetic stirring. This operation was carried out for about 1 hour, the temperature was kept close to $160^{o}C$ to avoid thermal degradation of the polymer samples. The reason for stirring at high temperature was to ensure that the polymer melt mixes properly with the solvent, thus transforming the suspension into a homogeneous solution. This procedure should result in disentanglement of long polymer chains. Disentanglement of the chains increases the efficiency of incremental crystallization that was carried out subsequently.

The vials, after the stirring at elevated temperatures had been achieved, were taken out of the diethylene glycol bath and quickly transferred into the oven which was at 160°C. The next step was the crystallization of the polymer which was done by slow cooling from 160 to -10°C. In preliminary studies it was observed that the polyolefins were eluted at temperatures <120°C. Hence, the polymer-solvent mixtures in the oven were cooled relatively fast in the 160 to 130°C temperature range. The cooling from 160°C to 130°C was performed rapidly (5 hours) in the air oven and the vials were rapidly transferred to the liquid bath when the temperature had decreased to 130°C. The final cooling was carried out by decreasing the temperature at 1.5°C/h from 130°C to –10°C. The samples were removed from the bath after they had been cooled to -10°C and stored in a freezer at -10°C until used for TREF analysis.

The total cooling time for crystallization was approximately 100 hours (over 4 days). The long time required for the crystallization of polymer samples is the reason for using two temperature baths because several samples can be cooled simultaneously.

3.2.2 SAMPLE LOADING IN THE TREF COLUMN

The crystallized polymer obtained after the cooling process was separated from the solvent by using an Anodisc inorganic filter having a pore size of 0.02 μm. The cold polymer suspension from the freezer was poured on the disc and the solvent was drawn out by a vacuum, generated by vacuum pump. Meanwhile a TREF column, of dimensions as described in the section 3.1.3 was filled to 60% height with Celite, a diatomaceous earth packing material. The bottom of the column was connected to vacuum and the crystalline polymer was washed with acetone from the filter disc into the column. When all the polymer has thus been transferred, more Celite was added at the top of the column. In this step all the operations are performed at sub-zero temperatures to prevent any dissolution of the polymer during this transfer operation. The ends of the column were capped with the previously described reducer fittings containing frits with 7 micron pore size. The loaded column was kept inside a freezer before being placed into the oven for elution of the polymer.

The efficiency of the polymer sample recovery, i.e., transferring the crystallized polymer from the suspension in the vial to the filter disc was a concern as good efficiency in collection of crystallized polymer was one of the necessary conditions for reproducibility of TREF profiles. The "dry" weights of the polymer sample (before crystallization step) and the particular filter disc were taken separately using the previously mentioned electronic balance. The weight of the filter disc with the polymer on it (after crystallization) was taken after keeping this disc at ambient conditions overnight. The overnight exposure removed acetone and solvent residuals from the crystallized polymer that might have remained in the polymer sample during its deposition on the filter disc. This operation was performed on 4 samples, and the recovery efficiency was found to be above 99.5 %. Thus, a high degree of efficiency in transferring the crystallized polymer from the suspension in the vial to the filter disc was noted.

3.2.3 ELUTION FROM THE COLUMN

The elution of the crystallized polymer from the packed TREF column is the step which separates the polymer according to the amount of side chain branching , i.e., methyl group concentration for polyolefins. The reproducibility of the TREF results largely depend on the reliability of this elution step. The following procedure was found to produce reliable results in most cases. As pointed out below, difficulties were encountered occasionally and the cause(s) of these problems has not been fully identified.

The equipment used for the elution had to be prepared before introducing the packed TREF column to the air bath. This consisted of flushing the solvent lines (heated to 130°C by heating tapes) downstream from the TREF column with solvent (ortho-DCB) for about 30 minutes. Subsequently, the air bath, with the column in its chamber, was cooled to -10°C. The flushing of the transfer lines was done to remove any residual polymer or column packing material from the lines; these materials may cause blockages in the transfer lines during subsequent steps of the procedure. After the air bath had been cooled to -10°C, the solvent pump was turned off, and a previously prepared TREF column was removed from the freezer and was installed in the TREF circuit. The solvent flow was started again at a rate of 1 ml/min when the bath temperature was steady at -10°C.

Several minutes of solvent flow was required to remove air from the column and lines. Spikes in the output signal from the IR cell, which was kept at 130°C even when not in use, indicated the passage of air bubbles through the IR cell. Up to 30 minutes were required to stabilize the IR signal. If necessary, the zero was adjusted on the IR cell before starting the elution. The temperature programmer of the air bath and the OPTO22 data acquisition system were readied while the oven temperature was stabilizing. The frequency of data acquisition for the various temperatures and pressures listed in section 3.1.6 was 2 s for most experiments. It was found that this rate of data acquisition was sufficiently fast to capture all of the peaks in the TREF profiles.

The temperature ramp for the air bath was started (2°C/min for most experiments); the run was usually terminated when the temperature reached 120°C for polyethylenes and 130°C for polypropylene samples. Data recorded by the OPTO22 system has been described in section 3.1.6. The TREF apparatus was not left unattended during the elution because problems were encountered during many of the elutions, especially in the early stages of the work. The TREF runs done are listed in Table A.1 in Appendix A, and the experiments in which problems were encountered are identified.

The problem most commonly encountered was a rapid increase in the pressure at the exit of the pump; pressures at the exit of the pump at times increased to 400 bar. At this pressure the pump automatically shut off. These pressure excursions occurred most frequently with HDPE with narrow molar mass distributions when the elution temperature was in the 85 to 100°C range. Pressure rises also occurred with higher frequency in preparative TREF (20 mg sample) than in analytical TREF (5 mg sample). The reason(s) for these pressure excursions is not known, but they were possibly due to blockage of the 7 μm pores in the frit located in the reducing union at the exit of the column. The use of frits with larger pores is not a viable alternative since carry over of the column packing would result. The blockage could be caused by agglomerates of polymer molecules which were not totally disentangled during the dissolution. The blockage could also be caused by re-crystallization of HDPE in the pores of the frit. Possible swelling of the polymer prior to the dissolution could also block the flow in the column packing. Blockage due to swelling could be the reason for the higher frequency of pressure excursions during preparative TREF.

If a pressure excursion was noticed (by following the pump pressure displayed on the PC), the pump was stopped and the air bath temperature was increased to 150°C by overriding the programmed temperature increase. After heating the air bath to 150°C, the pump was started and the flow blockage had always disappeared. Hence, the increase in temperature dissolved the polymer which had caused the blockage.

The parts of the TREF profile before the flow stoppage contain some useful information, but only results in which no flow stoppage occurred are used in the discussion in the next chapter. Typical TREF results, IR signal, column temperatures and the air chamber temperature as a function of time, are shown in Figure 3.6. It was observed that the shapes of the TREF profiles were affected noticeably if the pressure at the exit of the pump exceeded 3 bar.

Another less frequent upset which resulted in unusable results was a solvent leak. Leaks occurred much less frequently than the pressure excursions. Leaks occurred either at the pump or in the seal around the IR windows. The pump was immediately turned off once a leak was noticed, and the o-DCB which had leaked out was removed very carefully following all the safety precautions listed in Appendix B.

The solvent exiting the IR cell was discarded in analytic TREF and the only result from an analytical TREF experiment was the TREF profile. In preparative TREF, a larger sample of crystallized polymer was placed into the column (20 mg compared to 5 mg for analytical TREF), and the solvent leaving the IR cell was not discarded. The solvent, which contains the dissolved polymer, was collected in small vials; a total of 15 to 20 samples were collected sequentially during each preparative TREF run. The collection time for a typical fraction was 3 to 4 min; this corresponds to a 6 to 8°C change in the elution temperature for the usual rate of temperature increase. The temperatures at the column exit, T_5 displayed in column 7 on the PC screen, was used to determine the start and the stop times for collection of the fractions. The fractions collected during a preparative TREF experiment were subsequently analyzed by SEC.

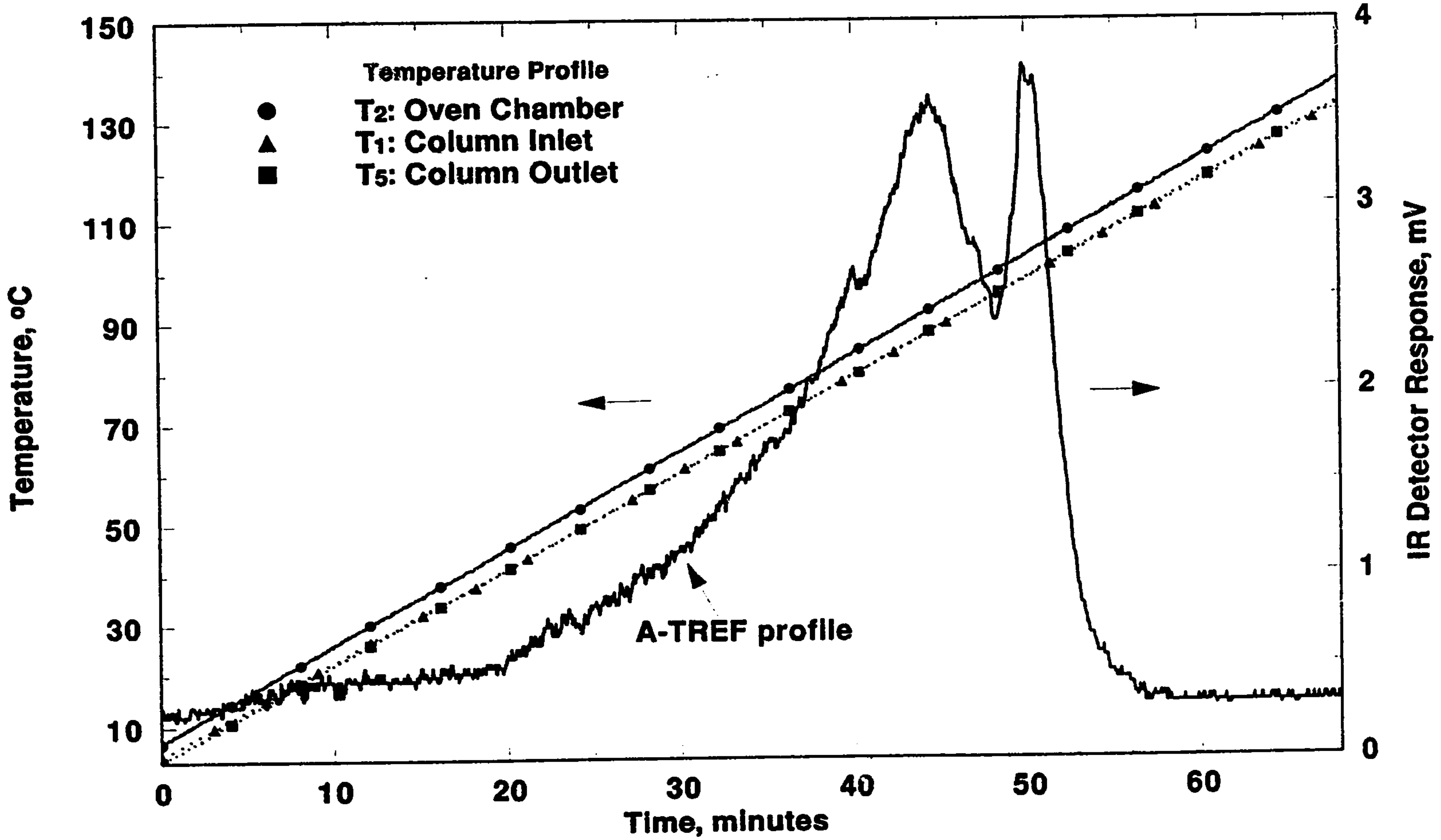


Figure 3.6 : Analytical TREF and temperature profiles (plotted with time) of a commercial LLDPE sample.

3.3 CROSS FRACTIONATION

Preparative TREF runs were done in order to have samples of polymer separated on the basis of the degree of side chain branching with SEC subsequently used to determine the molar mass distribution of the polymer in these samples. This type of sequential analysis in which a mixture is separated into different fractions on the basis of two different types of properties is referred to as cross fractionation. In the current work the cross fractionation consisted of first separating the polymer on the basis of side chain branching by TREF and then separating the polymer in the TREF fractions according to size of polymer molecules (molar mass) by SEC.

A Waters 150-C ALC/GPC was used for determining the molar mass distributions. All the SEC analyses were done by Ms. Naiyu Bu who is responsible for the operation of Waters SEC in the Department of Chemical Engineering. Only a brief description of the SEC (GPC) procedure will be presented since these experiments were not done by the author.

The TREF fractions were loaded into the Waters sample carousal in order of increasing TREF elution temperatures and the carousal was placed into the injection compartment of the SEC. The sample compartment was heated to 140°C and 0.3 ml samples of the TREF fractions were automatically injected into the SEC after the baseline had stabilized. Two injections were done for each TREF fraction and the time between injections was about one hour. The TREF fractions were analyzed in the order of increasing TREF elution temperature. It is important to adhere to this sequence of injections because pressure problems occasionally occurred during SEC analysis of high temperature TREF fractions.

Four Shodex GPC/AT-80M/S columns in series were used to separate the polymers on the basis of molar masses (size). These columns have an I.D. of 8 mm and are 250 mm long; they are packed with styrene - divinylbenzene gels. The carrier solvent was 1,2,4-trichlorobenzene and the flow rate used was 1.0 ml/min. The column temperature was kept constant at 140°C. A refractive index (RI) detector was used to determine the concentration of polymer as a function of retention time. The retention time is a function of molar mass, and polystyrene and polyethylene samples of known molar masses were used to obtain a calibration curve for converting retention time to molar masses. A typical molar mass distribution determined by SEC is shown in Figure 3.7.

The cross fractionation results can be displayed on 3-D plots of polymer concentration (output of RI detector) as a function of molar mass and methyl group concentration (TREF elution temperature). The 3-D plots showing this information are shown in Figure 3.8. The 3-D plots were prepared using the Axum software.

The elution temperatures plotted in Figure 3.8, as well as in other figures, were the temperatures at the exit of the column (T_5) at the time the IR signal was being recorded and the P-TREF fractions were being collected. No corrections were made for the holdup in the IR cell and the transfer lines downstream from the column. The dead volume of the transfer line between the exit of the column and the IR cell was 0.24 cm^3, the dead volume of the IR cell was 0.28 or 0.14 cm^3 (depending on the thickness of the lead spacer), and the dead volume of the transfer line from the exit of the IR cell to the point at which cross fractionation samples were collected was 0.71 cm^3 . The standard solvent flow rate was 1.0 cm^3/min and the standard rate of temperature increase was 2°C/min. Hence, the maximum correction to the elution temperature for solvent holdup is 2.5°C; this correction is not significant compared to the range of temperature at which elution takes place.

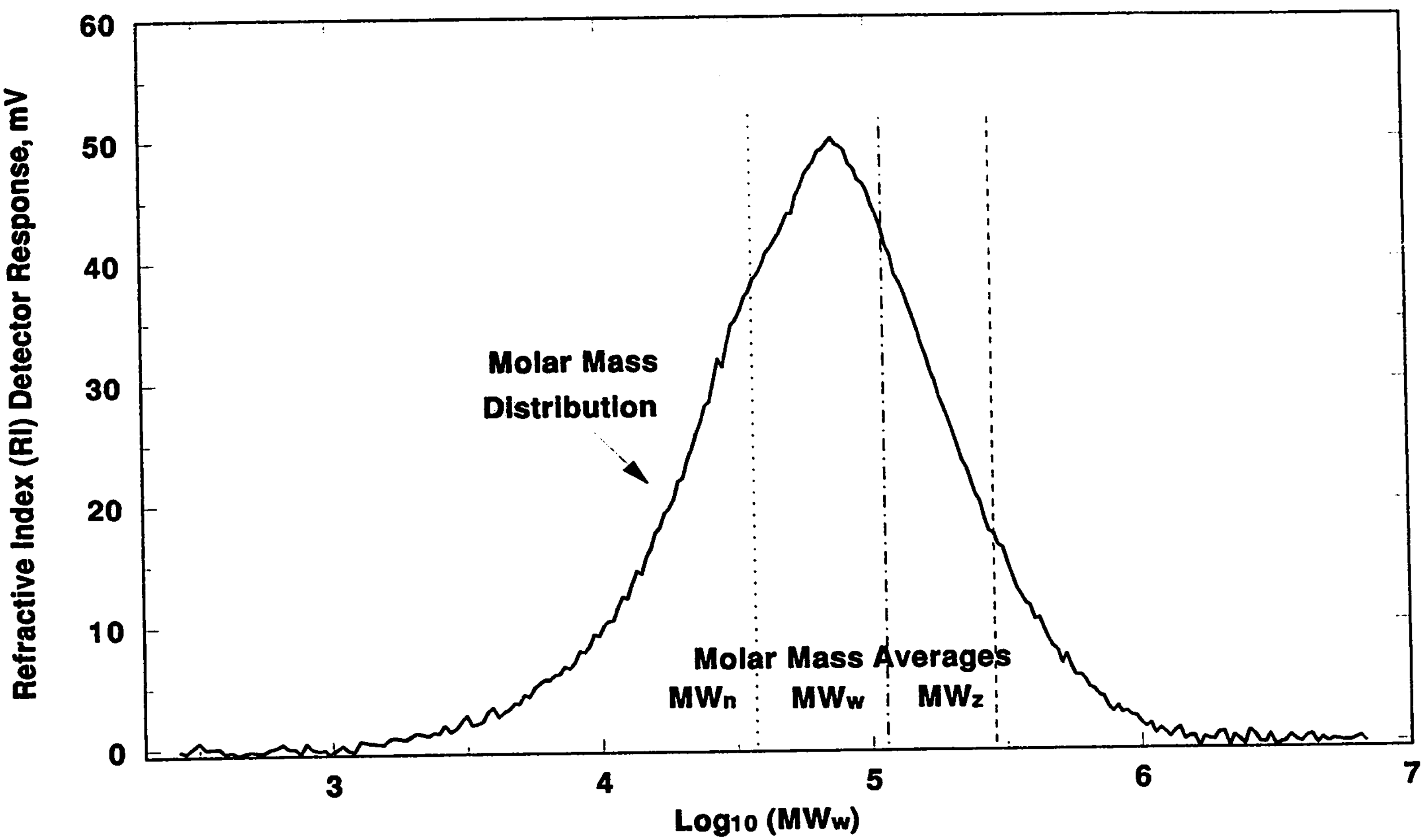


Figure 3.7 : Molar mass distribution and molar mass averages (bulk) derived from the SEC analysis of LLDPE P sample.

