CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Theory

2.1.1 Polyethylene [6]

Despite ethylene's simple structure, the field of polyethylene is a complex one with a very wide range of types and many different manufacturing processes. From a comparatively late start, polyethylene production has increased rapidly to make polyethylene the major tonnage plastics material worldwide (45×10^6 t capacity in 1995).

During the 1950s three research groups working independently discovered three different catalysts which allowed the production of essentially linear polyethylene at low pressure and temperature. These polymers had densities in the region of 960 kg/m^3, and became known as high-density polyethylene (HDPE), in contrast to the polymers produced by the extensively commercialized high-pressure process, which were named low-density polyethylene (LDPE). These discoveries laid the basis for the coordination catalysis of ethylene polymerization, which has continued to diversify. Of the three discoveries at Standard Oil (Indiana), Phillips Petroleum, and by Karl Ziegler at the Max-Planck-Institut fur Kohlenforschung, the latter two have been extensively commercialized. More recently the observation that traces of water can dramatically increase the polymerization rate of certain Ziegler catalysts has led to major developments in soluble coordination catalysts and later their supported variants.

The coordination catalysts allowed for the first time the copolymerization of ethylene with other olefins such as butene, which by introducing side branches reduces the crystallinity and allows a low-density polyethylene to be produced at comparatively low pressure. Although DuPont of Canada introduced such a process in 1960, worldwide

the products remained a small-volume specialty until 1978 when Union Carbide announced their Unipol process and coined the name linear low-density polyethylene (LLDPE).

2.1.1.1 Properties of Polyethylene

<u>Molecular structure and morphology</u>

Figure 2.1 shows schematic structures for the three polyethylenes, with the main features exaggerated for emphasis. LDPE has a random long-branching structure, with branches on branches. The short branches are not uniform in length but are mainly four or two carbon atoms long. The ethyl branches probably occur in pairs [7], and there maybe some clustering of other branches [8]. The molecular mass distribution (MMD) is moderately broad.
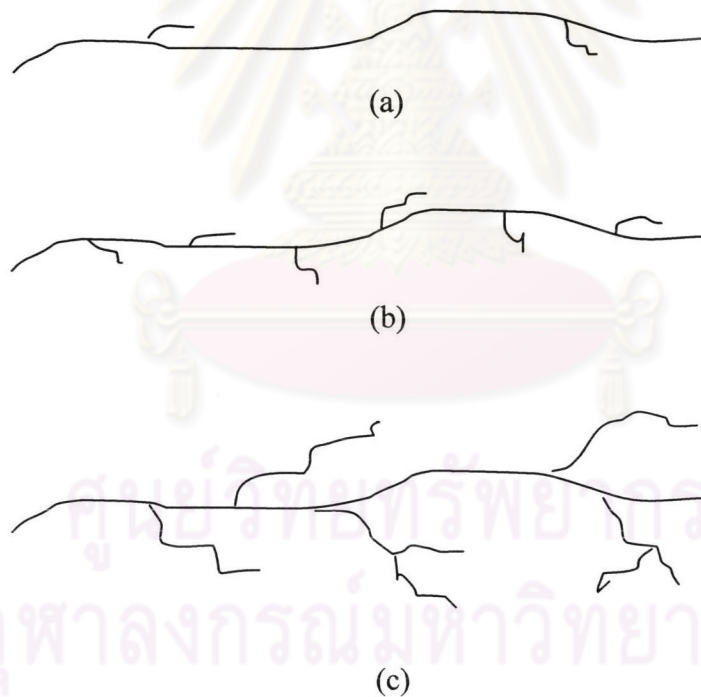

Figure 2.1 Schematic illustration microstructures of Polyethylene; (a) HDPE, (b) LLDPE, and (c) LDPE.

LLDPE has branching of uniform length which is randomly distributed along a given chain, but there is a spread of average concentrations between chains, the highest concentrations of branches being generally in the shorter chains. The catalysts used to minimize this effect generally also produce fairly narrow MMDs.

HDPE is essentially free of both long and short branching, although very small amounts may be deliberately incorporated to achieve specific product targets. The MMD depends on the catalyst type but is typically of medium width.

Polyethylene crystallizes in the form of platelets (lamellae) with a unit cell similar to that of low molecular mass paraffin waxes [9]. Due to chain folding, the molecular axes are oriented perpendicular to the longest dimension of the lamella and not parallel to it as might be expected (Figure. 2.2). The thickness of the lamellae is determined by the crystallization conditions and the concentration of branches and is typically in the range of 8-20 nm. Thicker lamellae are associated with higher melting points and higher overall crystallinities. Slow cooling from the melt or annealing just below the melting point produces thicker lamellae. Where long molecules emerge from the lamella they may either loop back elsewhere into the same lamella or crystallize in one or more adjacent lamellae, thereby forming "tie molecules".
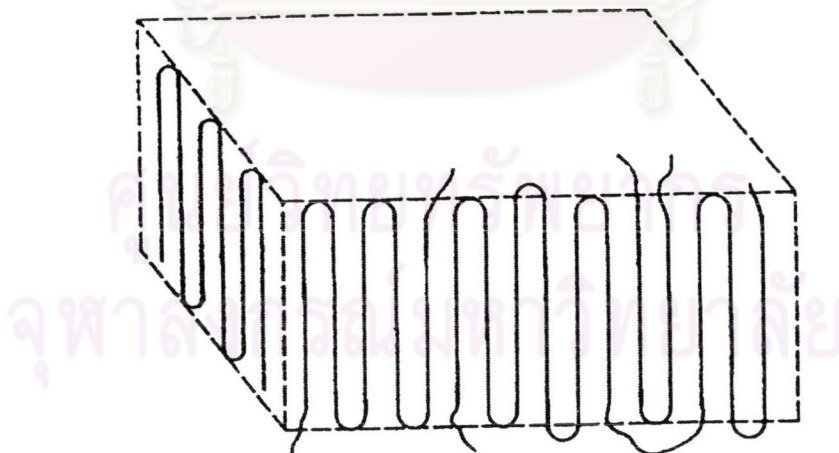
Figure 2.2 Folded-chain lamellar crystal of polyethylene [6].