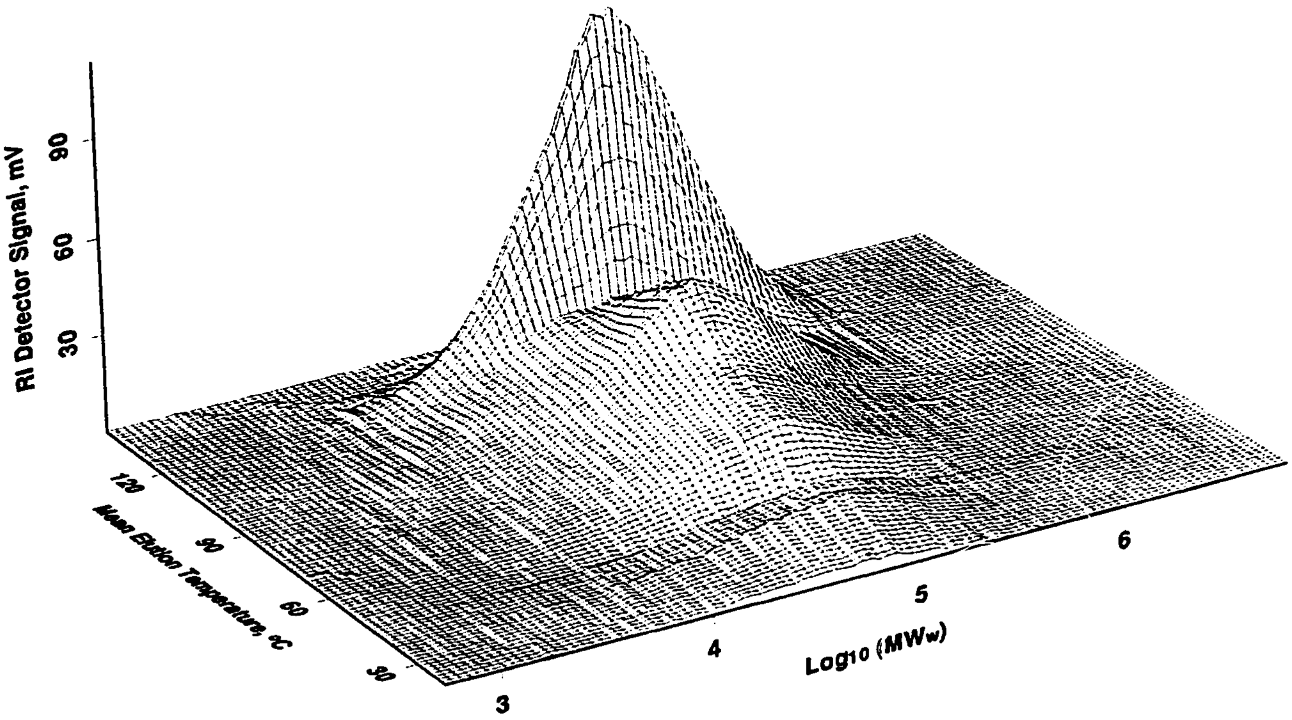


Figure 3.8 : A 3-D plot derived from the cross-fractionation data of laboratory prepared ethylene-propylene copolymer (Product No.: LPLMFI01)

4.0 RESULTS AND DISCUSSION

In Chapter 3, descriptions of the construction of the TREF equipment and the methodology were provided. In this chapter the results obtained by performing analytical and preparative TREF on polyolefin samples is discussed in detail. At the onset, it should be mentioned that the results are not discussed in their chronological order rather they have been separated on the basis of the type of polyolefin being investigated. The results are divided into sections on homopolymers, physical mixtures of homopolymers, commercial copolymers and laboratory prepared polymers. The polymers investigated in this study are described in the Table 4.1.

A cooling rate of 1.5°C/h during crystallization and a heating rate of 2°C/min during elution was used for all of the analytic and preparative TREF results presented in this chapter. Sample sizes of 5 mg of polymer in 5 ml of ortho-DCB for analytical TREF and 20 mg in 20 ml of ortho-DCB for preparative TREF were used. No high pressure excursions occurred, except in one case, during the TREF experiments presented in this chapter. A complete list of TREF experiments, including the preliminary experiments and experiments which encountered rapid pressure increases, is presented in Table A.1 in Appendix A.

4.1 RESULTS WITH HOMOPOLYMERS

Homopolymers are polymers that are synthesized from only one kind of monomer. Various commercial and laboratory-prepared polyolefins of this category were used. Commercial homopolymers studied were LDPE and SRM 1475, and laboratory-prepared homopolymers were LPLPDE07 and GEGEDE09 (see Table 4.1 for detailed description). The laboratory-prepared homopolymers were synthesized by R. R. Santos (to be published).

Table 4.1: Description of polymers characterized by TREF

Polymer Designation	Description of polymer
SRM 1475	A linear polyethylene supplied by the National Bureau of Standards (USA) with little or no short chain branching.
LDPE	Low density polyethylene obtained from Dow Chemicals. This type of polyethylene has high branching content.
LLDPE A LLDPE B LLDPE C	Linear low density polyethylenes, with 1-octene as copolymer, obtained from Dow Chemicals. These polyethylene have similar molar mass averages and distributions.
LLDPE G LLDPE P	Linear low density polyethylenes with 1-butene as copolymer. These copolymers were supplied by Novacor Chemicals.
LLDPE T	Linear low density polyethylene, with 1-hexene as copolymer, supplied by Novacor Chemicals.
LPLMFI01 LPLMFI02 LPGMFE01	Ethylene-propylene copolymer produced in our laboratory using propylene copolymerization catalysts. The copolymer synthesis conditions were different for each case.
GEGEDE09	High density polyethylene prepared in our laboratory.
LPLPDE07	Homopolypropylene prepared in our laboratory.

The objective of performing TREF on homopolymers was to determine the resolving power of the equipment and procedure developed during this study. From the literature reviewed in Chapter 2, it is known that highly branched polyethylenes elute at low temperatures while high density, linear polyethylenes elute at a higher temperature. The SRM 1475 is a high density homopolymer while the LDPE is a highly branched polymer. The TREF profile for SRM 1475, shown in Figure 4.1, has a peak at elution temperatures of 95 to 105^{o}C; this peak is typical of polyethylene with few short chain branches.

The TREF profile for LDPE, shown in Figure 4.2, has a peak in the 50 to 90^{o}C range. Peaks in this range of elution temperatures are due to polymer with low crystallinities (high concentration of chain branches). The broad nature of the peak in Figure 4.2 indicates that the chain branching distribution in the LDPE was broad. Figures 4.1 and 4.2 also show the gauge pressure at the exit of the pump as a function of the elution temperature; these results show that no significant changes in pressure occurred during the elution.

The results, obtained with the polyethylene homopolymers showed that the TREF apparatus, the off-column crystallization and the elution procedure resulted in TREF profiles similar to those reported in the literature (Wild and Ryle, 1977 and Kelusky et al. 1987). The TREF profiles with the polypropylene homopolymers was done to determine whether TREF separates HDPE and isotactic polypropylene. Two laboratory prepared samples, one a homopolyethylene polymer (GEGEDE09) and the other a homopolypropylene polymer (LPLPDE07) with similar molar masses were examined by TREF. The resulting TREF profiles are shown in Figure 4.3. The results in Figure 4.3 show that the maxima in the TREF peaks for the two homopolymers are separated by about 9^{o}C. This separation should be sufficient to obtain distinct peaks in samples which are a mixture of ethylene and propylene homopolymers.

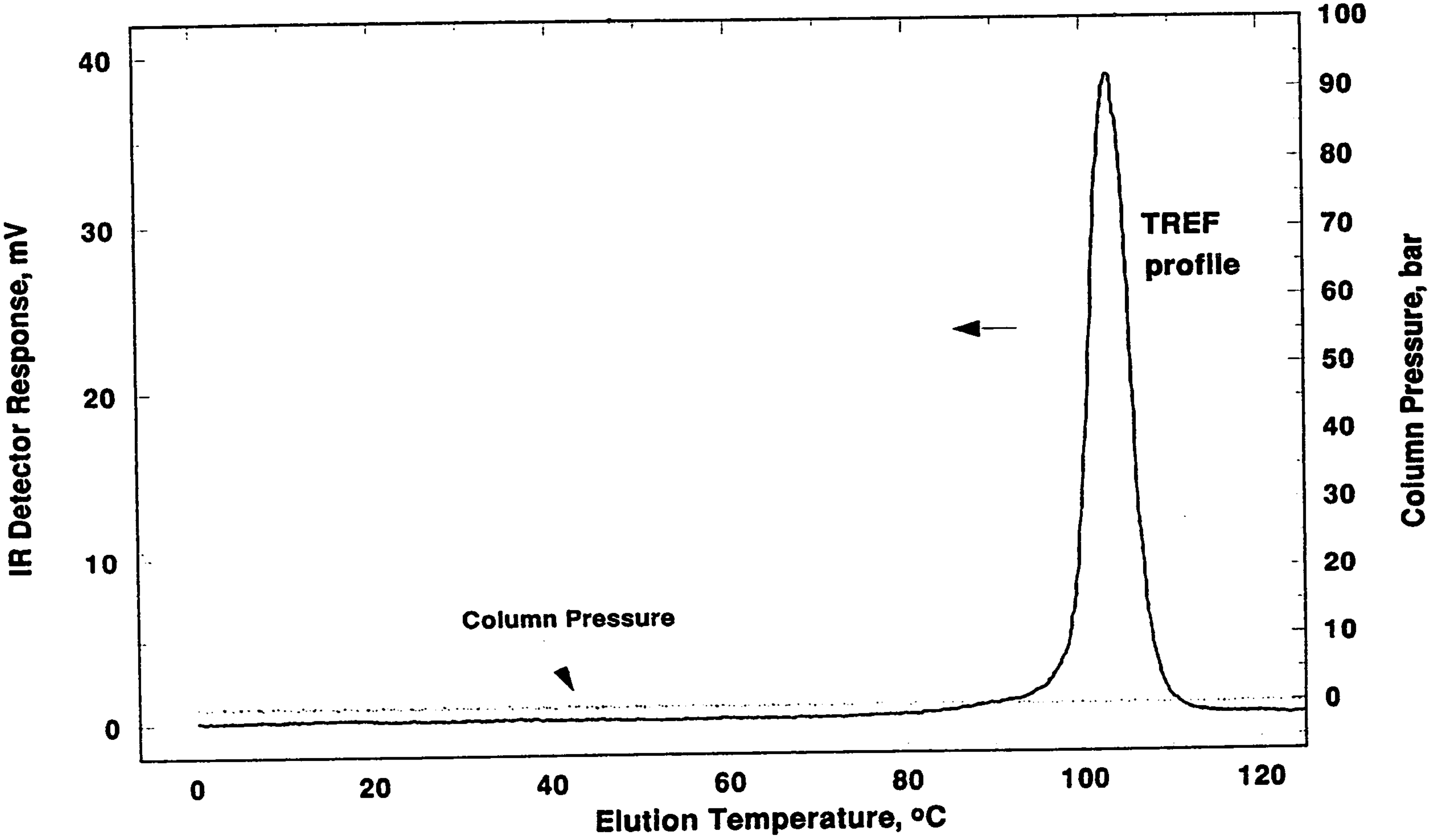


Figure 4.1 : Analytical TREF profile of high density polyethylene (Polymer: SRM 1475; Run No. : E921130D).

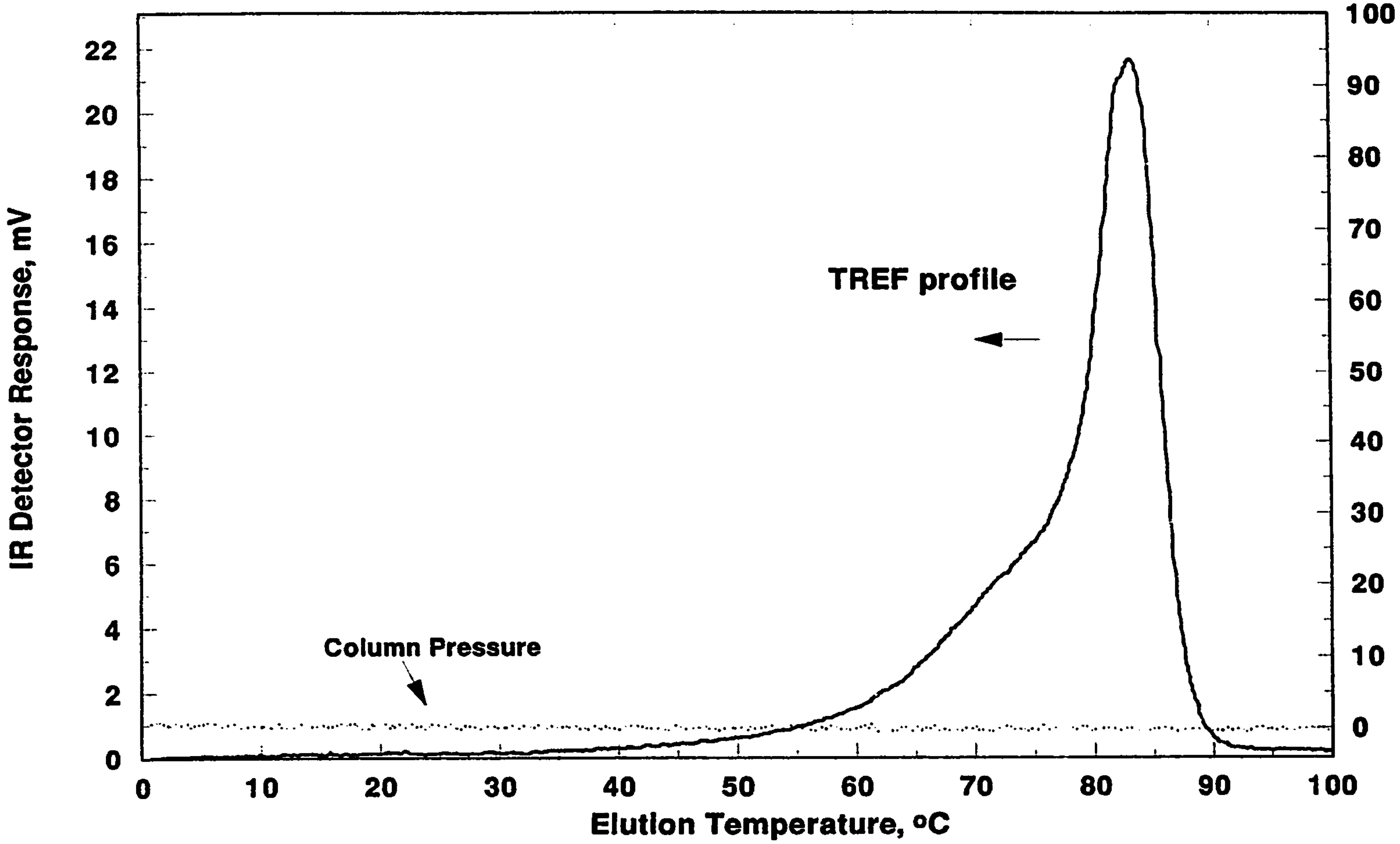


Figure 4.2 : Analytical TREF profile of high pressure low density polyethylene (Polymer: LDPE; Run No. : E930129D).

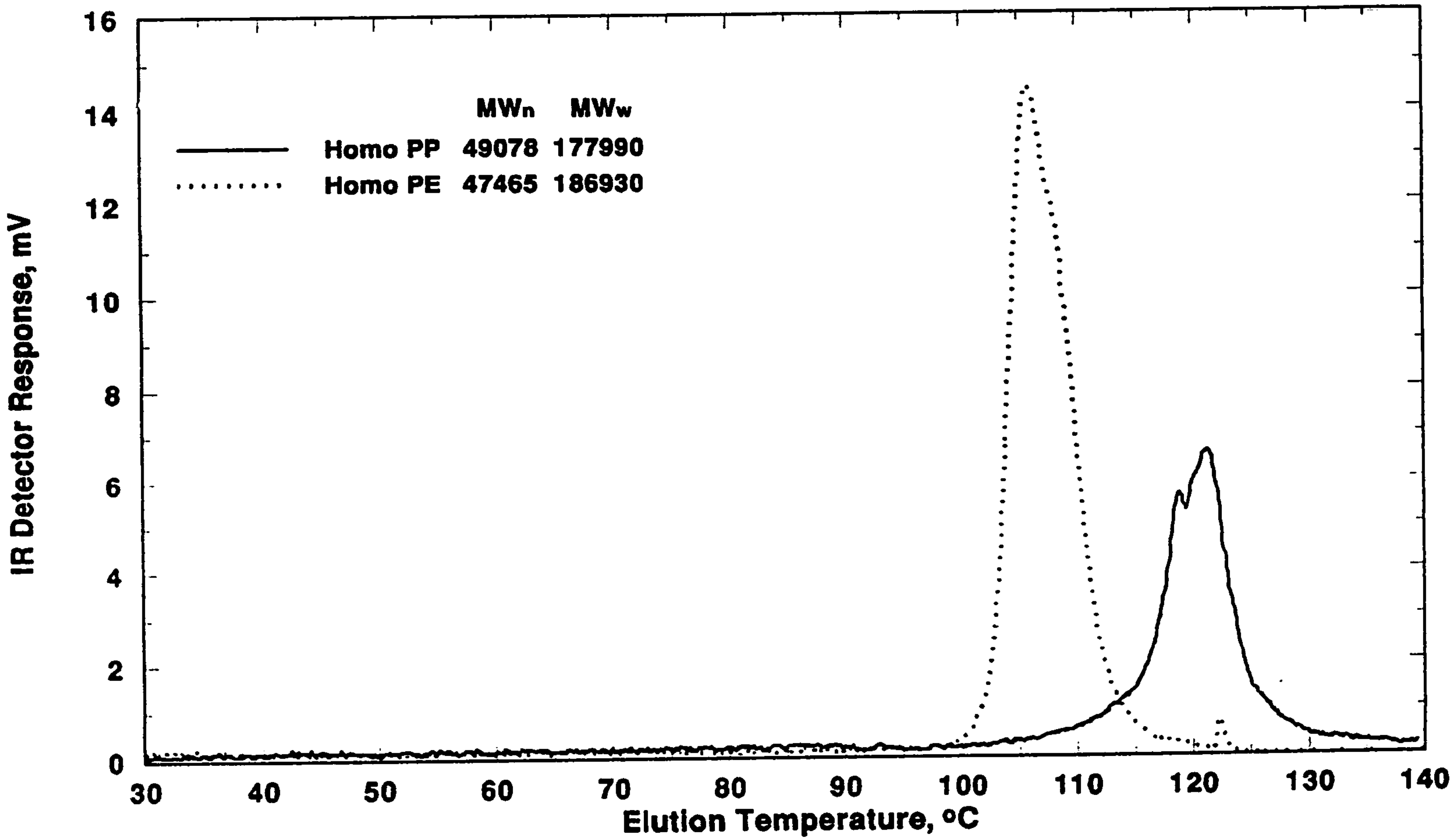


Figure 4.3: Analytical TREF profiles of laboratory-prepared homopolypropylene and homopolyethylene (Polymers: LPLPDE07 and GEGEDE09; run no.: E930508A and E930705A).

Examination of the intensity of the IR signals for the polyethylene and the polypropylene in Figure 4.3 shows that the integrated intensity (area under peak) for polypropylene is approximately one-half of the integrated intensity for the polyethylene even though the amount of sample was the same for both experiments. The reason for the lower IR signal for the polypropylene sample is the choice of IR frequency at which the detector was set. The 3.41 µm band corresponds to the CH_2 asymmetric stretch and polypropylene has about one half as many CH_2 groups as polyethylene; hence, the reduced IR signal for polypropylene.

TREF results with homopolymers have shown that LDPE, HDPE and polypropylene yield TREF peaks with maxima at significantly different elution temperatures; the results for these different homopolymers are shown in Figure 4.4. Physical mixtures of homopolymers were used to establish whether similar separations in elution temperatures occurred if different homopolymers were present in the sample. These results are discussed in the next section.

4.2 RESULTS WITH PHYSICAL MIXTURES OF POLYETHYLENE AND POLYPROPYLENE

To test further the resolution of our TREF facility, analytical and preparative TREF were performed on 1:1 mixtures, by mass, of ethylene and propylene homopolymers (GEGEDE09 and LPLPDE07). Samples of each homopolymers were separately shredded using the previously described cryogenic procedure (see Section 3.2.1). The shredded samples were mixed at a 1:1 mass ratio and analytical and preparative TREF was done on the physical mixtures.

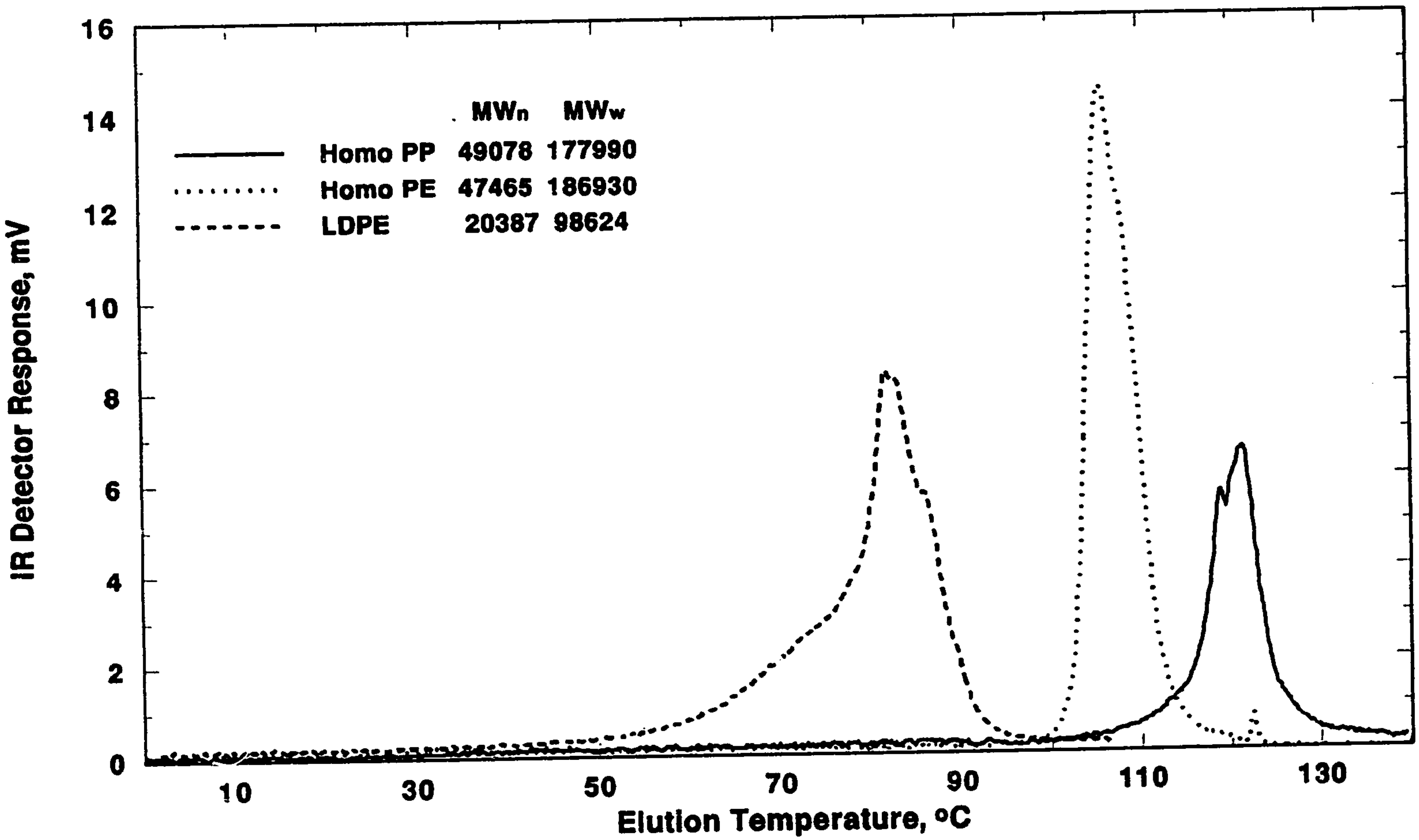


Figure 4.4: Analytical TREF profiles of homopolypropylene and homopolyethylene (Polymers: LPLPDE07, GEGEDE09 and LDPE; Run No.: E930508A, E930705A and E930208A).

The analytical TREF profile for the mixture is shown in Figure 4.5; it can again be noticed that the area under the polyethylene peak (elution temperature of 100 to 110°C) is about twice the area under the polypropylene peaks (elution temperature of 110 to 125°C). Another observation is that the peaks of the homopolymers were narrower for the physical mixture than in the case of individual homopolymers (compare profiles in Figure 4.3 and 4.5). The probable reason for the difference in sharpness of the peaks is the dependence of the resolution on the mass of polymer in each TREF fraction; the amount of PE and PP in the homopolymer samples were double those in the physical mixture.

Comparison of analytical TREF profiles with the preparative TREF profiles demonstrates the fact that resolution decreases with increasing sample size. The preparative TREF profile for the physical mixture of homopolyethylene polymer and homopolypropylene polymer is shown in Figure 4.6. The resolution of the PE and PP peaks in Figure 4.6 is much poorer than the resolution for analytical TREF (Figure 4.5).

Another feature apparent in Figure 4.6 is the occurrence of several small or unresolved peaks. Similar peaks were also noticed in analytical TREF profiles , e.g. the doublet peak in the PP profile in Figure 4.3 and the small peak at 124°C in the profile for the physical mixture (Figure 4.5), but the occurrence of these type of peaks was much less marked in analytical TREF than in preparative TREF. A possible cause of these additional maxima was nonuniform accessibility of the solvent to the crystallized polymer in the column. Additional experimentation, using different solvent flow rates, heating rates and/or column sizes is required to determine the cause(s) of these spurious peaks. However, the PE peak, with a maxima at 105°C, and the polypropylene peak, with a maxima at about 120°C, are clearly separated in Figure 4.6.

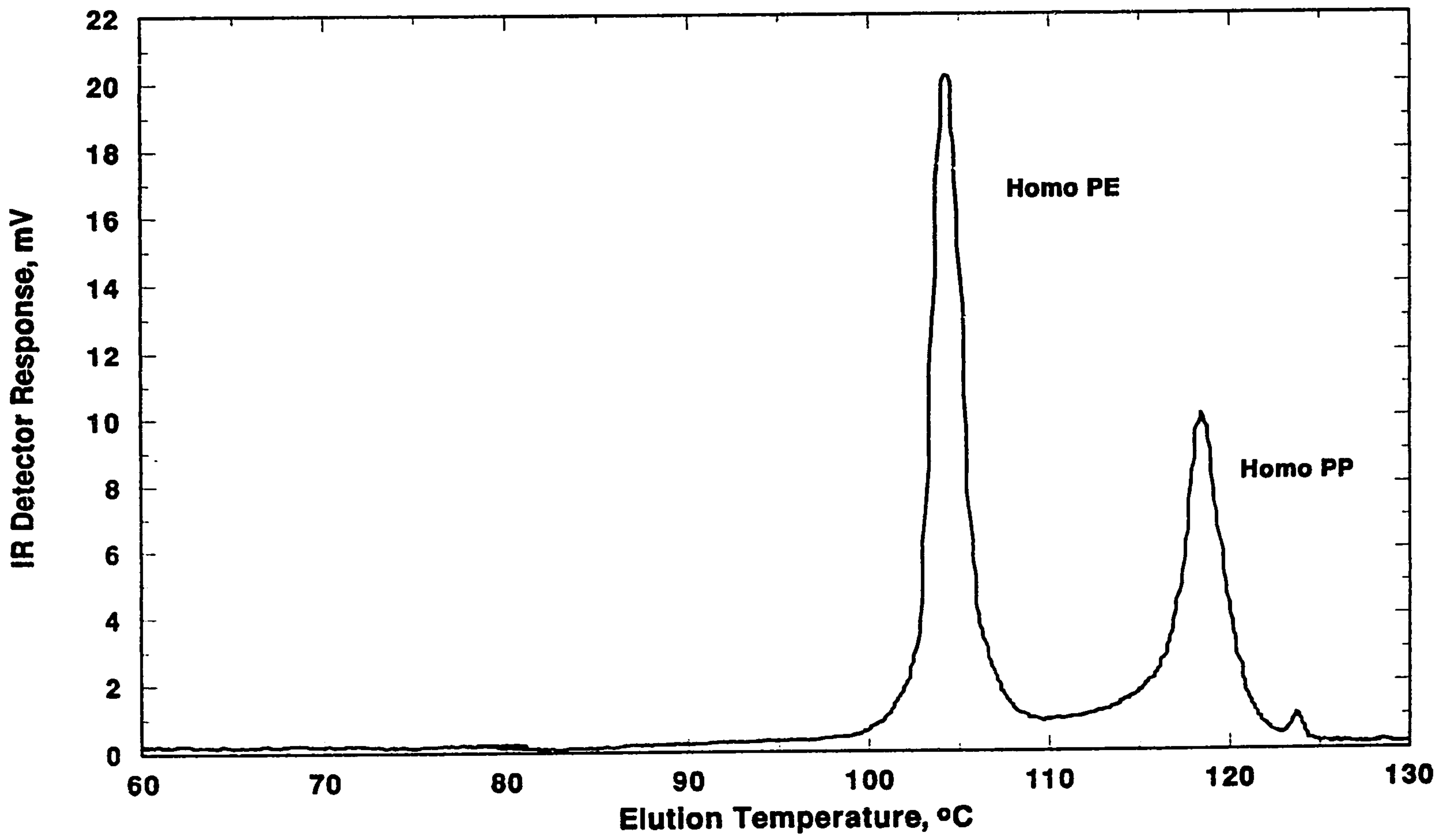


Figure 4.5: Analytical TREF profile of a 1:1 physical mixture of homopolyethylene and homopolypropylene samples (Polymers: GEGEDE09 and LPLPDE07; Run No.: E930713A).

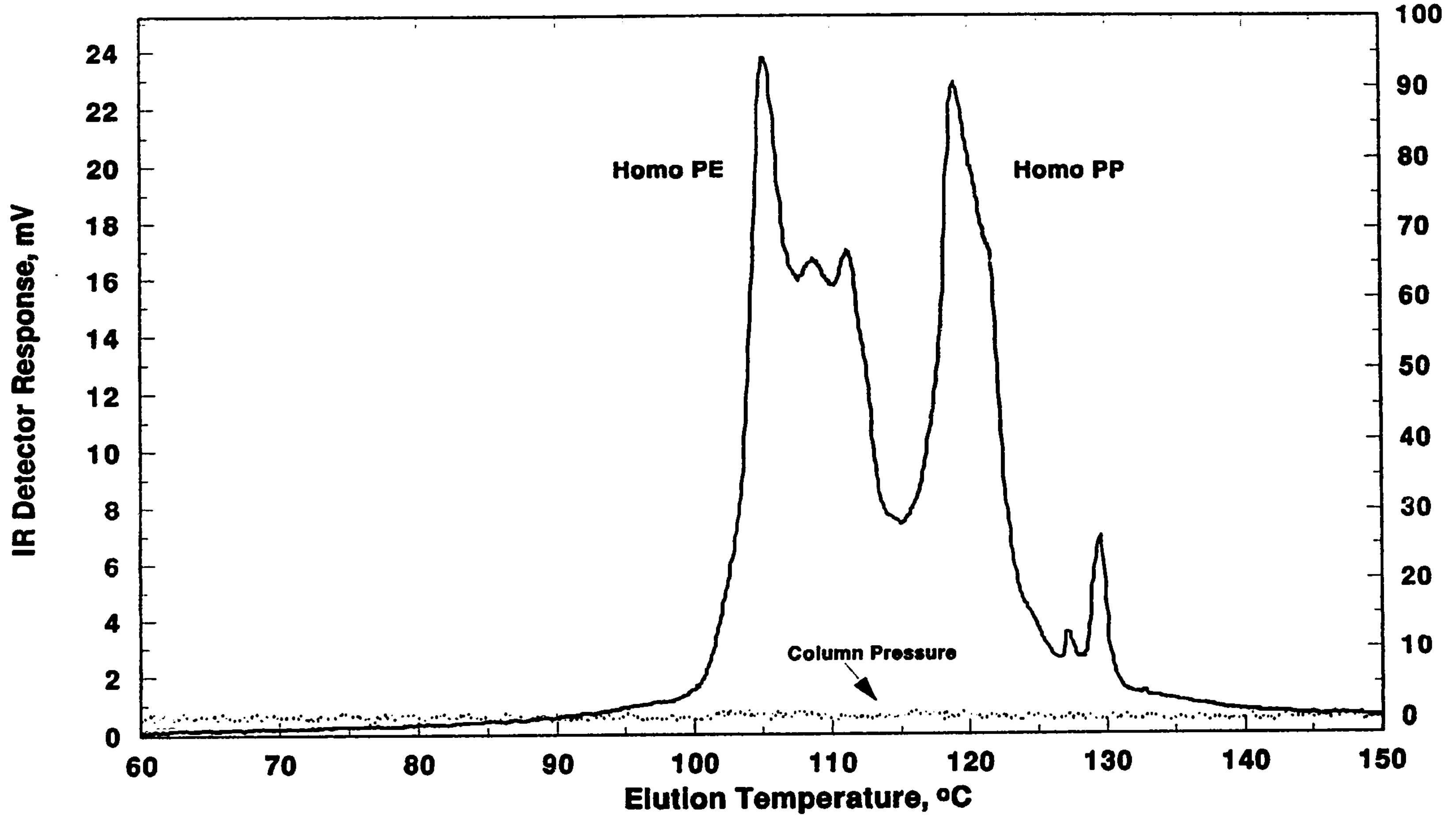


Figure 4.6: Preparative TREF profile of a 1:1 physical mixture of homopolyethylene and homopolypropylene samples (Polymers: GEGEDE09 and LPLPDE07; Run No.: E930516A).

The effluent from the preparative TREF run for the physical mixture was collected as 17 samples; the 17 elution temperature ranges over which these samples were collected were 21 to 31°C, 31 to 41°C, 41 to 53°C, 53 to 63°C, 63 to 73°C, 73 to 83°C, 83 to 90°C, 90 to 95°C, 95 to 100°C, 100 to 105°C, 105 to 110°C, 110 to 115°C, 115 to 120°C, 120 to 126°C, 126 to 131°C, 131 to 140°C, and 140 to 149°C. The molar mass distribution of the polymer in each of these fractions was determined by SEC. The molar mass distribution as a function of elution temperature are plotted in Figure 4.7. This 3-D plots clearly shows the PE and PP peaks which were also apparent in the TREF profile (Figure 4.6).

Another representation of the cross fractionation results is shown in Figure 4.8. Figure 4.7 clearly shows the separation according to crystallinity (elution temperature), while Figure 4.8 show the molar mass distributions of various TREF fractions more clearly. The breadth of the molar mass distribution and the short chain branching distribution are also clearly shown in the 2-D contour plot in Figure 4.9. The contour lines of this figure are lines of equal polymer concentrations; the plot shows that the PE and PP have similar molar mass distributions (similar MW_w and similar polydispersities). This is in agreement with the molar mass distributions of the whole (unfractionated) polymers. The molar mass averages (MW_w and MW_n) and polydispersity for PE were 186930, 47465 and 3.94, whereas, these values for PP were 177990, 49078 and 3.63.

4.3 RESULTS WITH INDUSTRIAL COPOLYMERS

Six commercial samples of ethylene-1-alkene copolymers were analyzed by TREF. Three of these copolymers (LLDPE A, LLDPE B and LLDPE C) were produced by a solution process with 1-octene as the comonomer. These three copolymers had

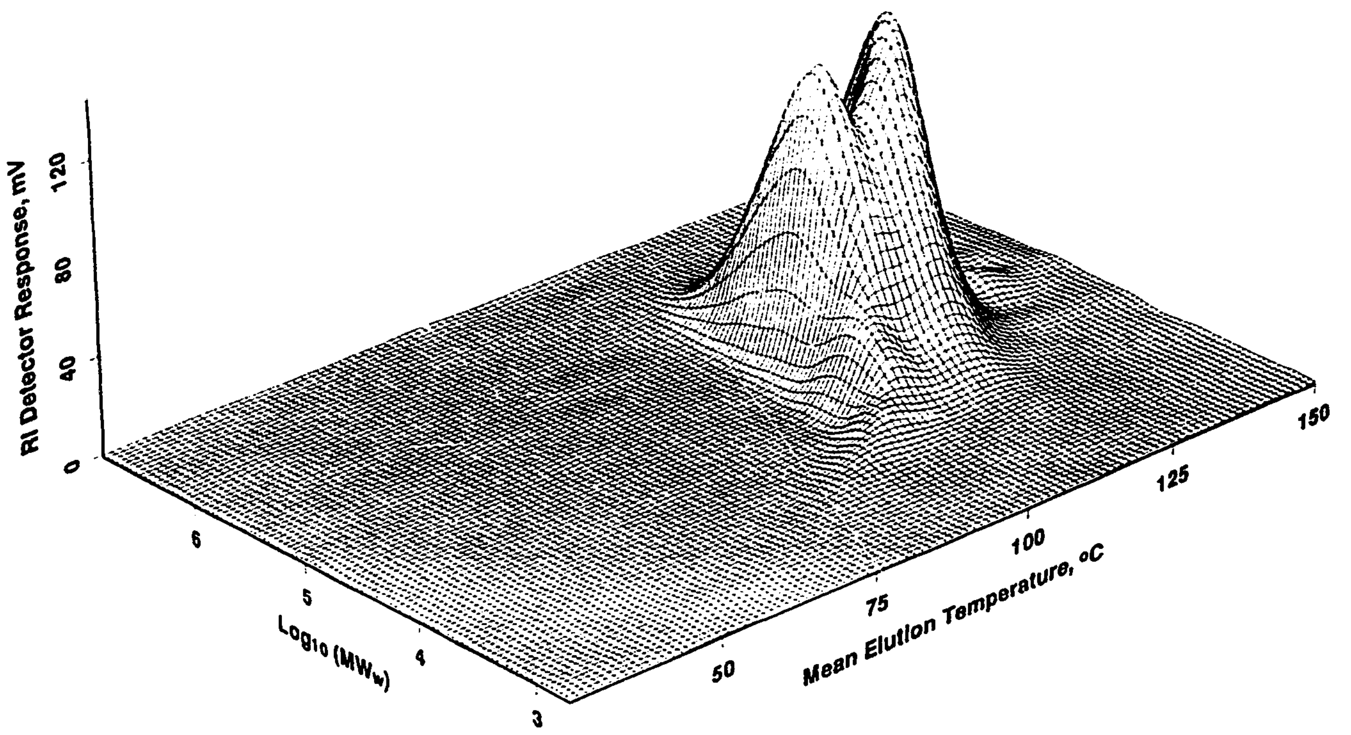


Figure 4.7 : Cross fractionation results for 1:1 physical mixture of ethylene and propylene homopolymers (Front view, polymer: GEGEDE09 and LPLPDE07 mixture; Run No. : E930516A).

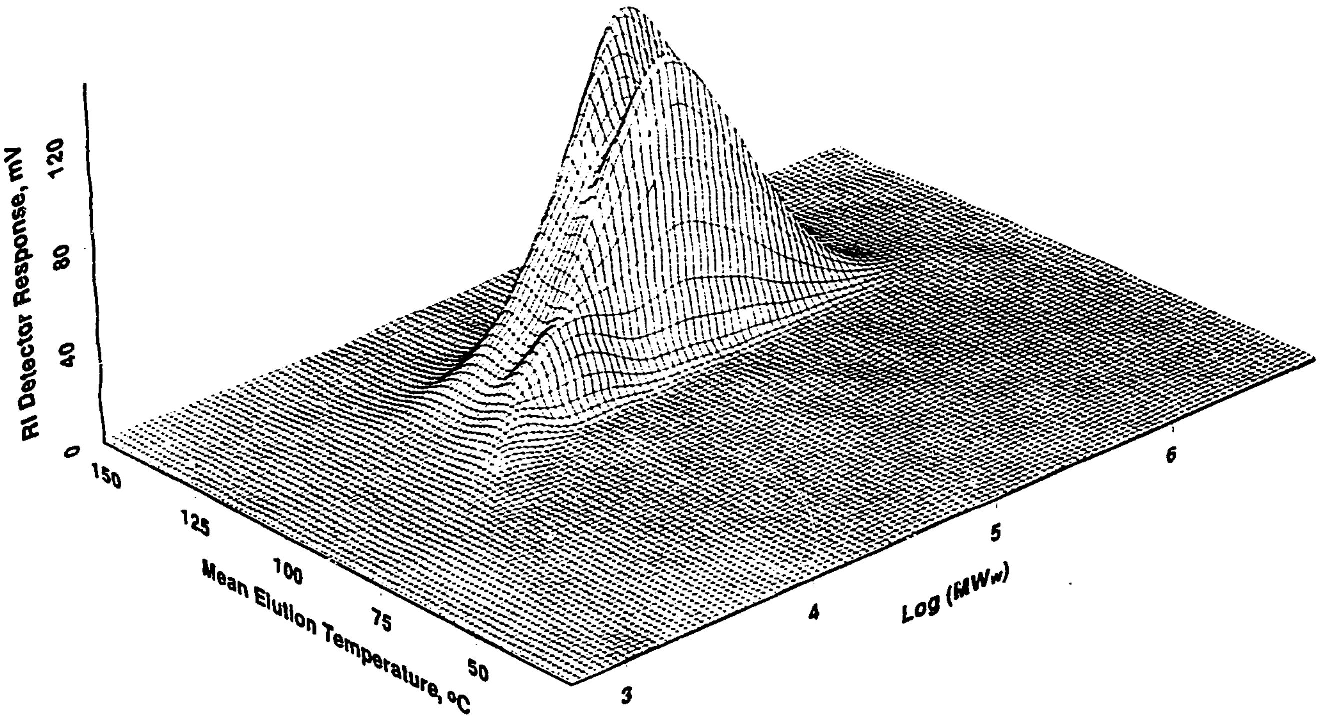


Figure 4.8 : Cross fractionation results for 1:1 physical mixture of ethylene and propylene homopolymers (Side view, polymer: GEGEDE09 and LPLPDE07 mixture; Run No. : E930516A).