Thermodynamically the side branches are excluded from the crystalline region because their geometry is too different from that of the main chains to enter the crystalline lamellae. Therefore, the branches initiate chain folding, which results in thinner lamellae with the branches mainly situated on the chain folds on the surface of the lamellae. However, on rapid cooling these energetically preferred placements may not always occur, and some branches may become incorporated as crystal defects in the crystalline regions.

A further result of a side branch is that having been prevented from folding directly into the same lamella, the polymer chain may form a tie molecule that links to one or more further lamellae.

Under moderately slow cooling conditions, crystallization may be nucleated at a comparatively small number of sites. Crystallization then propagates outwards from these centers until the surfaces of the growing spheres meet. The resulting spherulites show a characteristic banded structure under a polarizing optical microscope. The typical milkiness of polyethylene is due to light scattered by spherulites or other, less well defined aggregates of crystallites, rather than by the crystallites themselves, which are much smaller than the wavelength of light [10]. Ethylene copolymers may be transparent, although partially crystalline.

General Properties

LDPE and LLDPE are translucent whitish solids and are fairly flexible. In the form of films they have a limp feel and are transparent with only a slight milkiness. HDPE on the other hand is a white opaque solid that is more rigid and forms films which have a more turbid appearance and a crisp feel.
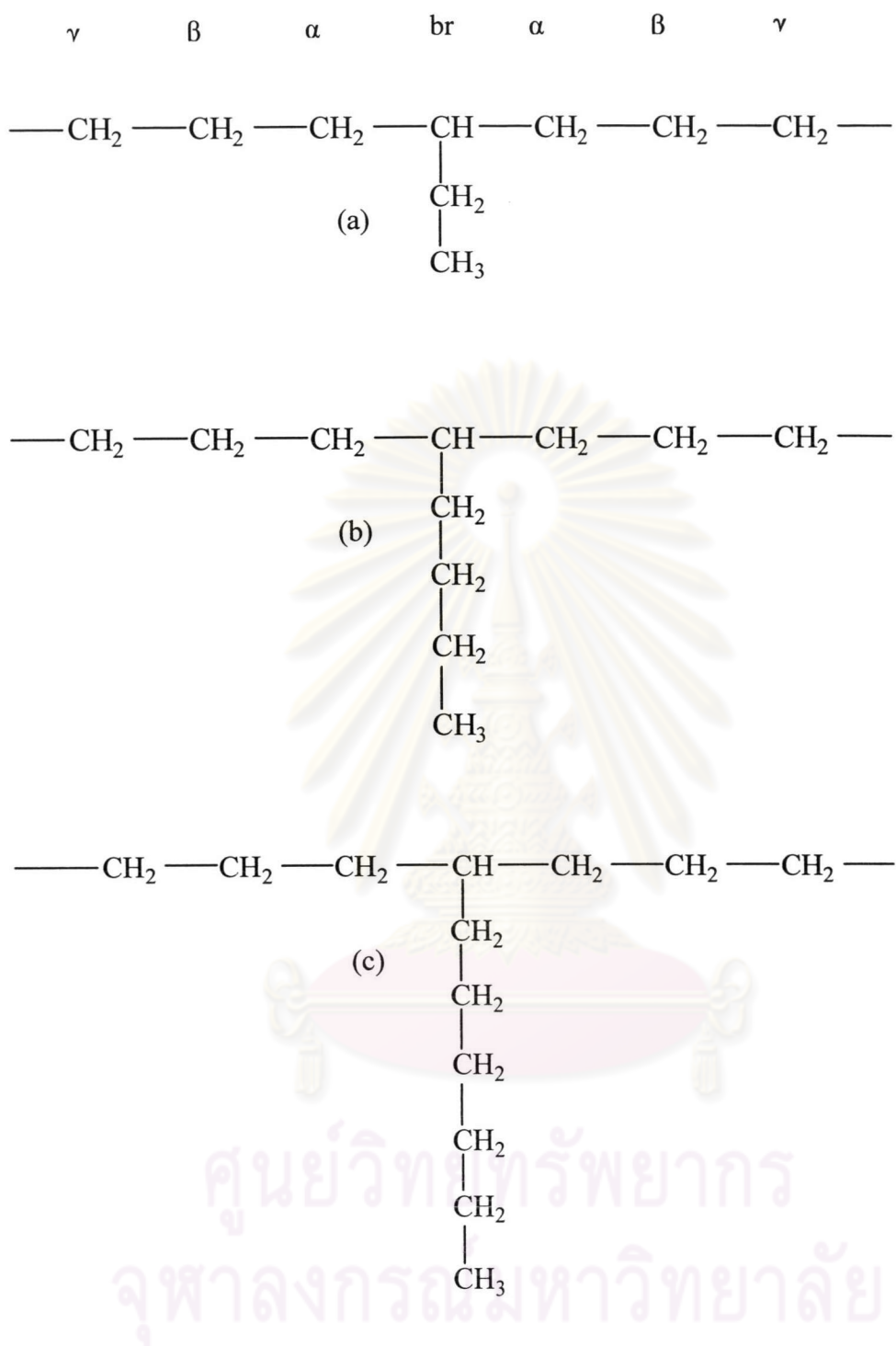
Polyethylene does not dissolve in any solvent at room temperature, but dissolves readily in aromatic and chlorinated hydrocarbons above its melting point. On cooling, the solutions tend to form gels which are difficult to filter. Although LDPE and LLDPE do

not dissolve at room temperature, they may swell in certain solvents with a deterioration in mechanical strength.

Currently LLDPE has the diversity of applications. LLDPE has short chain branching that are incorporated into the polyethylene backbone by random copolymerization with varying amounts of one or more alpha-olefins such as 1-butene, 1-hexene and 1-octene (Figure 2.3).