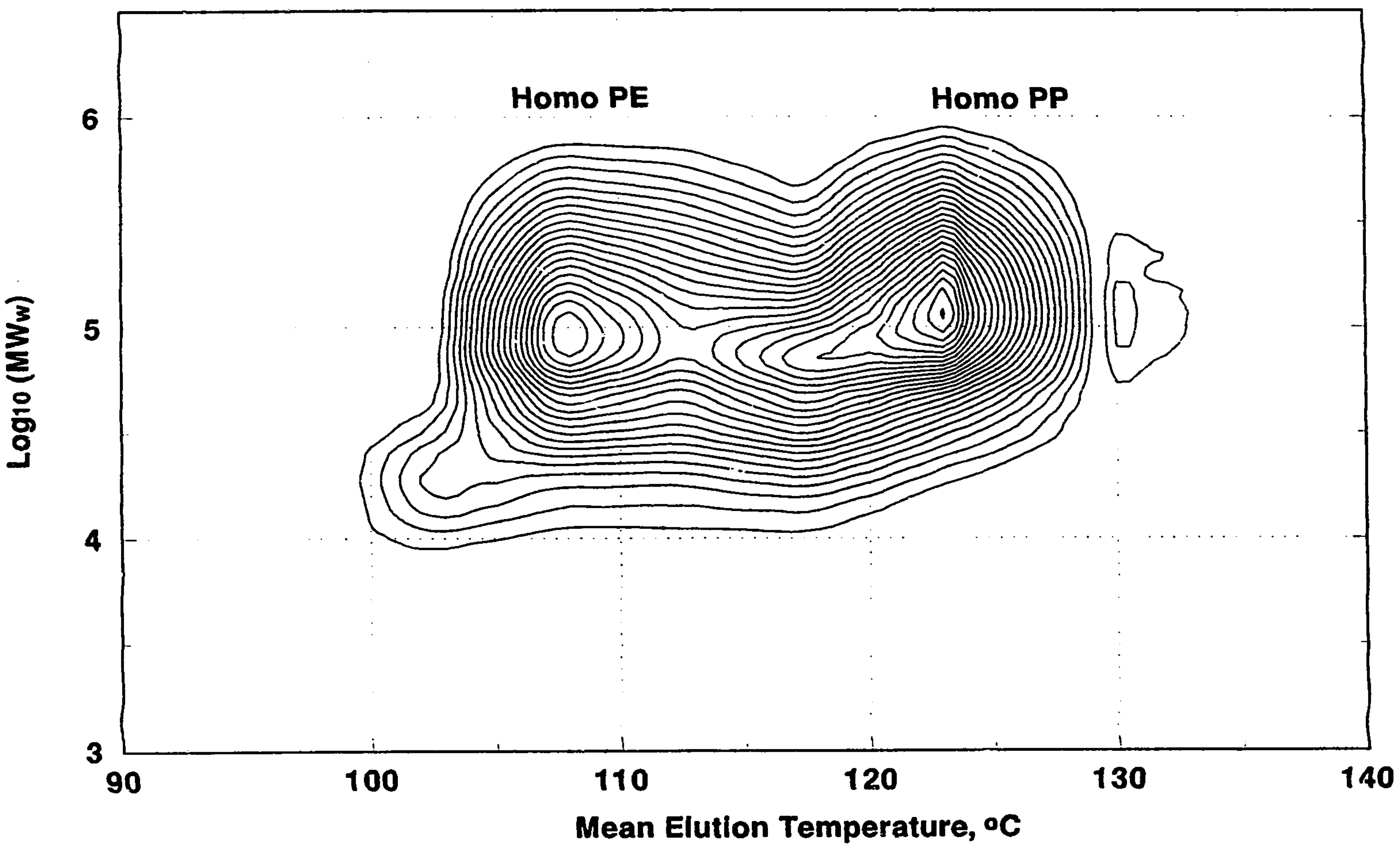


Figure 4.9 : Cross fractionation results of 1:1 physical mixture of ethylene and propylene homopolymers shown as a contour plot with lines of equal polymer concentration (Polymer: GEGEDE09 and LPLPDE07; Run No. : E930516A).

similar molar masses and mass distribution (see Table 4.2). TREF results, using the on-column method of crystallization , have been reported for these samples by Karbashewsky et al. (1991, 1992). The TREF profiles obtained in our study are shown in Figure 4.10, and these profiles are in excellent agreement with the profiles published by Karbashewsky et al. (1991, 1992). This shows that the more convenient off-column method of crystallization used in our study provides reliable TREF profiles.

Table 4.2 : Properties of commercial LLDPEs.

Sample Name	MW_n	MW_w	Polydispersity	Percent High Density
LLDPE A	29598	95640	3.23	30.03
LLDPE B	30058	98987	3.29	23.86
LLDPE C	31035	101915	3.29	29.64
LLDPE G	33087	102118	3.09	26.18
LLDPE P	37220	113326	3.05	25.78
LLDPE T	31274	110495	3.53	31.02

The TREF profiles in Figure 4.10 clearly show the presence of two different types of polyethylene; one type containing significant amounts of SCB (the peak at the lower elution temperature) and another type containing fewer SCB. In Figure 4.11, the TREF profiles for the three copolymers are compared with the previously shown profiles for highly-branched LDPE and the lowly branched HDPE (SRM 1475). An analysis of TREF

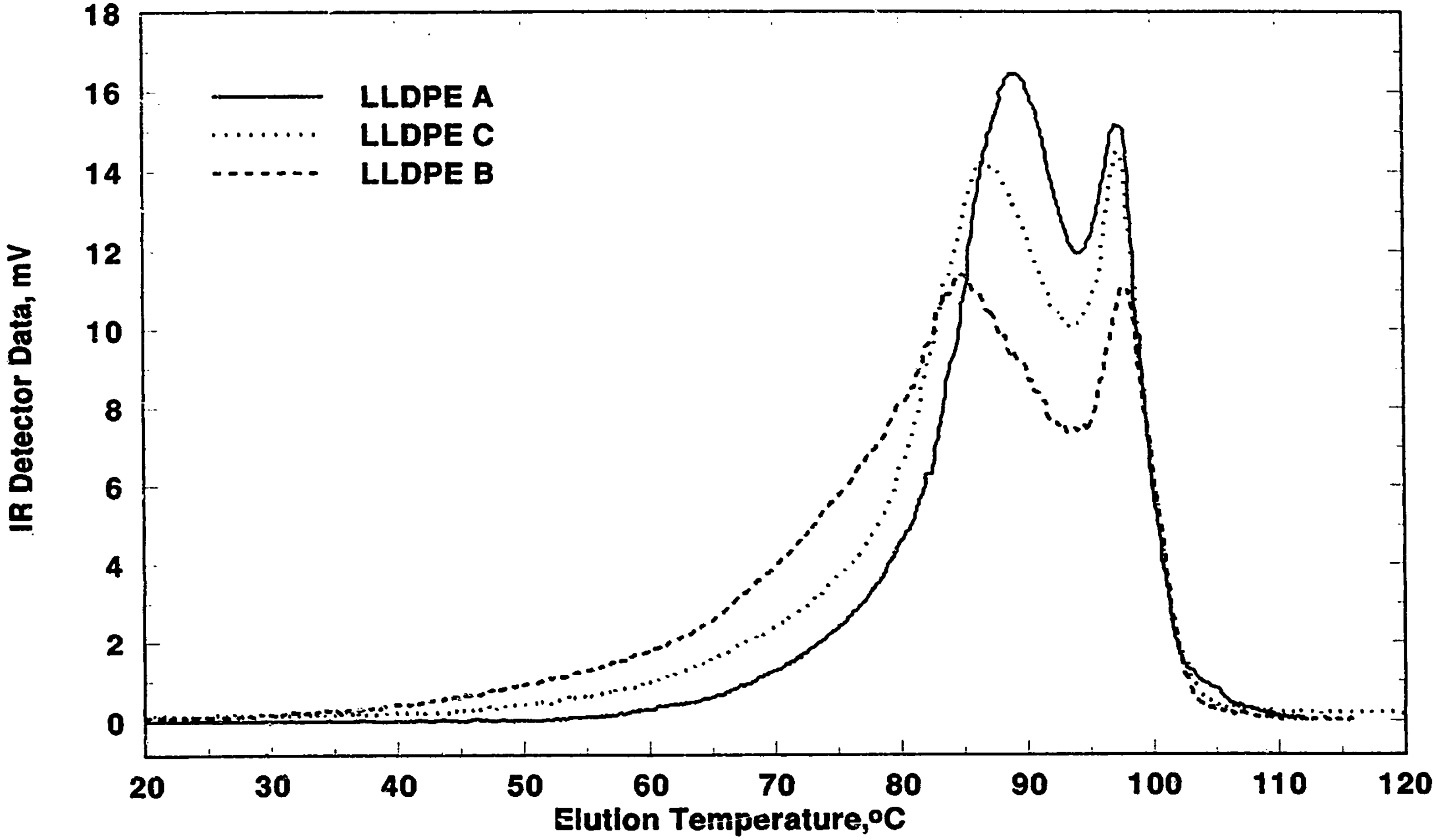


Figure 4.10 : Analytical TREF profiles for three commercial 1-octene LLDPE samples (Polymers: LLDPE A, LLDPE B and LLDPE C; Run Nos. : E921208C, E921209A, E921209D).

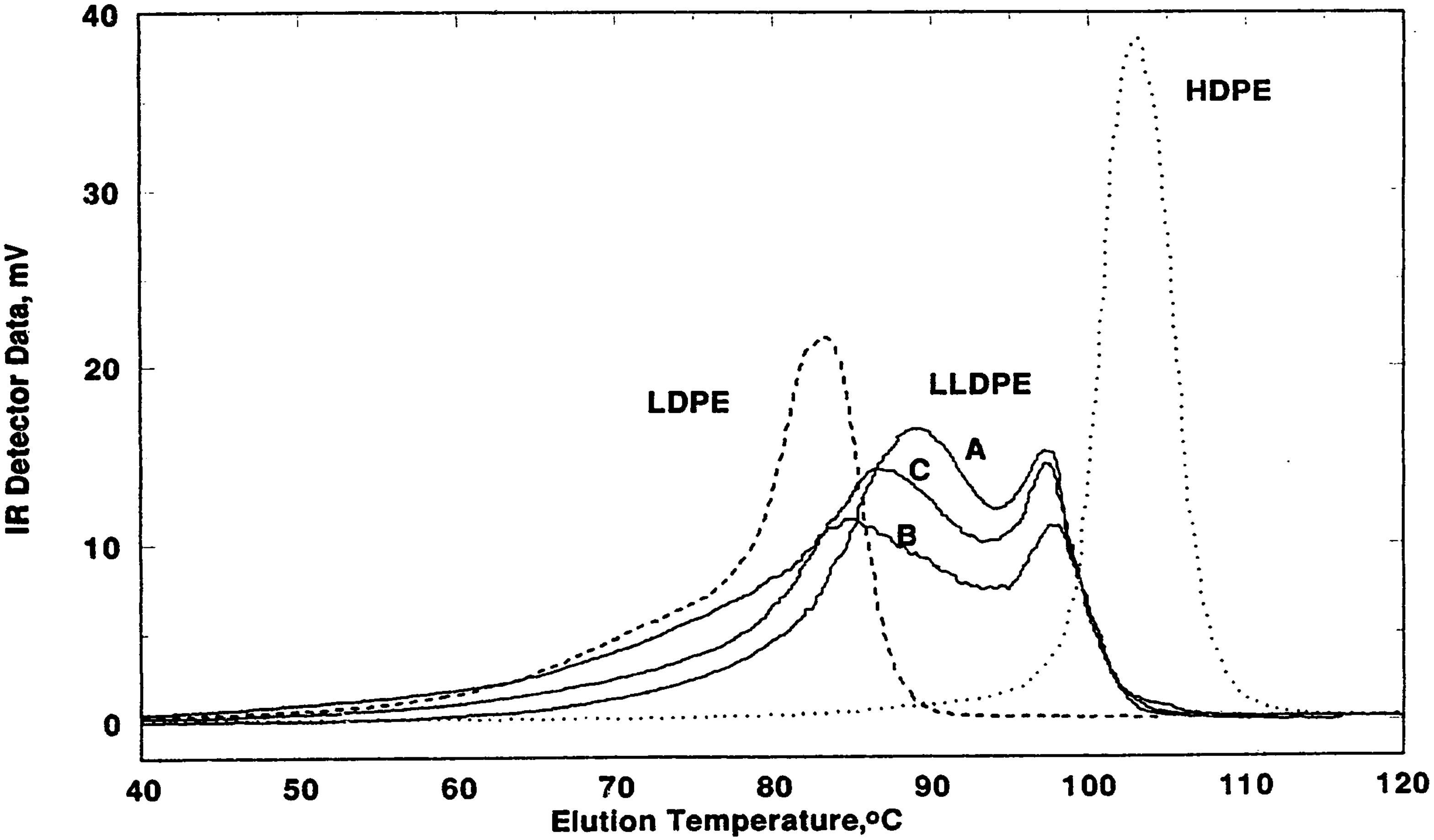


Figure 4.11 : Analytical TREF profiles for LDPE, LLDPE and HDPE samples (Polymers: LDPE, LLDPE A, LLDPE B, LLDPE C and SRM 1475: Run Nos. : E930129D, E921208C, E921209A, E921209D and E921130D).

profiles very similar to the ones shown in Figure 4.9 has been reported by Karbashewsky et al. (1991, 1992).

Sample LLDPE A was also used to determine the reproducibility of the apparatus and procedure developed during this study. A copolymer sample was chosen for determining the reproducibility because TREF is most useful for copolymers. The results of three analytical TREF experiments with LLDPE A are shown in Figure 4.12. These results show that excellent reproducibility was achieved.

The other three commercial copolymers were produced in gas-phase reactors. The comonomer for two of the samples (LLDPE G and LLDPE P) was 1-butene, and 1-hexene was the comonomer for LLDPE T. The TREF profiles of LLDPE G and LLDPE P are shown in Figure 4.13. These profiles show that there are small differences in SCBD in these two polymers; LLDPE P appears to be slightly more crystalline since the elution temperatures are higher for LLDPE P than for LLDPE G. However, the differences are minor.

The TREF profile for LLDPE T (1-hexene copolymer), however, is quite different from the TREF profiles for the 1-butene copolymers. This comparison is shown in Figure 4.14. The most significant difference is the relative size of the two peaks. The percentage of the total area under the TREF profile which is under the high temperature peak of the profile has been referred to as the percentage HDPE in the copolymer (Bibee and Dohrer, 1988). The percentage of the area under the high temperature peak was estimated for all six commercial LLDPE samples by using the PeakFit software for peak deconvolution. The result of these calculations are shown in the last column of Table 4.2. The heterogeneity of the copolymers increases with the increasing amounts of HDPE in the copolymers. According to this critereon, LLDPE T is less homogeneous than the two 1-butene copolymers.

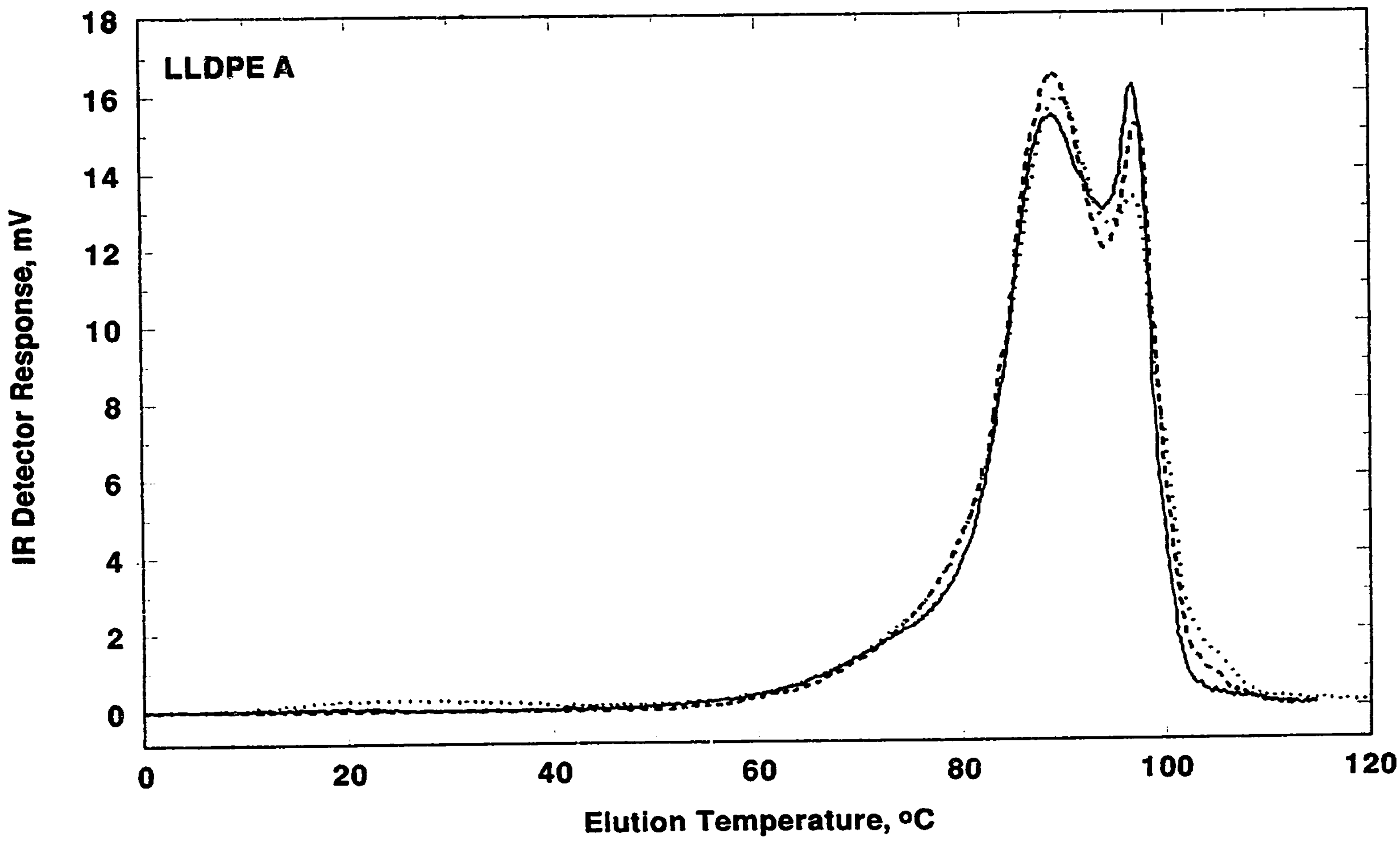


Figure 4.12 : Three analytical TREF profiles for LLDPE showing reproducibility of method (Polymer: LLDPE A; Run Nos. : E921208A, E921208B and E921208C).

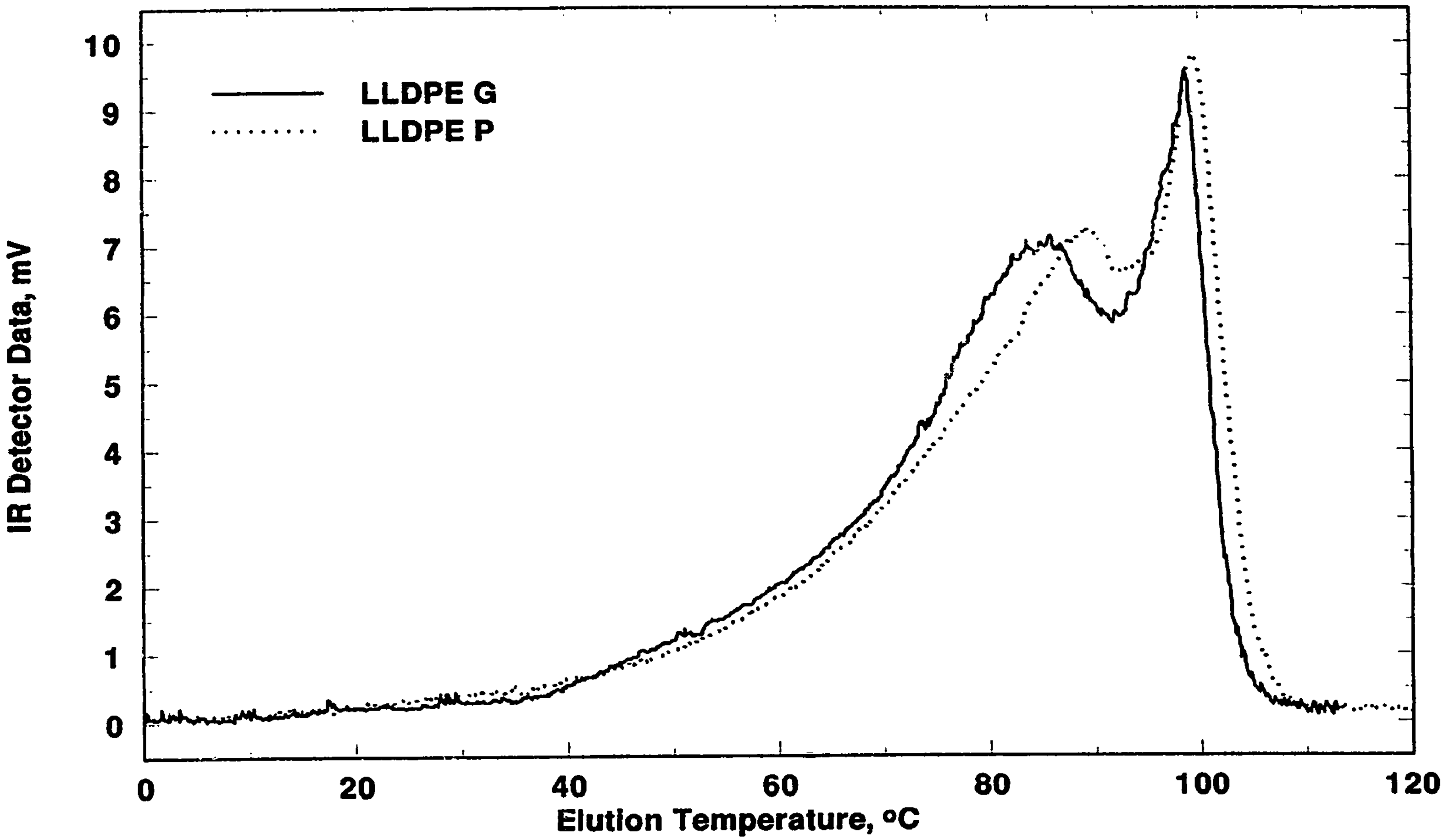


Figure 4.13 : Analytical TREF profile of two commercial 1-butene LLDPE samples (Polymers: LLDPE G and LLDPE P; Run Nos. : E921102A and E921113A).

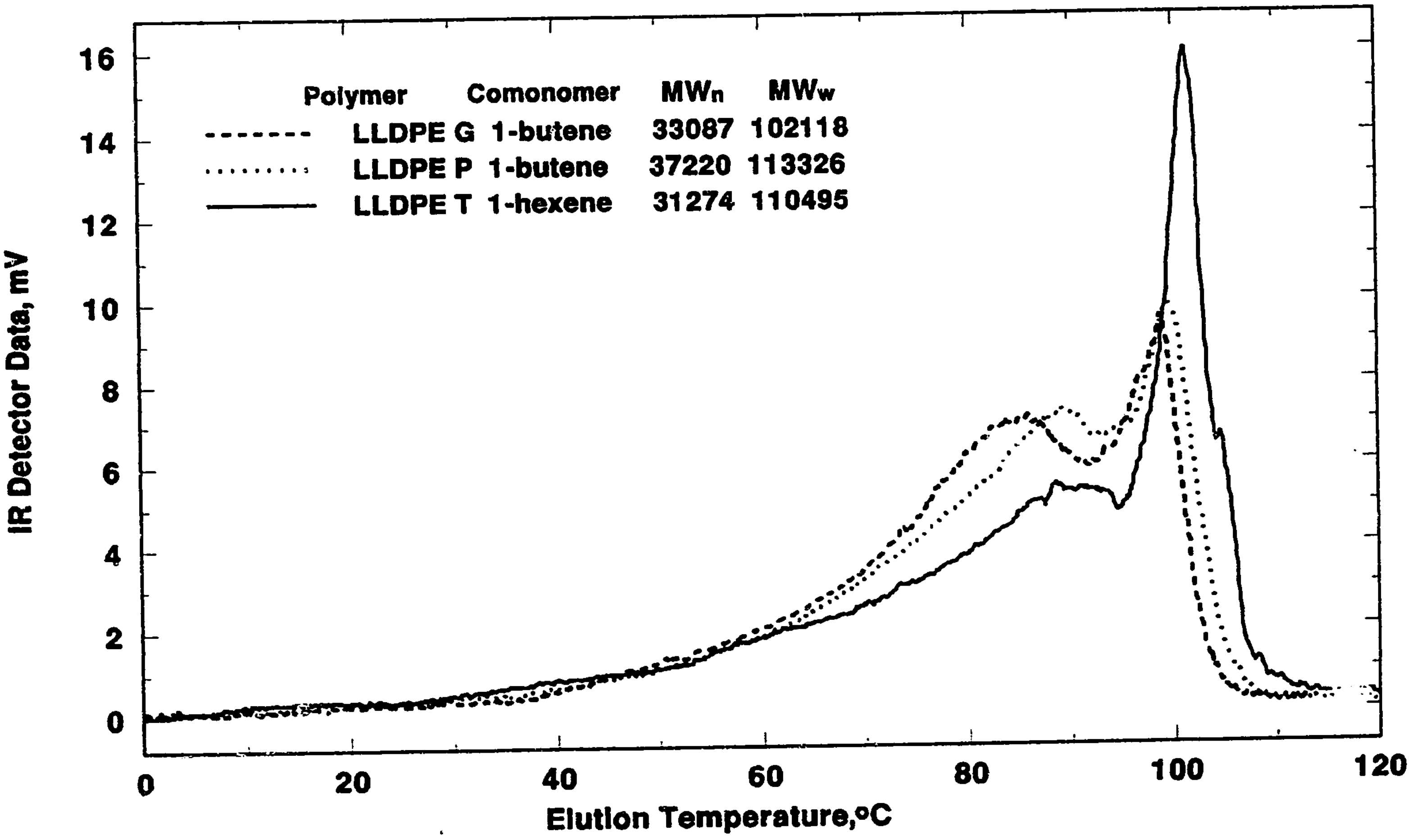


Figure 4.14: Analytical TREF profiles of three commercial LLDPE samples from the same manufacturer (Polymers: LLDPE G, LLDPE P and LLDPE T; Run No.: E921102A, E921113A and E921104D).

Further analysis of LLDPE P and T was done by performing preparative TREF studies on these polymers. For LLDPE P, 15 fractions were collected at the temperature ranges of 19 to 28°C, 28 to 38°C, 38 to 46°C, 46 to 54°C, 54 to 62°C, 62 to 70°C, 70 to 80°C, 80 to 86°C, 86 to 92°C, 92 to 97°C, 97 to 102°C, 102 to 108°C, 108 to 116°C and 116 to 125°C. For LLDPE T, 9 fractions were collected at the temperature ranges of 25 to 35°C, 35 to 45°C, 45 to 57°C, 57 to 70°C, 70 to 82°C, 82 to 94°C, 94 to 106°C, 106 to 118°C and 118 to 130°C. These fractions were subsequently analyzed by SEC. The molar mass distribution of each fraction along with the corresponding mean elution temperature of the fraction are plotted on 3-D plots. Two perspectives are given for each sample; Figure 4.15 and 4.16 for sample LLDPE P and Figure 4.17 and 4.18 for sample LLDPE T.

Figure 4.15 shows that LLDPE P has a broad short chain branching distribution (large range of elution temperatures). Figure 4.16 shows that the fractions containing more SCB (low elution temperature) have lower molar masses. A more quantitative representation of molar masses and polydispersity as a function of TREF fraction is shown in Figure 4.19. The molar masses and the polydispersity (MW_w/MW_n) of each fraction are plotted along with the TREF profile. As described in Chapter 3, under preparative TREF procedures, our method also yields a TREF profile while performing preparative TREF. The comparison of the TREF profiles obtained during the preparative TREF with those obtained during analytical TREF (see Figure 4.17) shows that the larger samples used in preparative TREF reduced the resolution of the TREF profile.

The results in Figure 4.19 show that for both LLDPE P and LLDPE T, the molar masses increased with increased elution temperature. The polydispersity on the other hand, generally underwent a gradual reduction. The results for the fractions with elution temperature below 50°C are not very reliable because the concentration of polymer in these fractions was very low. Hence, preparative TREF shows that the higher temperature

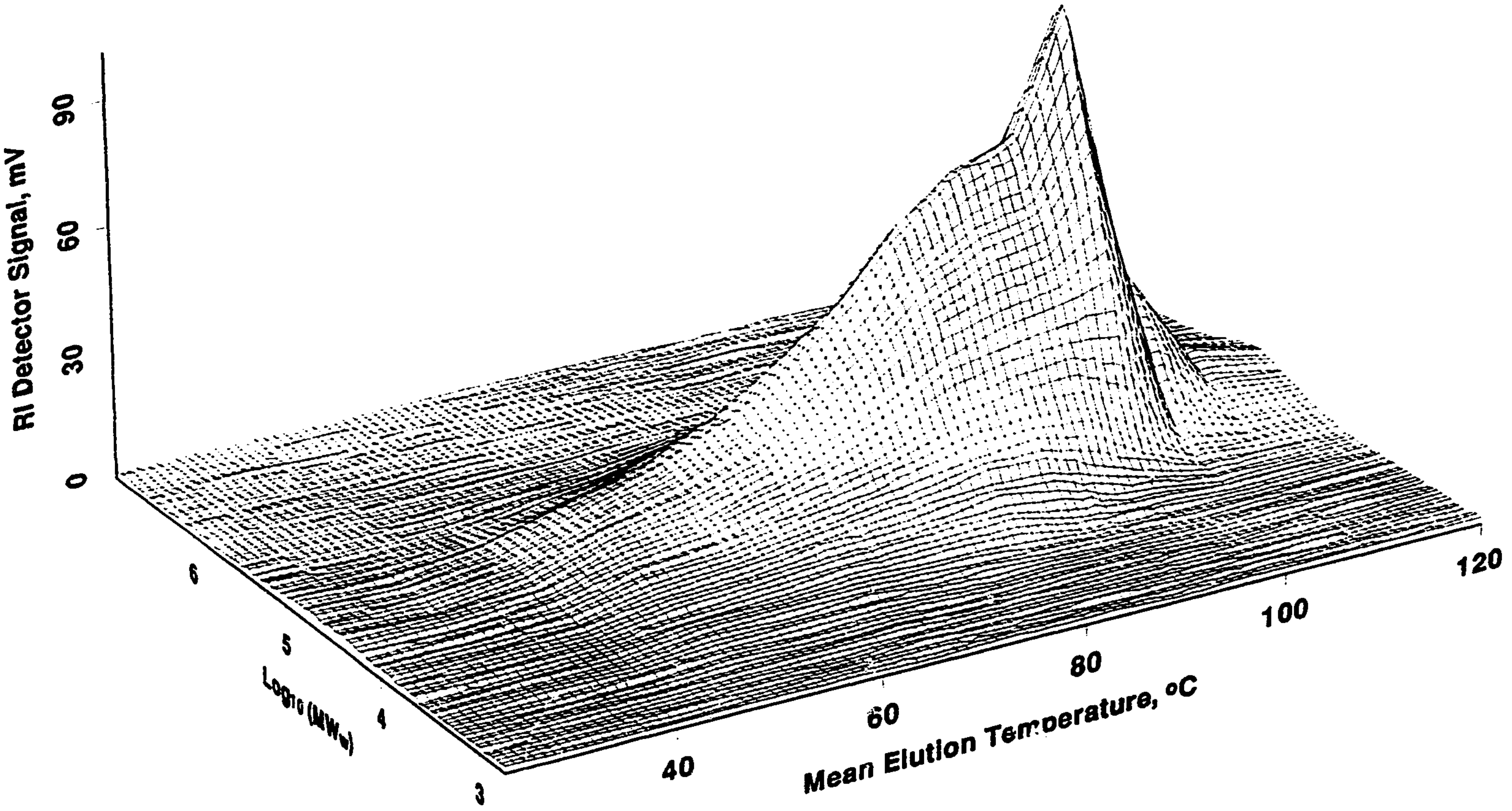


Figure 4.15 : Cross-fractionation results for LLDPE P (front view).

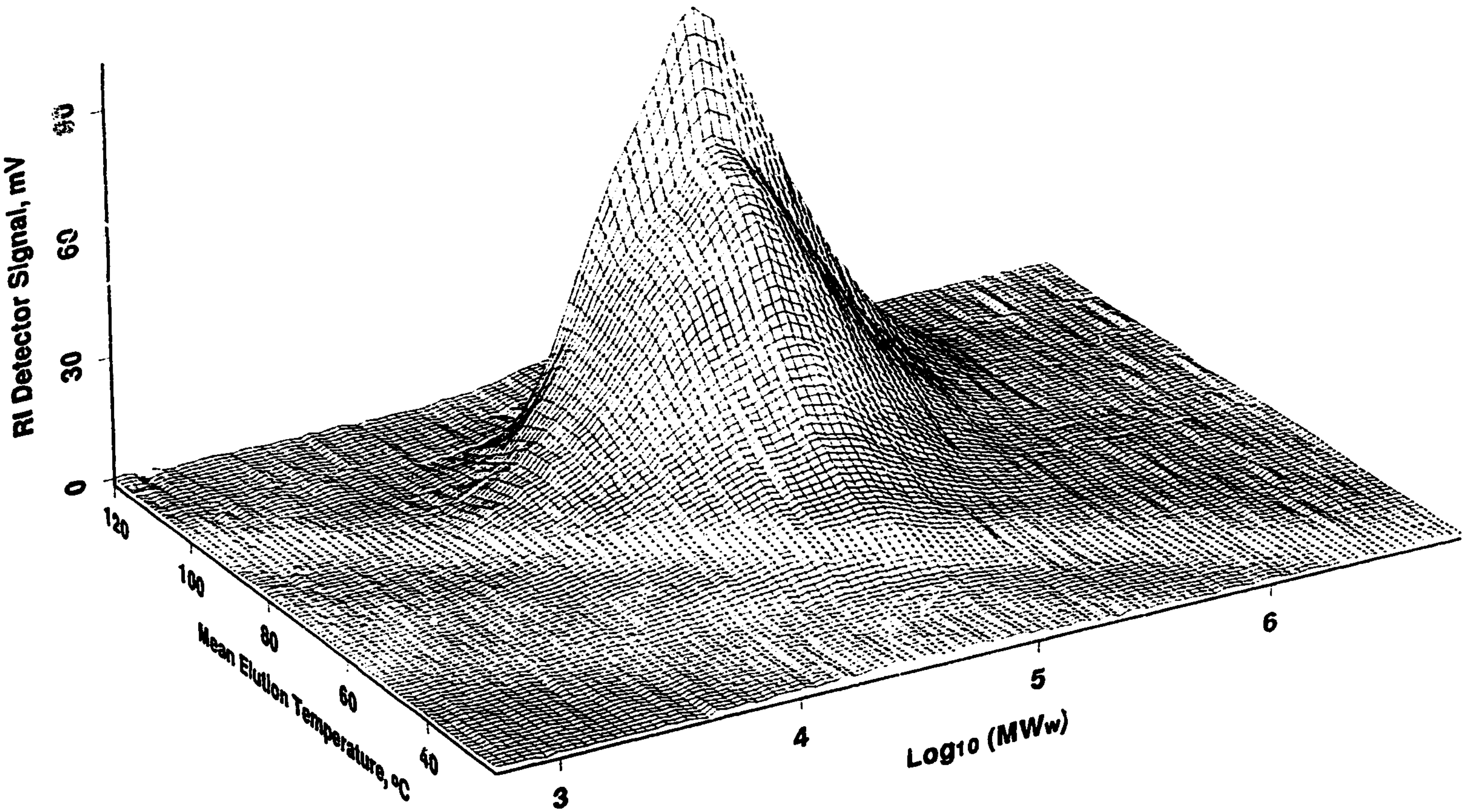


Figure 4.16 : Cross-[illegible] results for LLDPE P (side view).

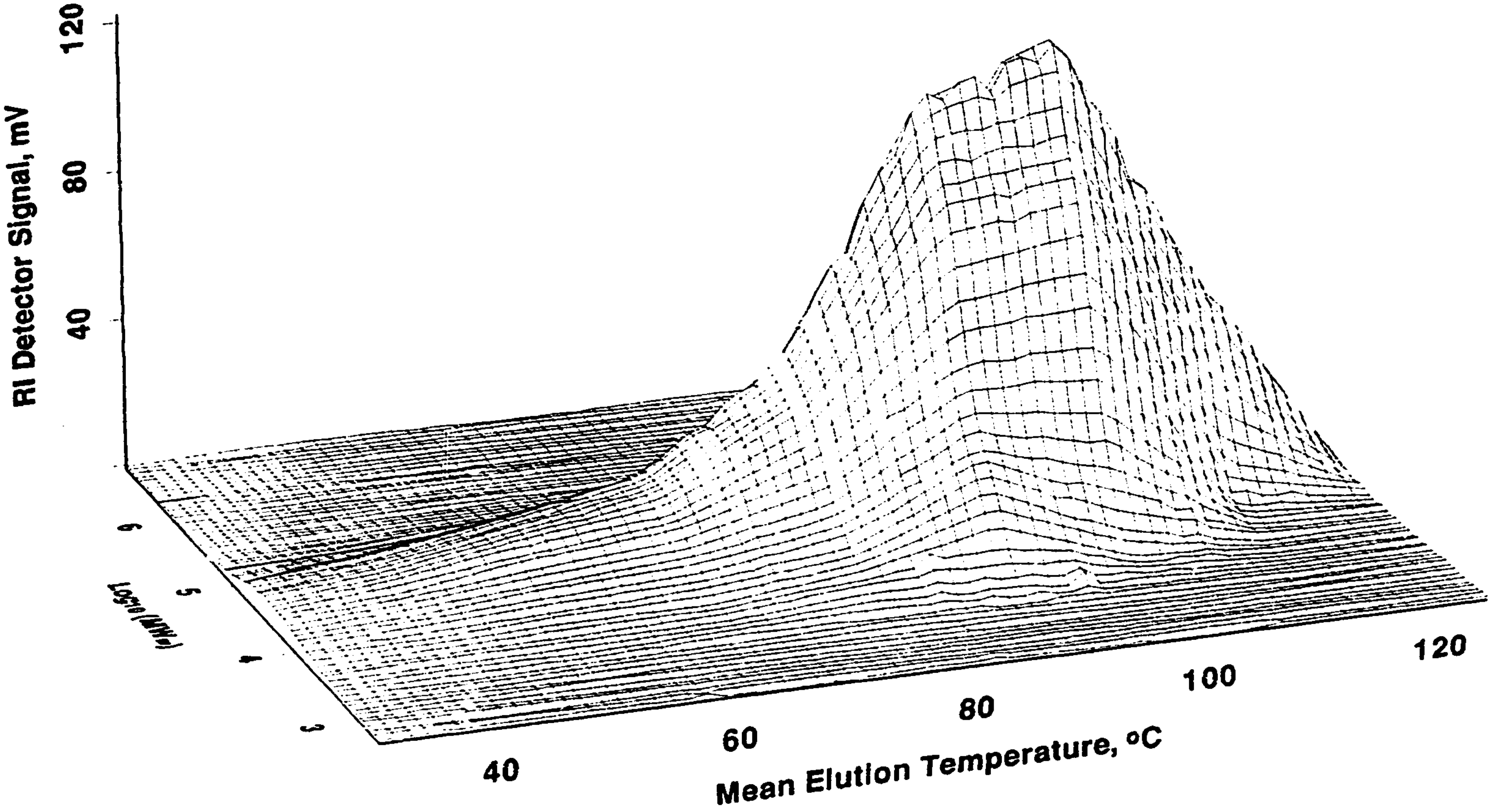


Figure 4.17 : Cross-fractionation results for LLDPE T (front view).