Detailed information about the molecular structure of polymers can be correlated to their macroscopic properties and therefore to their final applications. For instance, Figure 2.4 shows the property relationships with density, molecular weight and melt index for polyethylene. Take impact strength as an example. According to this figure, this property decreases when the density of polyethylene increases. Therefore, by lowering the density polyethylene, for example by copolymerizing ethylene with some other alpha-olefin, one can increase the impact strength. However, this does not give us the complete description of polymer because besides its composition we also have to be aware of its molecular weight. Figure illustrates how the properties of polyethylene vary with molecular weight. In the particular case of impact strength, this property is inversely proportional to the molecular weight. Since copolymers show distributions of both molecular weight and composition and, since not only the average values, but also the shape of these distributions can have a marked influence on the polymer properties, only the determination of this bivariate distribution can lead to a more complete understanding of the polymer behavior in end-use applications.

The determination of the averages compositions of copolymer or the average degrees of branching by FT-IR will not entirely define the polymer in question. The whole distribution of composition in addition to chain length is necessary in order to accomplish this task.

$$\overset{\gamma}{} \quad \overset{\beta}{} \quad \overset{\alpha}{} \quad \overset{br}{} \quad \overset{\alpha}{} \quad \overset{\beta}{} \quad \overset{\gamma}{}$$

$$-CH_2-CH_2-CH_2-CH-CH_2-CH_2-CH_2-$$

(a)

$$\underset{\overset{|}{CH_2}}{\underset{\overset{|}{CH_3}}{}}$$

$$-CH_2-CH_2-CH_2-CH-CH_2-CH_2-CH_2-$$

(b)

$$\underset{\overset{|}{CH_2}}{\underset{\overset{|}{CH_2}}{\underset{\overset{|}{CH_2}}{\underset{\overset{|}{CH_3}}{}}}}$$

$$-CH_2-CH_2-CH_2-CH-CH_2-CH_2-CH_2-$$

(c)

$$\underset{\overset{|}{CH_2}}{\underset{\overset{|}{CH_2}}{\underset{\overset{|}{CH_2}}{\underset{\overset{|}{CH_2}}{\underset{\overset{|}{CH_2}}{\underset{\overset{|}{CH_3}}{}}}}}}$$

Figure 2.3 Nomenclature adopted for the assignment of individual carbons of LLDPE; (a) C_4-LLDPE, (b) C_6-LLDPE, and (c) C_8-LLDPE.
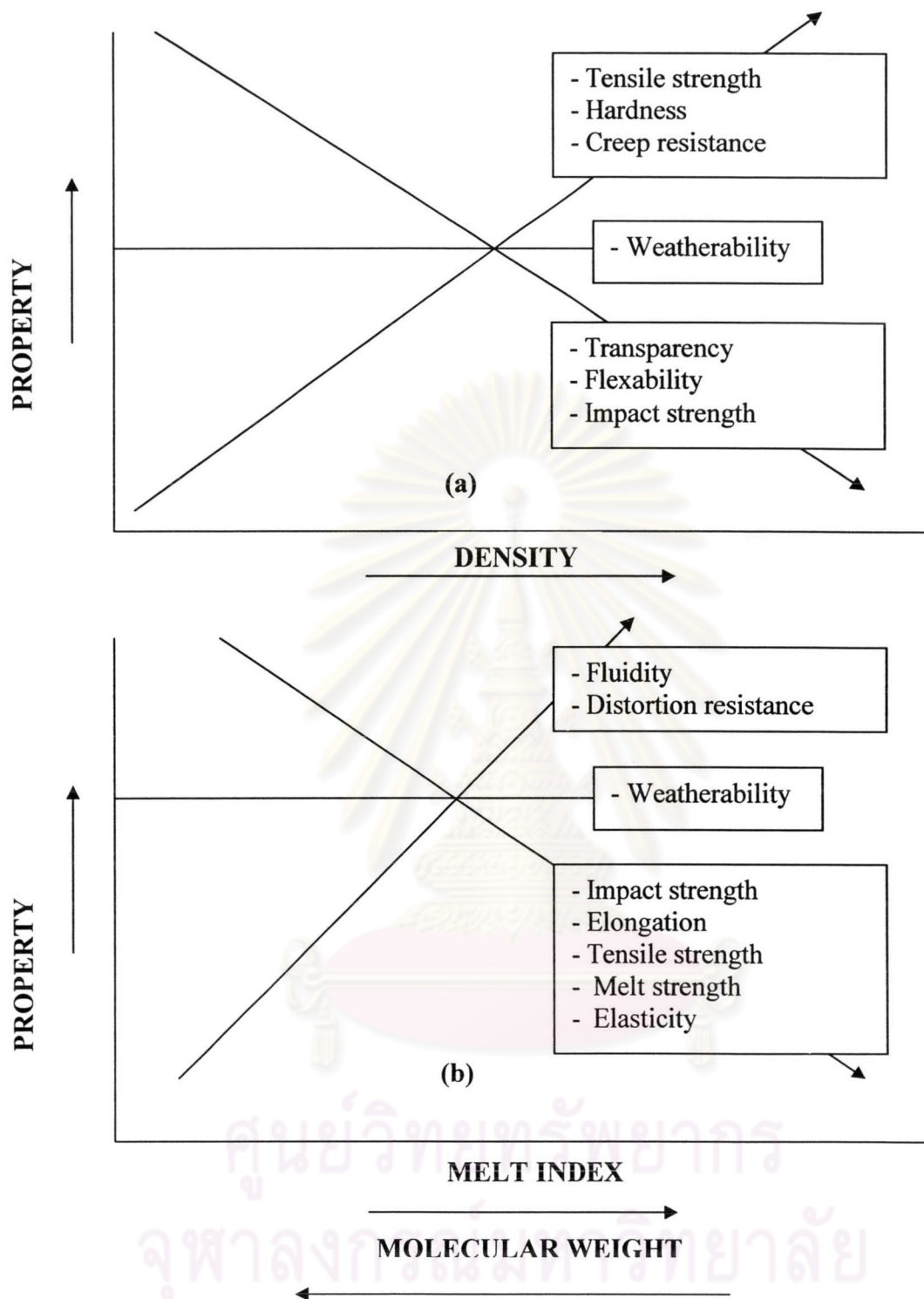
Figure 2.4 Property relationships of polyethylenes (a) density, (b) molecular weight, and melt flow index.

2.1.2 Temperature rising elution fractionation

Temperature Rising Elution Fractionation (TREF) is an analytical technique developed to separate semicrystalline polymers according to differences in molecular structure or composition. These molecular level differences lead to changes in crystallinity and solubility. TREF is helpful for the better understanding of the microstructure of polyolefins, polymerization mechanisms [11] and the nature of catalysts [12-14]. TREF has been applied to the characterization of polyolefins, including ethylene copolymers [15, 16], polypropylene [17, 18], propylene copolymers [19], polyolefin alloys [20] and metallocene-based polyolefins [21]. In polyethylene copolymers with alpha–alkenes, differences in crystallinities are caused by different amounts and distributions of primarily short chain branching (SCB).
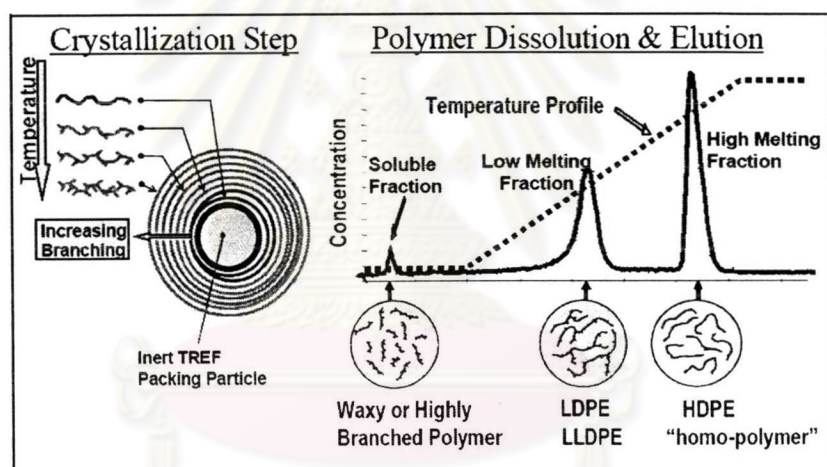
**Figure 2.5** TREF separation mechanism: crystallization and dissolution [22].

TREF can be divided into crystallization and elution steps, as illustrated in Figure 2.5. In the crystallization step, polymer is dissolved in a appropriate solvent, and then allowed to crystallize under controlled conditions by slowly decreasing the temperature. Crystallization may take place on an inert support or the support may be added later. In the elution step, solvent is pumped through a column packed with the polymer-support mixture while the temperature is increased. Polymer is elutes in the reverse order that it

was crystallized, with crystalline material eluting at lower temperatures followed by more crystalline polymer at higher temperatures.

2.1.2.1 Mechanism of fractionation

Figure 2.6 illustrates the principal types of macromolecular structures that can be fractionated by TREF. The upper structure represents a high density polyethylene (HDPE) chain. Due to its high structural order, HDPE is highly crystalline. However, if one of hydrogen attached to the backbone is substituted by another chemical group (R) that cannot crystallize with the other monomeric units, the structural order of the original chain is disrupted and its crystallization temperature will decrease.
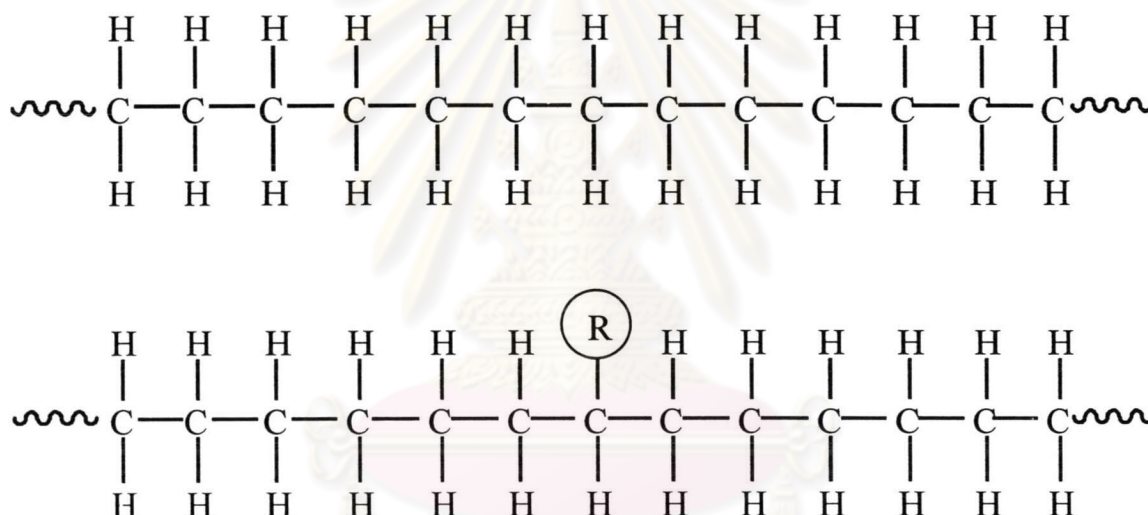
Figure 2.6 Some molecular structures that affect chain crystallinity and can be fractionated by TREF [23].

This is done commercially for the production of LLDPE using butane-1, hexene-1, or octene-1 as co-monomers. It is also important to realize that the crystallinity of copolymer chain will depend on not only taken into account when interpreting TREF results. TREF makes use of these differences in molecular structure to fractionate polymer chains according to their solubilities in a solvent at decreasing/increasing

temperatures. Influence of long-chain branching on TREF fractionation has not been thoroughly studied. From some limited observations. TREF does not seem to fractionate well according to long-chain branching behave essentially as main chains, and therefore have a little effect on crystallinity [24].