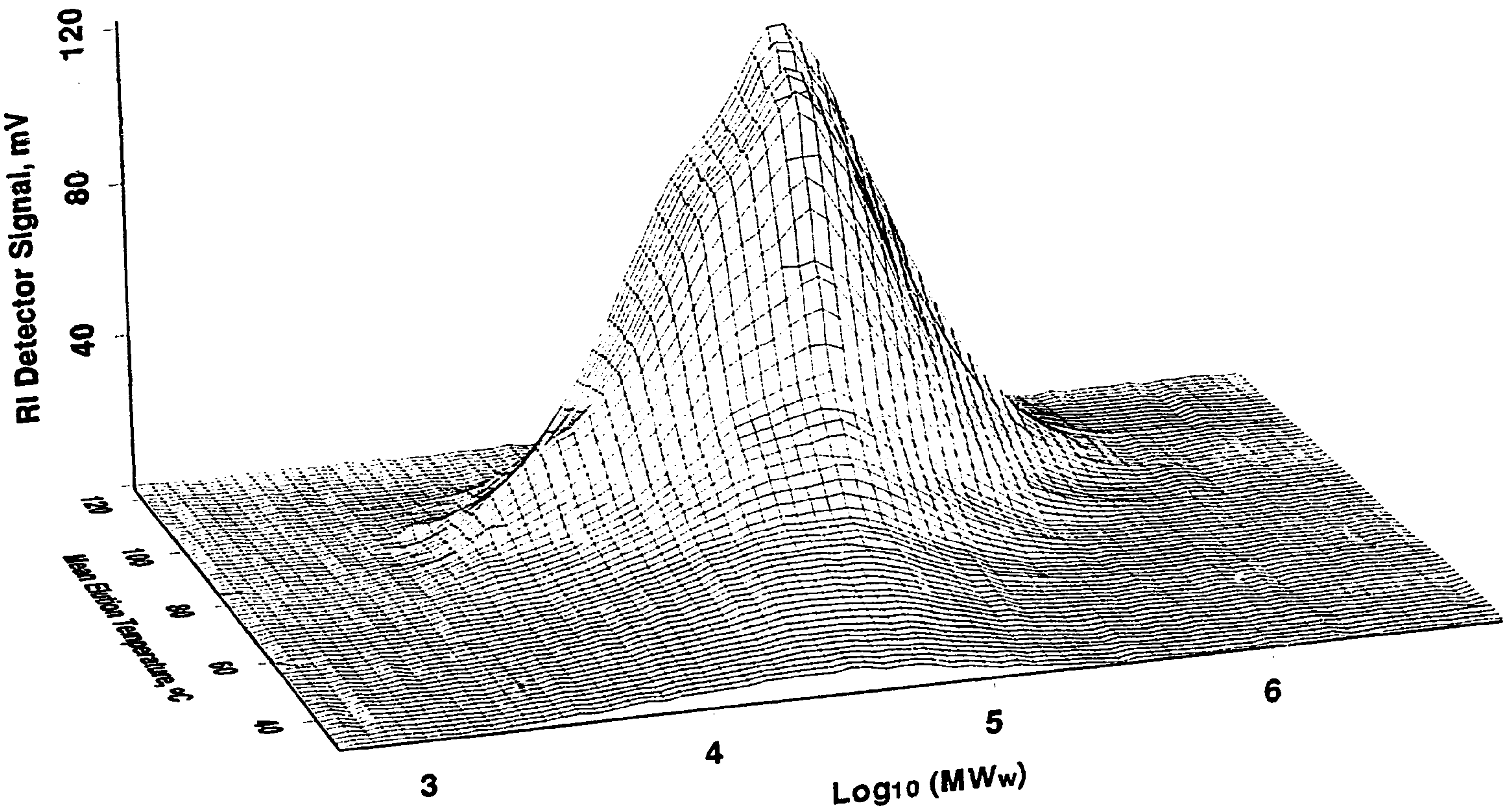
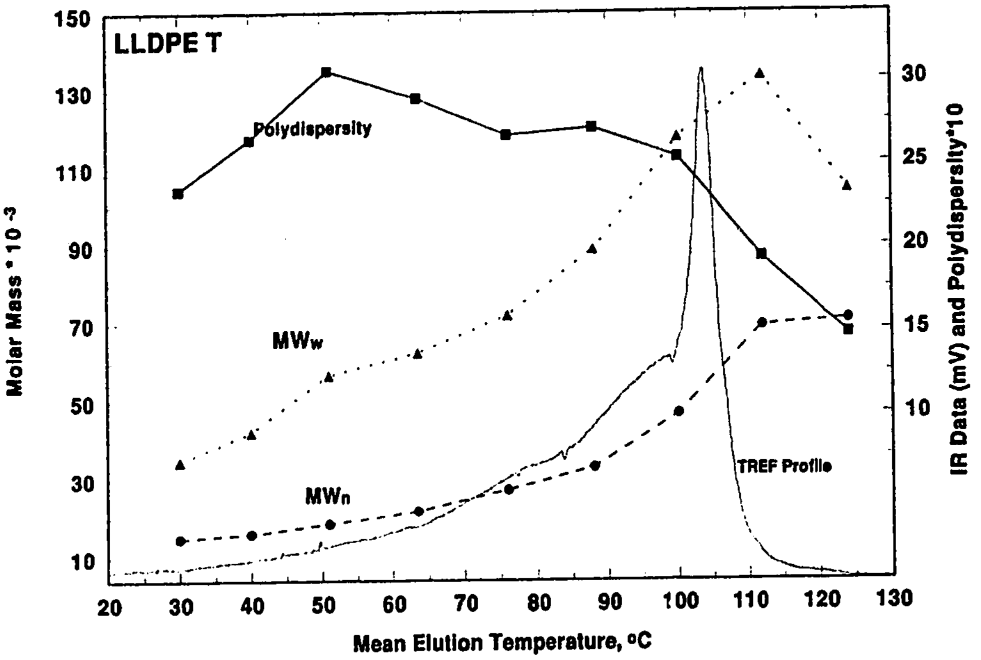


Figure 4.18 : Cross-fractionation results for LLDPE I (side view).



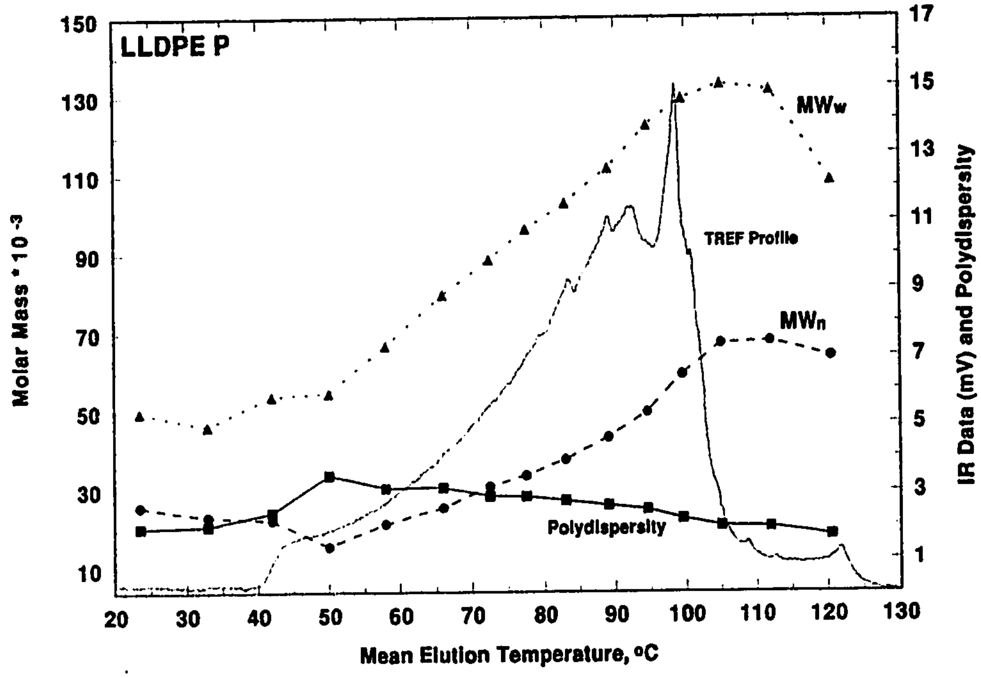


Figure 4.19 : Variation in molar masses and polydispersity of preparative TREF fractions for LLDPE T and LLDPE P.

fractions (i.e. lower side chain branching level) have narrower molar mass distributions. Similar trends of increasing molar masses and decreasing polydispersity were observed previously (Schouterden et al., 1987) with 1-octene LLDPE fractions obtained by a different fractionation technique called successive solvent fractionation (SSF).

The cross fractionation plots for LLDPE T in Figures 4.17 and 4.18 are similar to those for LLDPE P. Again, a distinct trend to higher molar masses with rising elution temperatures was observed for LLDPE T. This is clearly evident in Figure 4.19.

The results with the commercial resins showed that our system and procedure not only gave reproducible TREF profiles, but the profiles agree well with those in the literature for similar resins. The cross fractionation results showed how additional information on the molecular structure (chain branching and molar masses) can be obtained by this technique.

4.4 RESULTS WITH THE LABORATORY PREPARED COPOLYMERS

The department of Chemical Engineering at the University of Alberta has a polymerization laboratory where studies on polyolefin synthesis and characterization are in progress. While pursuing developmental work in TREF, some of the polyolefins synthesized in this laboratory were characterized by TREF and cross fractionation. All the polymers were synthesized by R. R. Santos and the procedures used for their synthesis will be described in the thesis of Santos (1994). The polymers examined included the already described homopolymers GEGEDE09 and LPLPDE07 as well as three ethylene-propylene copolymers (LPLMFI01, LPLMFI02 and LPGMFE01). The objective of the analysis on the last three polymers was to determine the effects of reactor operating conditions on polymer structure.

Analytical TREF profiles of LPLMFI01 and LPLMFI02 are plotted in Figure 4.20. It is readily apparent that these two polymers have significantly different TREF profiles.

The single, relatively sharp, TREF peak at 110°C for LPLMFI02 indicates that this sample consists largely of a crystalline homopolymer, probably homopolypropylene, since the TREF peak for LPLMFI02 is very similar to the TREF peak obtained with LPLPDE07 (see Figure 4.3). It appears that little or no copolymer was produced during the synthesis of LPLMFI02. The broad peak at elution temperatures of 0 to 100°C in the TREF profile of LPLMFI01 clearly shows the presence of noncrystalline copolymer. The high temperature peak for LPLMFI01 is probably isotactic polypropylene since this peak is similar to the one obtained for LPLPDE07 (see Figure 4.3). Hence, TREF was useful in providing information on the molecular structure of the polymer which is not readily available by other techniques.

Two TREF determinations were done on sample LPLMFI01 to check the reproducibility of the procedure on laboratory-prepared copolymer. These results are shown in Figure 4.21. A leak developed in the pump during Run E930209A which caused air bubbles to be introduced in the solvent, and these air bubbles caused the spikes in the IR signal. However, the results are still very reproducible even with this disturbance due to air bubbles (see Figure 4.21).

The TREF results for LPGMFE01 are shown in Figure 4.22. TREF profiles obtained with 5 and 20 mg sample sizes are shown in Figure 4.22. As with previously discussed results, the resolution in the peaks decreased with increasing sample size, but the two peaks are still clearly resolved even with the 20 mg sample. The profiles for LPGMFE01 are similar to those for LPLMFI01, i.e., copolymer and homopolymer were present in this sample. The small maximum at about 100°C, which was observed in both

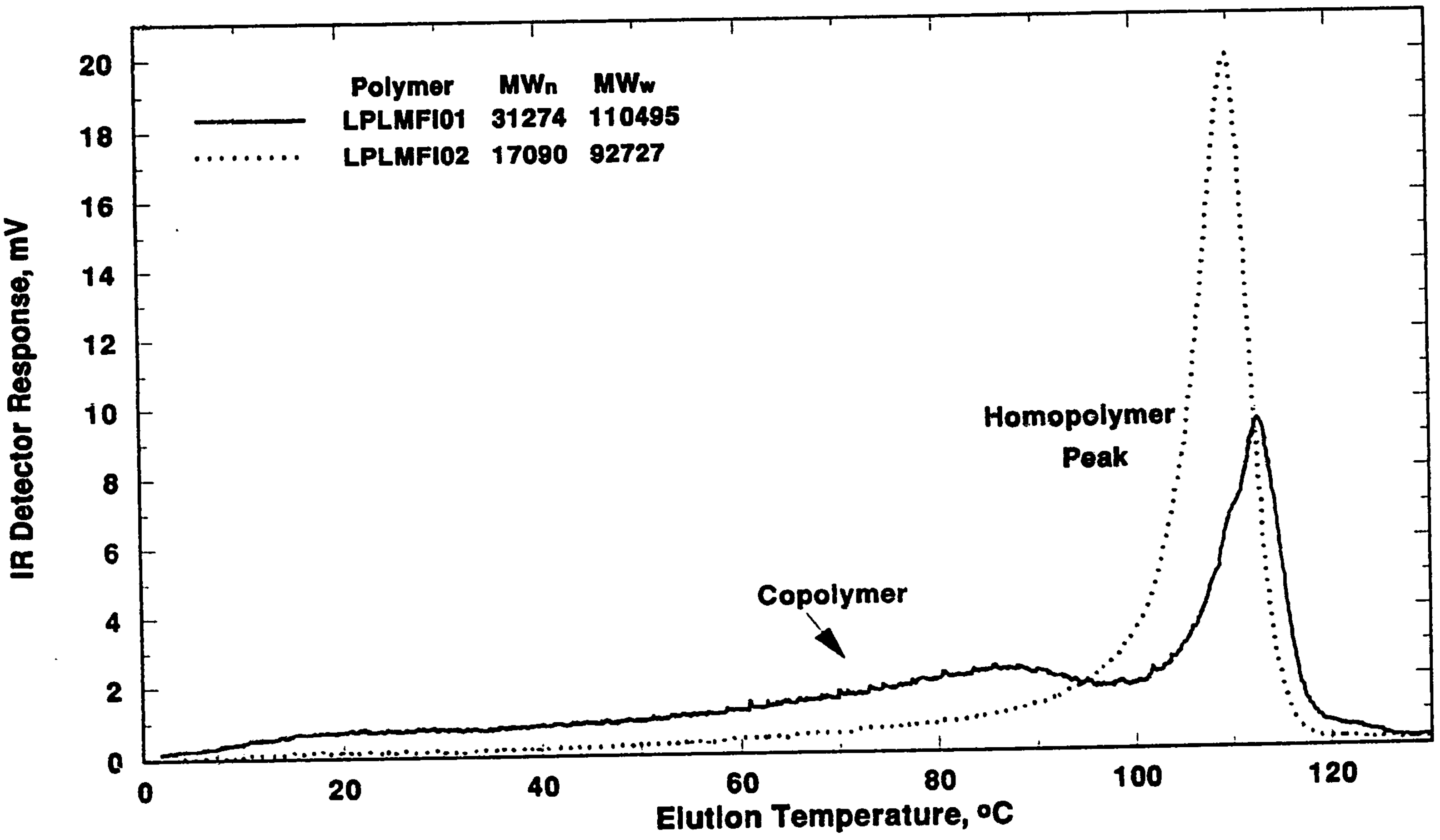


Figure 4.20: Analytical TREF profiles of two laboratory-prepared ethylene-propylene copolymers (Polymers: LPLMFI01 and LPLMFI02; Run No.: E930112D and E930126C).

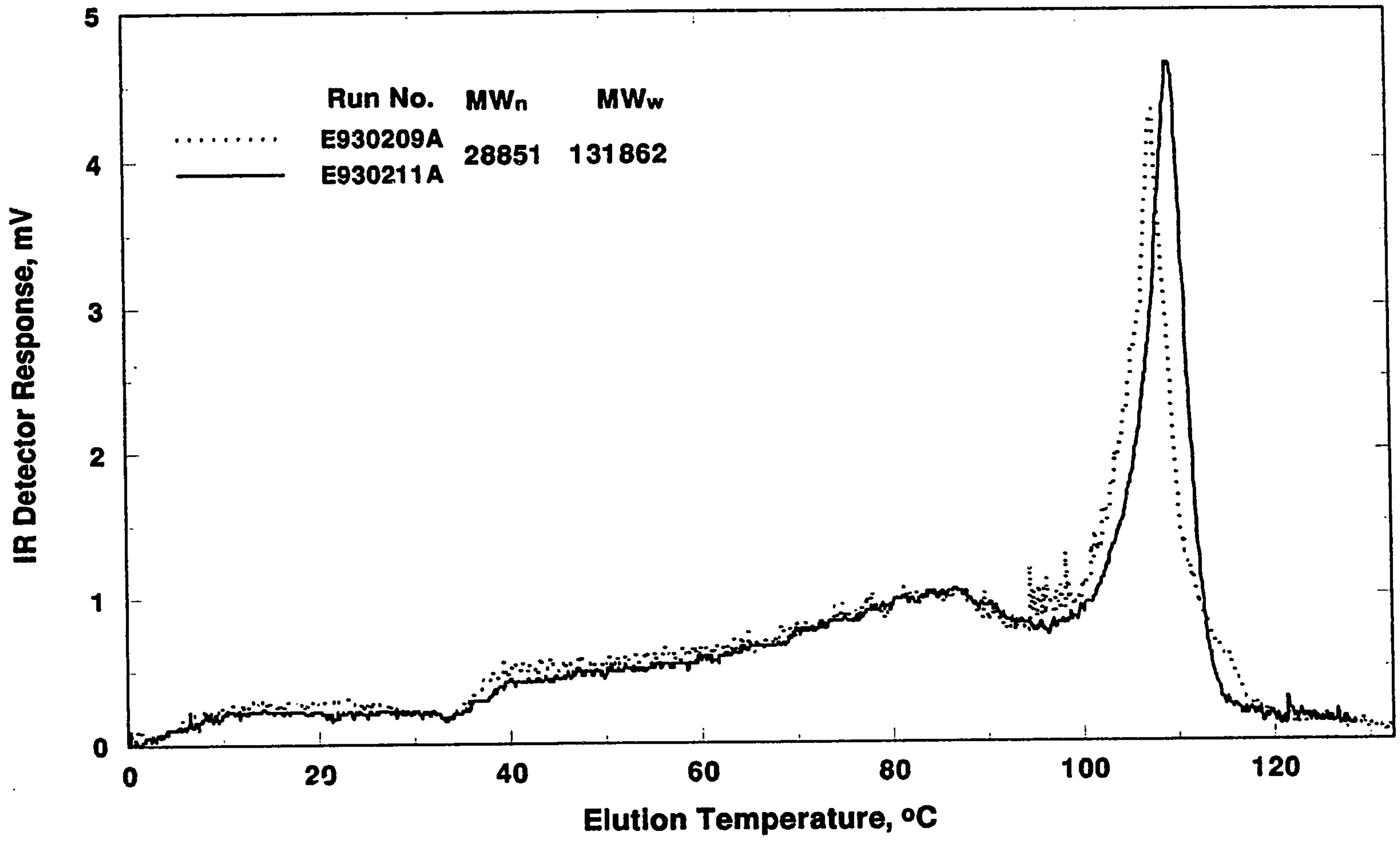


Figure 4.21: Results of repeated analytical TREF runs on the laboratory prepared ethylene-propylene copolymer (Polymer: LPLMFI01).