2.1.2.2 Basic TREF modes

The TREF process can be divided into two sequential stages, crystallization and elution. Polymer fractionation by crystallinity takes place during the crystallization step. Polymer, initially present in a dilute solution, is crystallized by slowly decreasing the temperature. Polymer chains of higher crystallinity precipitation at higher temperatures, while the ones of lower crystallinity precipitate at lower temperatures. Polymer can be crystallized from solution with or without the presence of a support. When crystallized without a support, it is necessary that the polymer be mixed with the support before the second step of fractionation.

The second step is performed in a column packed with the crystallized polymer and support. A good solvent flows through the column while the temperature is increased continuously or step-wise. In this way, the polymer chains are recovered in the reverse order they were precipitated. In preparative TREF, polymer fractions are collected at elution temperature intervals. These fractions are usually analyzed off-line to determine their microstructures by techniques such as carbon-13 nuclear magnetic resonance (^{13}C-NMR), infrared spectroscopy (IR) and size exclusion chromatography (SEC). In analytical TREF, an on-line detector is used to measure the concentration of polymer being eluted as a fraction of elution temperature. In this case, no further analysis is required if a calibration curve is available to relate elution temperature to the investigated property, for example degree of shot-chain branching in LLDPE. Table 2.1 compares the main characteristics of analytical TREF and preparative TREF.

**Table 2.1** Characteristics of analytical TREF and preparative TREF [23]

Preparative TREF	Analytical TREF
1. Fractionations are collected at predetermined temperature intervals.	1. Continuous operation
2. Information about structure is obtained off-line by other analytical techniques.	2. Information about structure is obtained online by a calibration curve.
3. Requires large columns and large sample sizes.	3. Requires small columns and small sample sizes.
4. Time consuming but can generate more detailed information about polymer microstructure.	4. Fast but generates less information about polymer microstructure.

2.1.2.3 Basic Apparatus

There are two modes used in TREF. For preparative TREF, fractions are recovered over a narrow temperature interval for further analysis. Relatively large samples (1-10 g) are required in order that a reasonable amount of polymer is available from each temperature fraction. Analytical TREF, refers to the technique in which the concentration of eluting polymer is continuously monitored by an on-line detector rather than being recovered. The latter TREF mode typically requires small quantities of polymer (< 200 mg).

The preparative TREF was described by Desreux and Spiegels [25] who fractionated high pressure, low density polyethylene using an apparatus that eluted polymer at gradually increasing temperature. They recognized that fraction produced were more dependent on polymer crystallinity than on molecular weight. Since that time

considerable effort has been directed towards the development of a faster technique with better quality of separation and resolution. Currently, modern analytical TREF has been reported Wild and Ryle [5]. Analytical TREF instrumentation was developed from SEC or gel permeation chromatography (GPC). Components commonly used in TREF systems are shown in Figure 2.7 and are as follows:
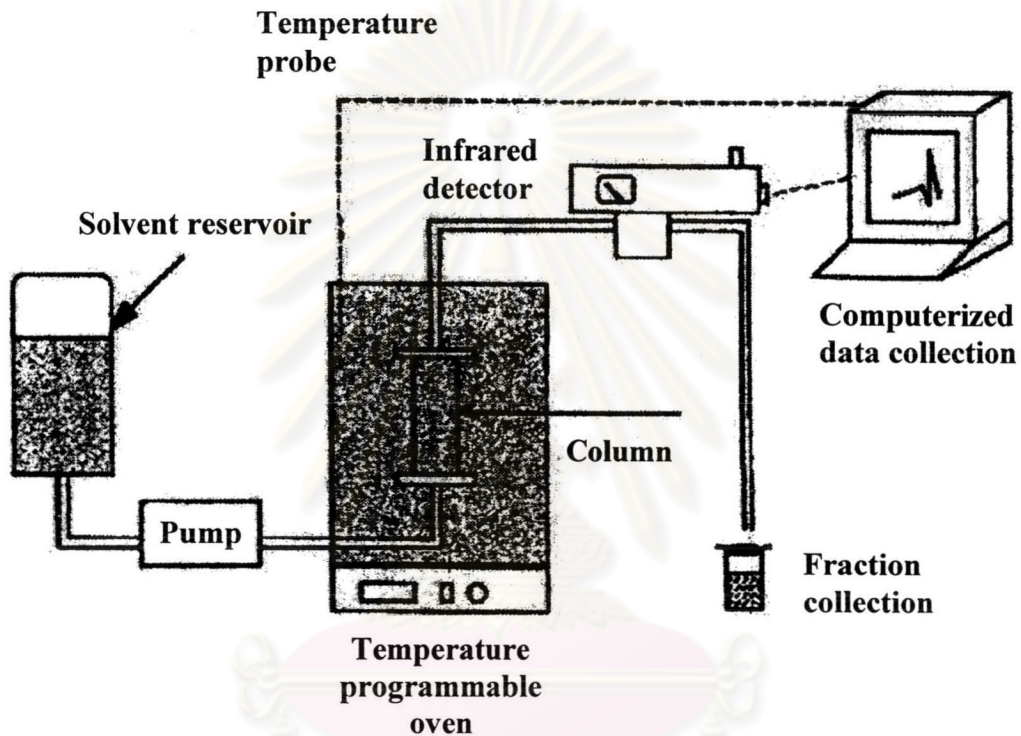
Figure 2.7 Schematic illustration of TREF apparatus [23].

Pumps from SEC or liquid chromatography (LC)

These are probably overkill as TREF systems can function at relatively low pressure (50 psi).

Columns

These are usually stainless steel made with dimensions varying from 7 x 0.9 cm to 38.1 x 2.5 cm (analytical TREF) and from 10 x 0.3 cm to 60 x 12 cm (preparative TREF).

Controlled crystallization and elution environments

These consist of a temperature programmable oil bath or SEC oven:

- Heat transfer in an air oven is poor compared to an oil bath. This can constitute a problem if a large size column is used for crystallization in an air oven. However, TREF heating rates are currently quite low.

- The convenience and case of changing sample columns in an air oven avoids messy oil.

- Decreased turn around time between runs is possible for an air oven due to the rapidity with which it can be cooled.

On-line detectors

Examples are refractive index (RI) or infrared (IR) detectors. IR presents less of a problem regarding baseline noise than RI; however, solvents with an IR window are required.

Degasser

The solvent is degassed prior to eluting so as to preclude bubbles interfering with the IR absorbance. It is observed that high-boiling trichlorobenzene (TCB) does not require a degasser, whereas low-boiling tetrachloroethylene (TCE) does.

Tubing

The tubing connecting the eluting column and the detector should be heated to a temperature above the highest elution temperature to avoid deposition of polymer (i.e. ~135°C for TCB and ~100°C for TCE).

2.1.2.4 Sample size

Sample size varies from 2 to 200 mg for analytical and from 0.02 to 10 g for preparative TREF. High sample loading has the advantage of producing TREF curves that are low in noise and large in signal. However, if the sample loading is too high, flow between support particles may be blocked, resulting in high back pressure.

2.1.2.5 Solvents

It is common to use the same solvent for both the crystallization and elution stages. Solvent type does not seem to affect the fractionation process. For four different solvents, calibration curves relating elution temperatures to SCB measured by the methyl content of fractions eluted at different temperature ranges were found to be almost parallel [23]. Absolute dissolution temperature may change with solvent type but relative changes of dissolution temperature with composition are similar in various solvents. Dissolution is affected by solvent power, the better the solvent, the lower elution temperature in TREF.

When an IR detector is used, the solvent should contain a suitable IR window for detecting polyalkenes. For IR detection dissimilar refractive indices between polymer and solvent are required. And increasingly important factor to consider on choosing solvents is the range of the temperature of operation. TREF equipment used for low crystallinity polymers must often operate at sub-ambient temperatures. Such a system requires a solvent that neither solidifies nor boils in the range of elution temperatures. Solvents

commonly used are xylene, ODCB (*o*-dichlorobenzene), α-CN (α-chloronaphthalene), TCB and TCE.

2.1.2.6 Support material

Typically used column packing materials (support) includes glass beads, Chromosorb P and steel shot. Glass beads have the advantage of better heat transfer and presumably higher cooling/heating rates can be used without generating undesired temperature gradients within the column. Chromosorb P appears to be the more general choice and posses an enormous surface area for crystal nucleation.

2.1.2.7 Elution

Continuous elution

The solvent flows continuously through the column as temperature is raised. Heating rates reported for analytical TREF range from 8 to 360°C/h and flow rate 1-6 ml/min.

Step-wise elution

This is mostly used for preparative TREF because it minimizes problems of temperature gradients common in large-scale TREF. A rise in temperature to the desired level is followed by a period of isothermal equilibration which depends on the temperature jump and dimensions of the column used. Sample elution in each step can be continuous or can be interrupted for equilibration (stop-flow elution).

2.2 Literature reviews

In 1987, Mirabella and Ford *et al.* [26] studied the cross- fractionation according to copolymer composition and molecular weight of C_4-LLDPE by using TREF technique and TCB as solvent. The polymer sample was dissolved in TCB at a concentration of 0.007 g/cc at 140°C. The polymer solution is deposited on a stainless steel column (250 mm x 10 mm I.D.) packed with an inert support, chromosorb P. The column is capped and cooled to room temperature at 1.5°C/h over about 3 days. The flow rate of TCB is 2.0 mL/min while the temperature is increased at 20°C/h. The four fractions were collected over the following temperature ranges 25-54, 54-81, 81-91, and 91-120°C. It was found that the branching content of each temperature ranges were 39.9, 15.6, 8.8, and 2.1 branches/ 1000 carbon, respectively.

In 1990, Springer and his coworker *et al.* [27] investigated the fractionation of LLDPE-1-butene copolymer by means of direct extraction and GPC. Solution crystallization was carried out in pure xylene at 23, 50, 65, and 80°C. The initial concentration was 8 g/L, and the total crystallization time took one day. The fractionation process was performed in seven steps using p-xylene as solvent. Extraction temperature was 125°C and BHT (2,6-di-tert-butyl-4-methylphenol) was chosen as stabilizer. It was concluded that the branching content of LLDPE were 25.2, 22.8, 0.0, 0.0, 20.0, 16.1, and 17.2 branches/ 1000 carbon. Both molecular weight and copolymer content can be obtained by using crossed-TREF technique.

In 1990, Wilfong and Knight *et al.* [28] studied on the crystallization phenomenon of spherulites of two C_8-LLDPEs by using TREF technique. The TREF system consisted of a stainless steel column (20 in. in length and 4 in. in diameter) packed with 0.028 in. stainless steel shot. The column was loaded by injecting a 0.5% solution of LLDPE in hot TCB. The polymer was crystallized onto the chromosorb P support as the solution was cooled at about 1.8°C/h. The column was then continuously eluted with TCB at about 40 mL/min while the temperature was increased at a programmed rate of 3.6°C/h. It was found that the branching content of two C_8-LLDPE were different in hexyl branch

concentration. LLDPE-A and LLDPE-B were fractionated into 12 and 17 fractions, respectively. The branching content of the LLDPE-A fractions ranged from 2.0 to 10.2 branches/ 1000 carbon and from 2.0 to 29.4 branches/ 1000 carbon for the LLDPE-B fractions. Moreover spherulites of the LLDPE fractions were less well developed, more uniform in size, and tended to progressively deteriorate and become smaller as the concentration of branches increased.