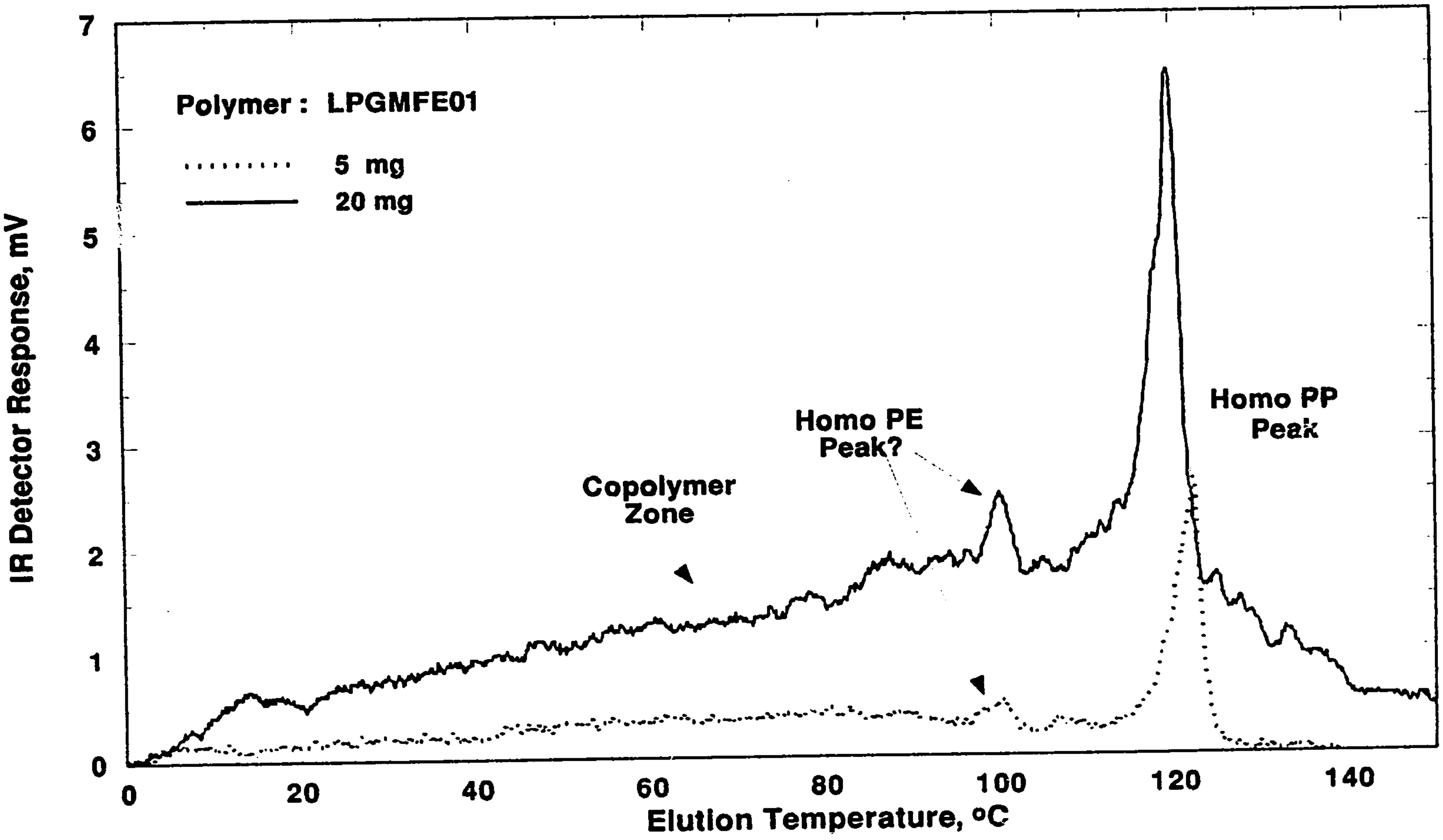


Figure 4.22: TREF profiles for 5 and 20 mg samples of a laboratory prepared ethylene-propylene copolymer (Polymer: LPGMFE01; Run Nos. E930511B and E930417A).

TREF profiles , could be HDPE. Hence, LPGMFE01 was possibly a mixture of ethylene-propylene (broad low temperature peak), HDPE (peak at 100°C) and isotactic polypropylene (peak at 120°C).

Cross fractionation was done on both of the copolymer samples. For LPLMFI01, twelve fractions were collected during the preparative TREF run; the fractions were collected over the following temperature ranges: 15 to 26°C, 26 to 38°C, 38 to 50°C, 50 to 55°C, 55 to 65°C, 65 to 75°C, 75 to 85°C, 85 to 95°C, 95 to 105°C, 105 to 115°C, 115 to 126°C, and 126 to 137°C. The molar mass distributions were determined for each fraction, and the results are shown on the 3-D plot in Figure 4.23. The bimodal, possibly even trimodal, nature of the resin is very apparent in Figure 4.23. The contour plot (lines of constant polymer concentration) in Figure 4.24 also shows the multimodal nature of the resin. The local maximum at an elution temperature of about 35°C is not very reliable because the amount of polymer in the low temperature fractions is very small (low concentrations).

The molar masses of fractions with elution temperatures <120°C appear to be relatively constant. A more quantitative representation of the average molar masses and the polydispersity is given in the top panel of Figure 4.25. This plot shows that the polydispersity decreases slightly with increasing elution temperature. The polydispersity of all fractions were lower than the polydispersity of unfractionated LPLMFI01 which was 4.6. The TREF profile included in the top panel of the Figure 4.25 has a "false" peak at about 125°C. This false peak occurred due to a pressure rise (partial flow blockage as discussed in Chapter 3). This TREF profile is the only profile discussed in chapter 4 for which a significant pressure rise occurred. The pressure rise did not have a significant effect on the result because it occurred after the vast majority of polymer had eluted from the column. The large increase in molar masses in the fractions eluted after the pressure rise are probably responsible for the flow blockage.

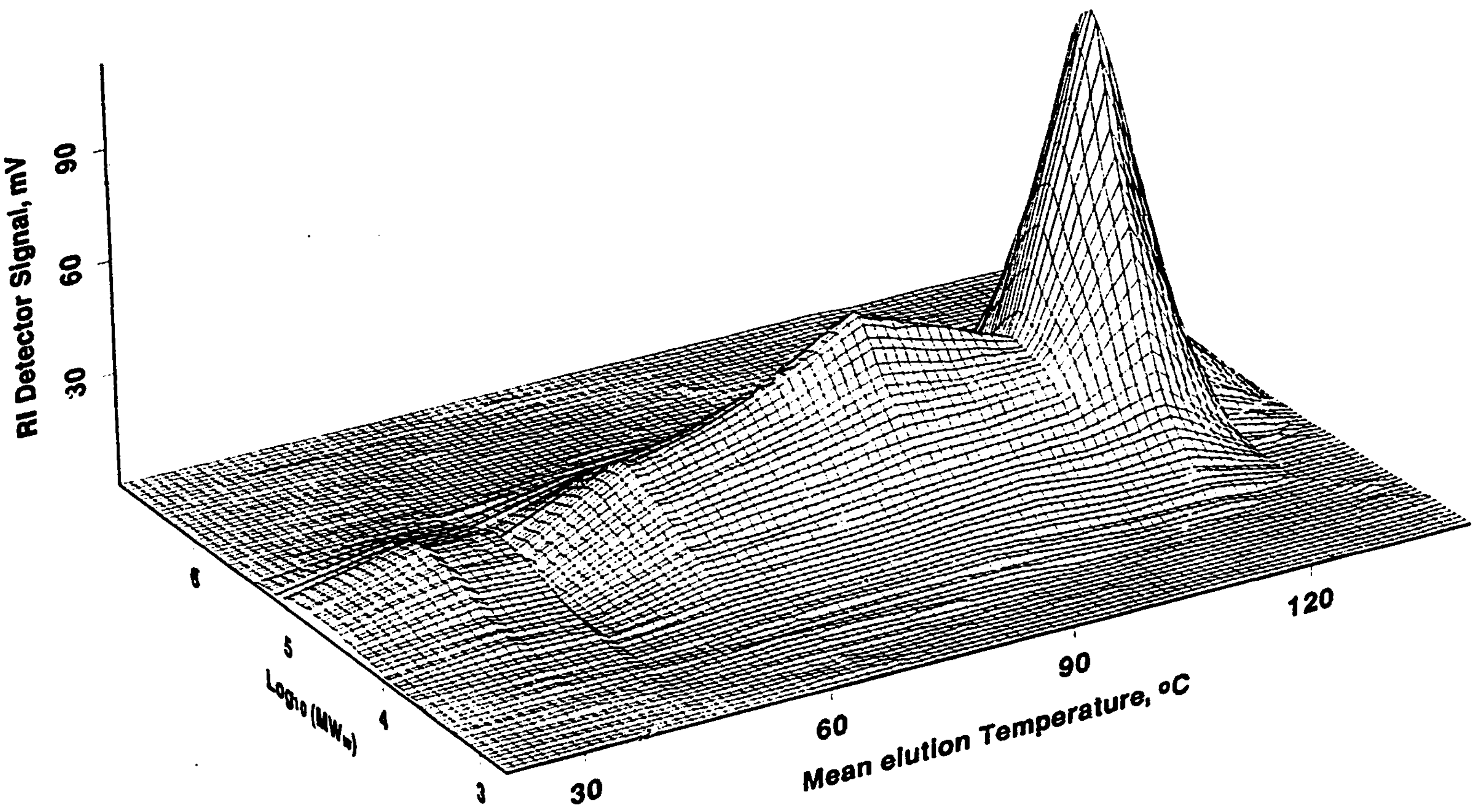


Figure 4.23: Results of cross fractionation for ethylene-propylene copolymer (Polymer: LPLMFI01, Preparative TREF run no.: E930226B).

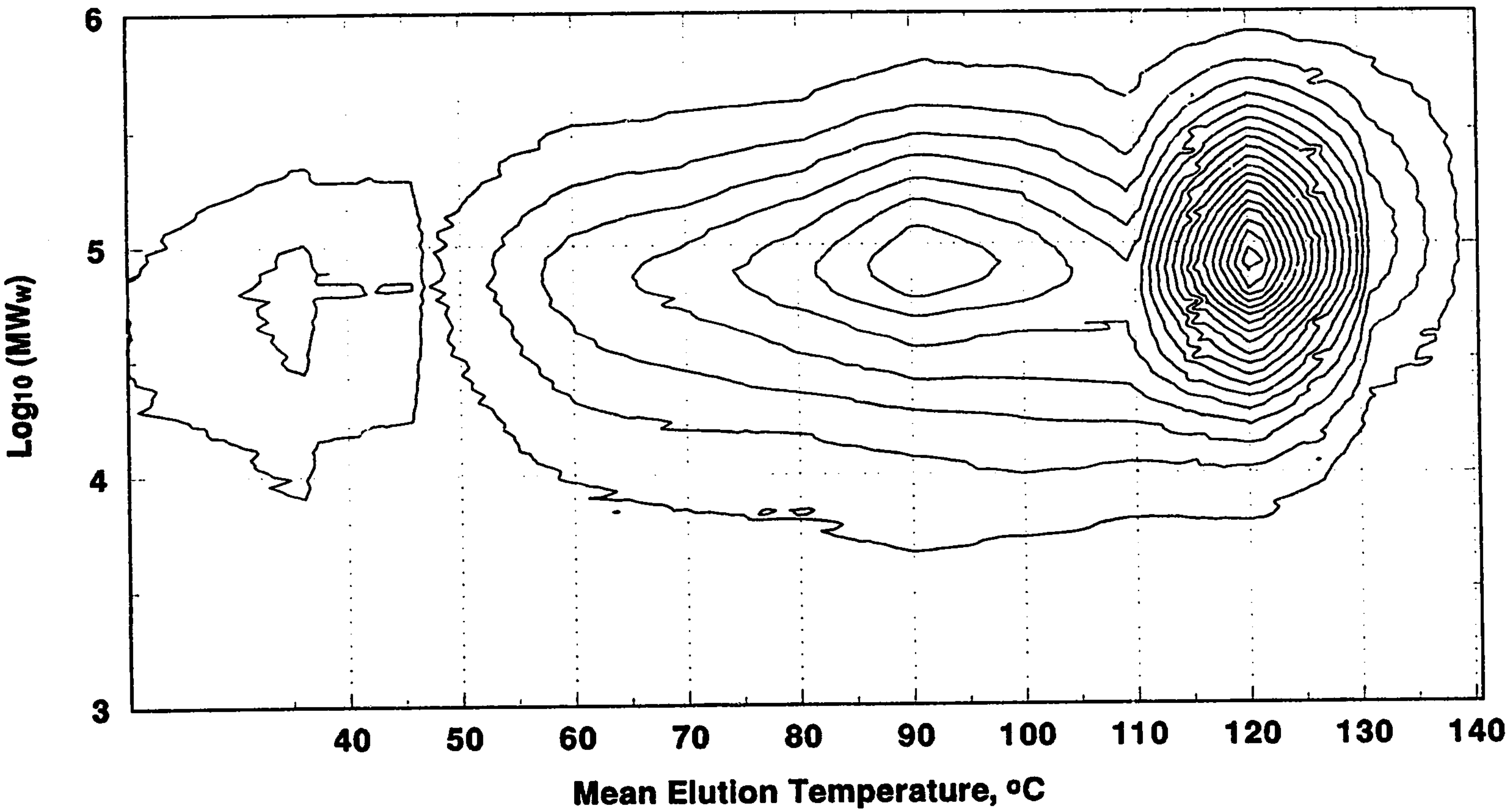


Figure 4.24: Contour plot of cross fractionation results (Polymer: LPLMFI01).

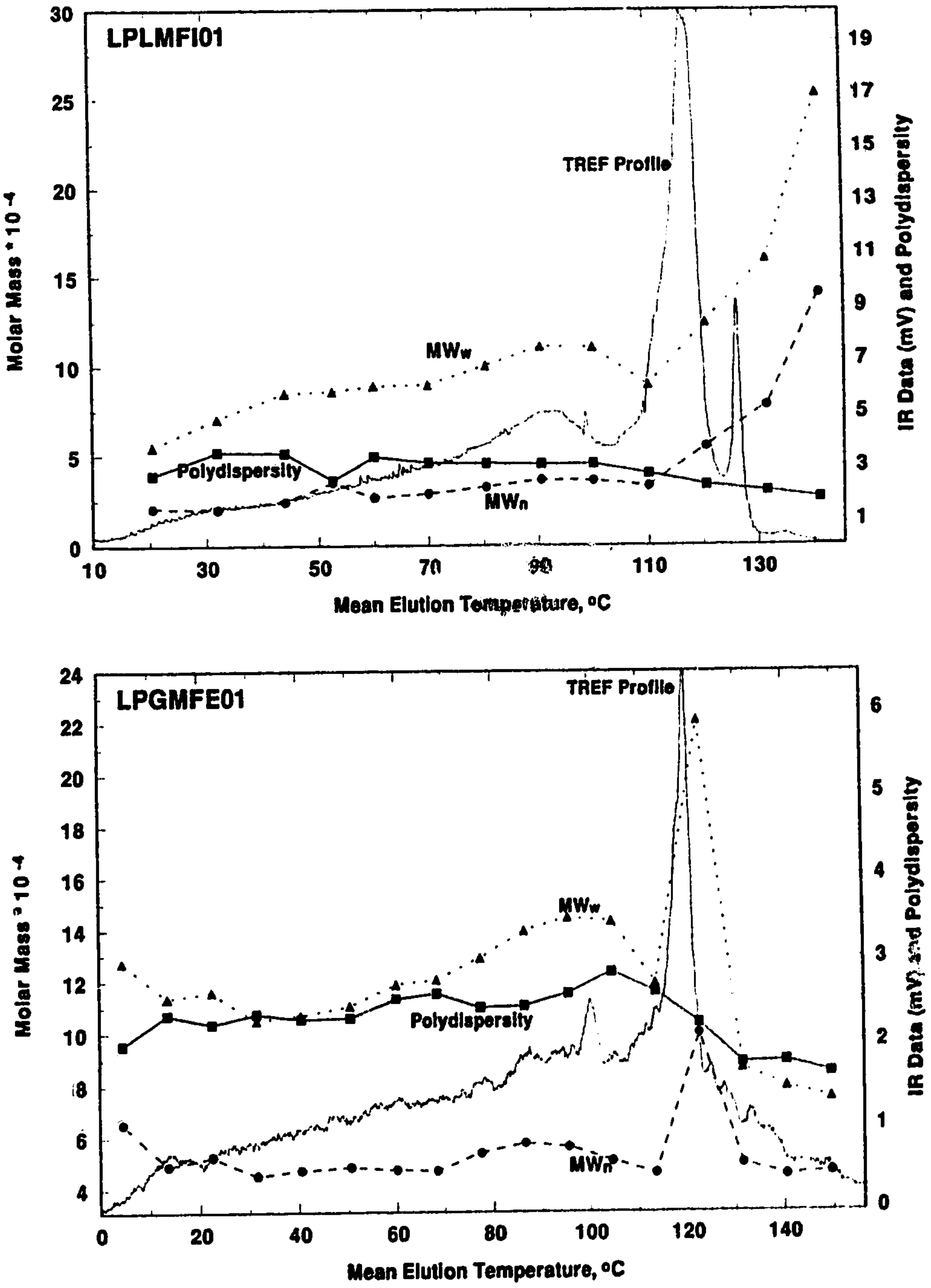


Figure 4.25: TREF profiles, and molar masses and polydispersities of preparative TREF fractions of LPLMFI01 and LPGMFE01 (Preparative TREF run nos. : E930226B and E930417A).

Preparative TREF was also done on LPGMFE01, and the results are shown in Figure 4.26 and the bottom panel of Figure 4.25. Sixteen fractions were collected for this analysis; the temperature range for these samples were the following : 0 to 9°C, 9 to 18°C, 18 to 27°C, 27 to 36°C, 36 to 45°C, 45 to 56°C, 56 to 64°C, 64 to 73°C, 73 to 82°C, 82 to 91°C, 91 to 100°C, 100 to 109°C, 109 to 118°C, 118 to 127°C, 127 to 136°C, and 136 to 145°C. The plots in Figure 4.26 shows that the molar masses increase with increasing elution temperatures, and that the molar mass distribution appears to be narrower for high temperature fractions than for the low temperature fractions. The high average molar mass for the TREF fraction corresponding to the TREF peak at 120°C is shown in the bottom panel in the Figure 4.25.

The results with the laboratory-prepared copolymers have shown that TREF and cross fractionation can yield valuable insight into the molecular structure of complex polymers. This type of information may possibly explain the subtle, but important, differences in processing properties observed for resins which have similar global properties such as melt index and density. This detailed structural characterization is also necessary to determine how reactor operating conditions and catalyst formulation influence the molecular structure during synthesis of the polymers. the TREF system developed during this project will be used extensively in the ongoing olefin copolymerization project in the Department of Chemical Engineering.