In 1993, Zhou and Hay *et al.* [29] studied the effect of branching distribution of LLDPE on molecular weight and heat properties by using crossed-fractionation chromatography combinating between TREF and SEC together. In TREF process, LLDPE was dissolved in xylene at a concentration of 0.05 g/cm^3 at 130°C, stabilized with Santanox R, and was then loaded on to the column preheated to 130°C. The column, filled with silica sand as support, was subsequently cooled to room temperature at a rate of 1°C/h. The different polymer fractions were eluted from the column by ramping the temperature from 40°C to 110°C in 5°C steps at a heating rate of 10°C/h. In order to achieve equilibrium elution, the column was kept at each temperature for 40 min. It was found that the degree of branching distribution did not influence on molecular weight but, the heat property did.

In 1995, Soares and Hamielec *et al.* [30] studied the microstructure of polyethylene. It displayed that TREF is a powerful technique for fractionating and characterizing semicrystalline polymers. When TREF is properly executed, it is regulated by the crystallinity of the polymer samples and is effectively independent of molecular weight and cocrystallization influences. Preparative TREF is a time consuming procedure but when combined with various complementary analytical techniques can provide very detailed information about the polymer microstructure. The information obtained by analytical TREF is more limited than that available from the preparative technique.

In 1995, Borrajo *et al.* [31] studied the modeling of fractionation process in TREF system. C$_4$-LLDPE and C$_6$-LLDPE, using Ziegler-Natta catalysts were examined. TREF of the copolymers was perfumed on a stainless steel column (300 X 80 mm I.D.) packed

with an inert support. Samples were dissolved in xylene (mixed isomers) at a concentration of about 0.012 g/mL, at 125°C, and deposited in the column. The column temperature was then slowly cooled down to 25°C, at 2°C/h. The column is kept at 25°C for a period of 4-5 h. The eleven fractions were obtained for each sample, by pumping xylene at column temperature, at 25°C, 40°C, 60°C, 70°C, 75°C, 80°C, 85°C, 90°C, 95°C, 100°C and 105°C. Solvent, 200 mL, were pumped through the column, at 10 mL/min, after allowing 30 min for equilibrium at the elution temperature. It was found that the results from model fit experimental TREF data, and correctly predict number average branch points for TREF fractions.

In 1996 Kim *et al.* [32] investigated the effect of branching distribution and heat behavior of HDPE on molecular weight distribution of not only unimodal but bimodal as well by using preparative TREF. The column is loaded with glass beads having a diameter of 2 mm, leaving a total free volume of 400 mL. The polymer sample was dissolved in hot xylene at a concentration of 0.015 g/cm^3, stabilized with BHT antioxidant, and then loaded into the column preheated to 132°C. The column was subsequently cooled to room temperature at the rate of 1.2°C/h. During the cooling of dilute solution of HDPE resin crystallizes onto the glass surface. The oil bath was heated at the rate of 10°C/h to the upper temperature of a desired range and was maintained at this temperature for 30 min. Six hundred milliliters of xylene, preheated to that temperature, was passed upward through the column at a flow rate of 1.5 mL/min and the eluted solution was collected as a fraction. The elution temperature ranges used in this study were as follows: 25-60, 60-68, 68-76, 76-84, 84-92, 92-100, 100-108, 108-120°C. It was found that the degree of branching distribution of four HDPE ranged from 0-5 branch/1000 C atom.

In 1996 Kim and Park *et al.* [33] studied the influence of short chain branching on the blown film properties of LLDPE. Preparative TREF was performed to characterize the SCBD of LLDPE. The polymer was dissolved in BHT stabilized hot xylene at a concentration of 0.015 g/cm^3 was crystallized from 132°C to room temperature at a rate of 1.2°C/h. The crystallized molecular species on glass beads were dissolved by heating

at a rate of 10°C/h to the upper temperature of a desired range. The elution temperature rages used in this study were as follows: below 55,55-60,60-65, 65-70, 70-75, 75-80, 80-85, 85-90, 90-95, 95-100, and 100-105°C. The yield of fractions eluted above 105°C was too poor to collect. From microstructure, it was found that not only mechanical strength but also morphology depended on the chain length of branching. Especially the dart drop impact strength, it was the highest when chain length was 8 C-atom. Whereas the Elmendort tear strength was increased when chain length was longer. In addition both chain length and branching distribution influenced on mechanical properties.

In 1996 Karoglanian and Harrison *et al.* [34] studied the similarity of compositional distribution information generated by differential scanning calorimeter (DSC) and TREF. In TREF process, the ultra low density polyethylene (ULDPE) sample was dissolved in hot TCB, to which was added heated inert support material (Chromosorb P). The polymer, support, and solution formed a sludge-like mixture which underwent controlled crystallization from 130°C to 30°C at a rate of 1.5°C/h at the same time and in the same oven as the previously mentioned DSC samples. During this cycle, separation on the basic of crystallizability occurs, in which the most crystallizable and least branched components crystallize first, followed by chains with increasing levels of branching and decreasing crystalizabilities. Six fractions were collected over the elution range, NMR was employed to determine branching content, and DSC to determine melting point. It was found that branching content of ULDPE ranged from 3.5-30.5 branches/1000 carbons.

In 1997, Mierau *et al.* [35] investigated the grafted impact-resistant polypropylene by TREF. The maleic anhydride grafted impact-resistant polypropylene, consisting of amorphous rubber and semicrystalline matrix were separated the rubber from the matrix by preparative TREF. The polymer samples were dissolved in xylene at 125°C and introduce into the column of the apparatus, packed with an inert support (ballotini, diameter about 200 μm). Subsequently, the column was closed and cooled to room temperature with a rate of 5°C/h. The following fraction was done with the same solvent by slow heating incremental steps of temperature and removing the polymer phases at

selected temperatures. The impact-resistant polypropylene was fractionated into three parts at the following temperature: 60, 96, and 128°C. It was found that TREF was an effective method to fractionate not only the virgin product, but also the modified one.