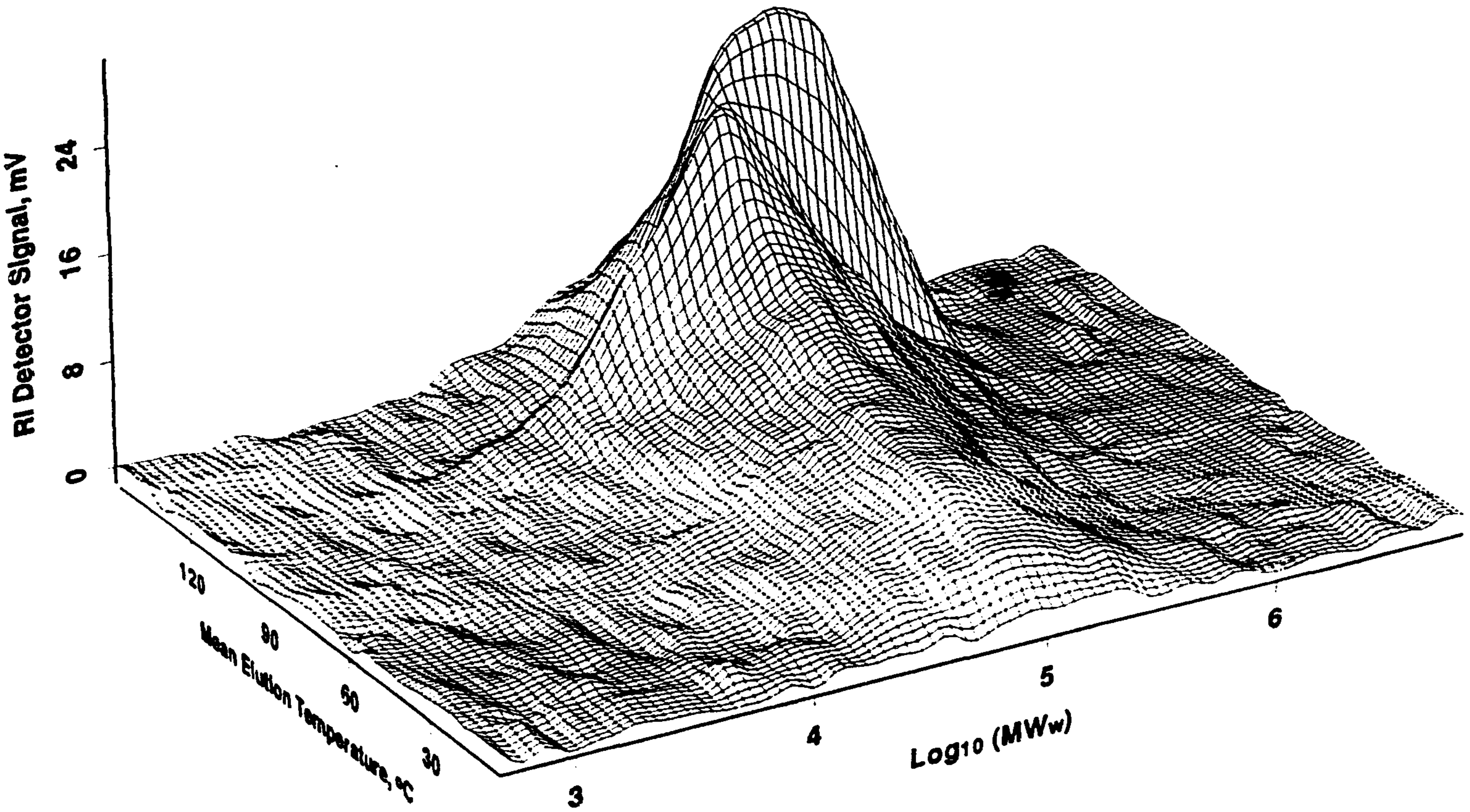


Figure 4.26: Results of cross fractionation for ethylene-propylene copolymer (Polymer: LPGMFE01; Run No.: E930417A).

5.0 CONCLUSIONS AND RECOMMENDATIONS

A TREF apparatus was built and operating procedures for analytic and preparative TREF were developed during this study. Polymers with known TREF profiles were used to test the performance of the equipment and operating procedures. On the basis of results from these experiments it is concluded that the assembled equipment and the developed procedures can produce reliable data.

Experiments with physical mixtures of HDPE and isotactic PP showed that TREF separates these two crystalline homopolymers. These results aided the interpretation of TREF profiles obtained for laboratory-prepared copolymers of ethylene and propylene. The results with the laboratory-prepared copolymers demonstrated the usefulness of TREF for copolymerization studies. The TREF system developed in this study will no doubt be used frequently in the continuing olefin copolymerization project at the University of Alberta.

The simple cross fractionation procedure developed in this study was very effective; high quality TREF-SEC data were obtained. The additional information provided by the molar mass distribution for each TREF fraction allowed fairly complete characterization of the molecular structure of polyolefins. This information is necessary for optimization of reactor conditions for the production of resins with tightly specified properties.

Notwithstanding the accomplishments of this project, further improvement of the equipment and the procedure are possible. The major problem encountered during many of the TREF elutions was a pressure excursion. The cause(s) of this problem should be identified so that equipment and procedure modification can be made which eliminate, or at least reduce this problem. Possible experimental approaches to solving this problem include changing the type and size of column packing, use of frits with large pores at the column exit, changes in the internal geometry of the column exit (e.g., smooth rather than abrupt transition from column to tube diameter), variation in the column diameter, different methods of loading the crystallized polymer into the column (e.g. slurry packing) and slower rates of temperature increase during elution.

Other modifications which would improve the equipment are a change in the design of the IR cell. The current cell is very fragile and leaks easily; alternate cell designs should be explored. The incorporation of an automatic sample collector for preparative TREF would decrease the work load. A final, and important, recommendation is to replace the o-DCB used as the solvent during the crystallization by xylene. Xylene is a better solvent for polyethylene than the o-DCB; lower temperatures can be used with xylene. This would reduce the risk of thermal degradation of the polymer and reduce the crystallization time.

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Appendix A

Table A.1 contains information on the TREF experiments performed on various samples of polyolefins. The experimental runs are listed chronologically and the letter E in the run number, stands for elution, the six numbers are the date on which the elution was done (year-month-day) and a letter after the date is used to identify runs if more than one elution was performed on a specific date. Unless mentioned otherwise, the rate of cooling during sample crystallization was 1.5°C per hour and the rate of temperature rise during elution was 2°C per minute. The solvent was 1,2-dichlorobenzene at a flow rate of 1 ml/min during elution. Celite was used as the filter aid material in the TREF column. All crystallizations were performed using the off-column procedure. The ASCII data files for each run were stored in files having names which are identical to the run number. Specific details for each run are provided in the column of remarks (see Table 4.1 for description of polymers).

Table A.1 : Details of TREF experiments

Run Number	Polymer Type	Sample Size (mg)	Remarks
E920514	LLDPE G	5	Cooling 5°C/h in air oven (old); IR detector malfunctioned; sample not ground; solvent was TCB.
E920515A	LLDPE G	5	Cooling 5°C/h in air oven (old);solvent TCB.
E920519	LLDPE G	5	Cooling: 5°C/h; Pressure increased at 90°C; Poor temperature ramps during heating and cooling (old controller),TCB used as solvent..
E920523	LLDPE G	5	Cooling: 5°C/h, TCB used as solvent.
E920529	GS9113	5	Cooling: 5°C/h; Laboratory prepared polyethylene in slurry phase with 1-hexene as comonomer; IR reading went beyond full scale; IR detector malfunction,TCB used as solvent..
E920617C	GS9113	5	Better heating and cooling ramps provided by the newly acquired automated THERMOTRON oven; Pump shut off due to pressure increase at 100°C ; solvent o-DCB used for this and subsequent experiments.

Table A.1 (contd.)

Run Number	Polymer Type	Sample Size (mg)	Remarks
E920624	GS9113	5	Rate of Cooling: 5^{o}C/h; IR reading went out of range.
E920625B	GS9114	5	IR reading went beyond the range; Pump shut off due to high pressure in column.
E920625C	GS9114	5	IR range reduced to 1/4, first sample with stirrer in the vial (stirrer used for all subsequent runs).
E920625D	LLDPE G	5	Profile not good as pressure increase occurred.
E920625E	LLDPE G	5	Profile better; pressure increase occurred.
E920627	GS9113	5	
E920628	LLDPE G	5	Pressure increased during 84 to 122 ^{o}C; Pump stopped.
E920629C	LLDPE G	5	Pressure increased during 111 to 122^{o}C.; Pump stopped.
E920707	LLDPE G	5	Pressure increased between 102^{o}C to 116^{o}C; Column downstream line size reduced to 1/16" from 1/8"; stirring of polymer solution in the vial now a routine.
E920708C	LLDPE G	5	Higher pressure encountered at 90 to 110^{o}C. Column length reduced from 71 to 58 cm.
E920722	LLDPE G	5	Pressure transducer signal port at the pump outlet connected to the OPTO22 to collect column pressure data. Changes made in the data acquisition program to collect the IR readings as positive values; Cooling rate: 2^{o}C/h.
E920723	LLDPE G	5	Cooling: 5^{o}C/h; Regular spikes observed due to IR detector bubble problem.
E920724	LLDPE G	5	Cooling: 2^{o}C/h.
E920724B	LLDPE G		Cooling: 2^{o}C/h.
E920726	LLDPE G	5	Cooling: 5^{o}C/h; Pressure to 10 bars at 95^{o}C.
E920801	LLDPE G	5	Crystallization in Liquid bath.
E920802B	LLDPE G	5	Crystallization in liquid bath; Pressure increased and pump stopped.
E920806	LLDPE G	5	Crystallization in liquid bath; Pressure increase 90 to 114^{o}C.
E920813A	LLDPE G	5	Pressure increased and pump stopped; Crystallization in temperature controlled (TC) air oven.
E920813B	LLDPE G	5	TC oven;
E920817B	LLDPE G	5	TC oven.
E920817D	LLDPE G	5	TC oven; Pressure increased to 50 bar between 97 to 105^{o}C.
E920820B	LLDPE G	5	Crystallization in liquid bath; Pressure increased to 400 bar; pump stopped; no stirrer used.
E920820C	LLDPE G	5	Crystallization in liquid bath.
E920826A	LLDPE G	5	TC oven; Pressure increased to 400 bar; Pump stopped.
E920827C	LLDPE G	5	TC oven; ; Pressure rise to 4 bars from 98 to 110^{o}C.

Table A.1 (contd.)

Run Number	Polymer Type	Sample Size (mg)	Remarks
E921012	LLDPE G	5	Crystallization in liquid bath cooling of 2°C/h used till E921023C; Solution in vial colored by Viton septa..
E921014	LLDPE G	5	Pump flow problem.
E921017A	LLDPE G	5	Reduced solvent flow :0.5 ml/min; Viton septa covered with Teflon.
E921018A	LLDPE G	5	
E921020	LLDPE P	5	Pressure increase to 25 bars at 98°C; Polymer filtered through the filter aid and not the membrane.
E921020B	LLDPE P	5	Polymer filtered through filter aid and not through the inorganic membrane.
E921023A	LLDPE G	5	Profile slightly distorted as pressure little higher in 100 to 110°C range; crystallization in liquid bath.
E921023C	LLDPE G	5	Crystallization in liquid bath.
E921102	LLDPE G	5	Down stream line of column (to the IR cell) further shortened to reduce dead volume.
E921103B	LLDPE P	5	
E921103C	LLDPE P	5	Pressure increase to 25 bar.
E921103D	LLDPE P	5	
E921104A	LLDPE P	5	
E921104B	LLDPE T	5	
E921104C	LLDPE T	5	
E921104D	LLDPE T	5	
E921110A	LLDPE G	5	
E921112B	LLDPE G	5	
E921114B	LLDPE G	5	Pressure Increase to 200 bar.
E921114C	LLDPE G	5	
E921125B	LLDPE T	5	
E921125C	LLDPE T	5	
E921126A	LLDPE T	5	
E921130A	LLDPE T	5	
E921130B	SRM 1475	5	
E921130C	SRM 1475	5	
E921130D	SRM 1475	5	
E921208A	LLDPE A	5	
E921208B	LLDPE A	5	
E921208C	LLDPE A	5	
E921209A	LLDPE B	5	
E921209B	LLDPE B	5	
E921209C	LLDPE A	5	

Table A.1 (contd.)

Run Number	Polymer Type	Sample Size (mg)	Remarks
E921209D	LLDPE C	5	
E921209E	LLDPE C	5	
E921210A	HDPE with 1.5% butene.	5	
E921210B	HDPE with 1.5% butene	5	
E921227C	LPLMFI01	5	
E930111A	LLDPE P	5	Crystallization in liquid bath used till E930114C.
E930112A	Ethylene propylene copolymer.	5	Trial ethylene propylene copolymer made under unknown conditions
E930112B	Ethylene propylene copolymer.	5	
E930112C	LPLMFI02	5	
E930112D	LPLMFI01	5	
E930112E	LPLMFI02	5	
E930113A	LPLMFI01	5	Pressure increased in 97.5 - 110°C range noticed.
E930114B	LLDPE G	5	Pressure increased to 210 bar in 95 - 115 °C noticed.
E930114C	LLDPE G	5	
E930122A	LLDPE P	5	TC oven used now onwards unless mentioned otherwise.
E930126A	LPLMFI01	5	Pressure increase to 100 bar in 100-115°C range.
E930126B	LPLMFI02	5	
E930126C	LPLMFI02	5	
E930126D	LPLMFI01	5	
E930127A	LPLMFI02	5	
E930127B	LPLMFI01	5	
E930128A	LLDPE G	5	
E930128B	LLDPE G	5	
E930129B	HDPE with 1.5% butene.	5	Pressure increased to 250 bars in 88-135°C range.
E930129D	LDPE	5	
E930208A	LDPE	5	IR cell repaired and lead spacer changed to 0.5 mm.
E930208B	LPLMFI01	5	
E930209A	LPLMFI01	5	Bubble problem in the solvent pump.
E930211A	LPLMFI01	5	
E930211F	LLDPE D	5	
E930212C	LLDPE G	5	

Table A.1 (contd.)

Run Number	Polymer Type	Sample Size (mg)	Remarks
E930225A	LLDPE T	20	P-TREF performed; Pressure increase to 400 bars between 90-120^{O}C.
E930225C	LLDPE T	20	P-TREF performed.
E930226B	LPLMFI01	20	Pressure increase to 20 bar between 105 to 124^{O}C.
E930226D	LLDPE B	5	Pressure increase to 15 bar between 98-110^{O}C.
E930331C	GEGEDE09	5	Crystallization in liquid bath used now onwards, Pressure increase to 10 bar between 98 to 108^{O}C.
E930407A	GEGEDE09	5	Pressure increase to 280 bars between 88 to 145^{O}C.
E930409A	LPGMFE1	5	
E930409B	LPGMFE1	5	
E930416A	LLDPE P	20	P-TREF performed.
E930416C	LLDPE A	20	P-TREF performed; Pressure increases encountered throughout.
E930417A	LPGMFE1	20	P-TREF performed.
E930417B	LLDPE A	20	P-TREF performed; Pressure increase to 60 bars between 88 to 120^{O}C.
E930421B	LLDPE A	5	
E930504A	LPLPDE07 and GEGEDE09 physical mixture.	5	Pressure increase to 10 bar between 118 to 124^{O}C.
E930504C	LPLPDE07 and GEGEDE09 physical mixture.	5	
E930504D	GEGEDE09	5	
E930507B	GEGEDE09 and LPLPDE07 physical mixture.	5	
E930508A	LPLPDE07	5	
E930509A	LPLPDE07	5	Pressure increase to 5 bars between 115 to 125^{O}C.
E930509B	GEGEDE09	5	Pressure increase to 10 bar at 105^{O}C.
E930511A	HDPE with 1.5% butene.	5	Pressure increase to 200 bars between 95 to 143^{O}C.
E940511B	LPGMFE1	5	

Table A.1 (contd.)

Run Number	Polymer Type	Sample Size (mg)	Remarks
E930512B	LLDPE, HDPE blend (Dow:T024-S1)	5	LLDPE and HDPE blend was prepared in the laboratory extruder (from L. Wardough). TREF profile resulted in a distinct LLDPE profile followed by an irregular profile in the higher temperature region.
E930512C	LLDPE, HDPE blend (Dow:T024-S1)	5	Pressure increase to 30 bars between 100 to 120°C.
E930513A	LLDPE, HDPE blend (Dow:T024-S1)	5	Pressure increase to 18 bars between 90 to 116°C.
E930514A	LLDPE B	5	
E930516A	GEGEDE09 ad LPLPDE07 physical mixture	20	P-TREF performed.
E930630	GEGEDE09	5	
E930705A	GEGEDE09	5	
E930713A	GEGEDE09 ad LPLPDE07 physical mixture	5	

APPENDIX B

SAFETY PRECAUTIONS DURING TREF EXPERIMENTS

While performing TREF experiments various chemicals such as solvents, fluids for temperature baths, anti-oxidants, silica based filter aid and polymers were used. There also was equipment with moving parts that required safe operational procedures.

SAFETY WHILE HANDLING OF CHEMICALS

The liquid chemicals that were used during TREF were 1,2-dichlorobenzene (used as solvent), acetone (used as wash liquid) and diethylene glycol (liquid bath cooling/heating agent). The solvent 1,2-dichlorobenzene (UN 1591) requires stringent safety precautions while in use because it is highly poisonous. The maximum allowable exposure limit is 50 ppm (OSHA). For further information refer to the materials safety data sheet (MSDS) of 1,2-dichlorobenzene. It is toxic by ingestion and mildly toxic by dermal absorption. Therefore, certified hand gloves, chemical splash goggles (Fisher Scientific catalogue no. 11-401-10) and respirators (Fisher Scientific catalogue no. 13-995-11) were used during handling.

All the vessels containing 1,2-dichlorobenzene were kept in fume hoods (Sisco Scientific, Laboratory fume hood, Model no. 5601CB) with continuous operation of the exhaust system. The 1,2-dichlorobenzene vapors are heavier than air, therefore, the fume hood should remain slightly open while in use. The containers used for solvent storage in the TREF apparatus were plastic coated (Kontes, HPLC reservoir, catalogue no. 953901) to avoid spillage by breakage. Spills were cleaned up by thoroughly mopping the affected area and placing the towels in special containers for later disposal by the waste disposal authorities.

For acetone (UN 1090) and diethylene glycol (Cas. no. 000111-46-6), the safety precautions were similar to that of 1,2-dichlorobenzene. For further information consult the materials safety data sheet (MSDS) of acetone and diethylene glycol.

The 2,6-di-tert-butyl-4-methylphenol (Cas. no. 128-37-0), which was used as an antioxidant is a solid and while handling, certified hand gloves, chemical splash goggles and laboratory overalls were used to avoid any dermal contact. For further information refer to the materials safety data sheet (MSDS) of 2,6-di-tert-butyl-4-methylphenol.

All the polyolefin materials handled during the TREF experiments were typically less hazardous to dermal contact. Certified gloves and chemical splash goggles were used when polyolefins were handled.

While using Celite (Manville Products Corp., Denver, CO, USA) as a column packing material, gloves for hand protection; respirators for avoiding inhalation of fine Celite dust, and chemical splash goggles for eye protection were used. Celite contained crystalline Silica Quartz (Cas. no. 14808-60-7) and Christobalite (Cas. no. 14464-46-1).

SAFETY DURING OPERATION OF EQUIPMENT

The ultra centrifugal mill (Brinkmann Retsch, type ZM1) was used to shred the polymer extrudates. The ultra high speed of the rotor (78.5 m/sec at the rotor periphery) requires that the rotor compartment be properly closed by tightening the rotor nut and the compartment hatch. For further details consult the operating instruction manual of the centrifuge.

Care was taken not to interfere with the movement of the moving parts while using the HPLC pump and the vacuum pump.

The liquid bath (Neslab, model: RT-220) and the controlled temperature oven (Thermotron, model: S5.5C) performed the heating (maximum temperatures encountered:

160°C) and cooling (minimum temperature encountered: -10°C) during the TREF experiments. Hand gloves and laboratory overalls were used to avoid dermal contact with these equipment. While operating the liquid bath, safety precautions, similar to that necessary while using 1,2-dichlorobenzene, were taken.