In 1998 Xu *et al.* [36] studied the effects of internal and external donors of four catalyst systems; $MgCl_2/TiCl_4$-$AlEt_3$, $MgCl_2$/di-*n*-butyl phthalate (DNBP)/$TiCl_4$-$AlEt_3$, $MgCl_2/TiCl_4$-$AlEt_3$/diphenyl dimethoxyl silane (DPDMS) and $MgCl_2$/DNBP/$TiCl_4$-$AlEt_3$/DPDMS using preparative TREF and ^{13}C-NMR . A 1 g sample of polymer and 3% antioxidant were added in a 1000 mL flask containing 250 mL xylene. The polymer was dissolved at 130°C. Sea sand was heated to the same temperature and added to the flask and maintained at 130°C for 2 hr. The mixture was cooled to room temperature at a rate of 1.5°C/h. The cooled sand wrapped with polymer was transferred into a steel column with a temperature controlling unit. The polymer was recovered by evaporating the xylene solvent and drying in a vacuum oven. It was found that electron donor had an important influence on the tacticity distribution of polypropylene sample. Some key fractions were characterized by ^{13}C-NMR. The results showed that the fractionation was performed mainly according to tacticity and that electron donors increased the percentage of isotactic fractions.

In 1998, Abiru *et al.* [37] characterized microstructure of propylene-butene-1 copolymer using TREF. One gram of polymer was dissolved in 150 of *n*-heptane with 0.1% of 2,6-di-*tert*-butyl-*p*-cresol (DBPC) as an antioxidant at 90°C in a 500 mL flask, and then 280 g of glass beads (a range of particle diameter of 75-125 μm) were added to the solution. The system was maintained at 90°C under rotation for 30 min and cooled to room temperature at 5°C/h. The *n*-heptane was then evaporated very slowly under reduce pressure. After complete removal of *n*-heptane, 200 mL of methanol was poured into the flask. Thus methanol slurry, containing glass beads coated with whole polymer, was obtained. The methanol slurry was packed into a double-walled glass column (30 mm I.D. 600 mm length) connected with the temperature controlling unit. The first fraction was obtained at 5°C by pouring approximately 400 mL of *n*-heptane into the column.. In this procedure, about 150 mL of *n*-heptane was needed to flush out the methanol from the

column. The temperature was then raised stepwise at an interval of $5^{\circ}C$ from 5 to $80^{\circ}C$. A typical volume of 400 mL of each fraction was collected in a 1000 mL beaker for 2.5-3 h. It was found that the solubility of polymer fraction is regarded as the main mechanism for separating polymer fractions using TREF. A propylene-butene-1 copolymer sample used was shown to have a wide butene-1 composition distribution from 12 to 47 mol%.

In 1998 Fonseca and Harrison *et al.* [38] investigated the co-crystallization of LDPE/HDPE blends using DSC and TREF. TREF was perfumed on pure LDPE, HDPE and LDPE/HDPE 75/25 blend. Polymers were dissolved at $160^{\circ}C$ in TCB and the loaded on to a heated inert support (Chromosorb P). Samples were either crystallized by quenching the hot slurry in an ice-water bath, or they were slowly crystallized in a microprocessor-controlled crystallization oven on reducing the temperature from $130^{\circ}C$ to $30^{\circ}C$ at a rate of $1.5^{\circ}C/h$. Subsequently, the mixture was loaded into a column, and placed in a elution oven. A controlled heating rate of $40^{\circ}C/h$ was applied simultaneously with an eluent flow rate of 4 mL/min. It was found that DSC and TREF of LDPE/HDPE blend manifested co-crystallization behavior when crystallization rates are high. The unique advantage of TREF is that it permits, for the first time, separation and analysis of those materials involved in the co-crystallization stage for those systems showing partial co-crystallization (multiple dissolution/melting peaks). In this case, it is possible to determine not only the relative composition of a LDPE/HDPE co-crystal, but also to demonstrate that only selected portions of the pure homopolymers are involved in co-crystal formation.

In 1999, Xu *et al.* [39] characterized the isotactic polypropylene prepared with dimethylsilyl bis(1-indenyl)zirconium dichloride supported on methylaluminoxane pretreated silica by preparative TREF. The polymers were dissolved in xylene at concentration of 0.005 g/mL at $130^{\circ}C$. This solution was deposited on an inert support (sea sand) packed in a steel column. The column was cooled to room temperature at a rate of $1.5^{\circ}C/h$. Then the deposited polymer was heated in incremental steps of temperature and eluted with xylene. Some of fractions were analyzed by ^{13}C-NMR, DSC and intrinsic viscosity. It was found that in the first seven fractions isotacticity had a

larger effect on the fractionation, but in the last six fractions molecular weight affected it predominantly.

In 1999, Wang *et al.* [40] characterized the C_8-LLDPE synthesized with constrained geometry catalyst by TREF. The sample dissolution and precipitation was carried in a 2 L glass kettle under ultra-high purity nitrogen. The weighed copolymer sample, about 1 g, 1 g of antioxidant Santanox R, and 0.6 L of celite chromosorb P were charged into the glass kettle with 1 L of TCB. After a 2 h dissolution at 140°C, the system was cooled down to room temperature at a constant rate of 1.8°C/h. The polymer coated support was then loaded into a TREF column (30 cm. X 5 cm I.D.). The first fraction was collected at the room temperature by filtering and washing the support with fresh TCB. Consecutive fractions were eluted by increasing the elution temperature stepwise to 130°C at a TCB flow rate of 2.0 mL/min. Some key fractions were analyzed by ^{13}C-NMR and DSC. It was found that the branching content of C_8-LLDPE ranged from 11-16 branches/1000 carbons. ^{13}C-NMR and DSC measurements showed that the short chain branching density decreased with increasing elution temperature and that a direct linear relationship existed between the melting temperature and the elution temperature.

In 2000, Silva Filho *et al.* [41] investigated C_4-LLDPE and C_8-LLDPE sample produced with a heterogeneous Ziegler-Natta catalyst using preparative TREF, crystallization analysis fractionation (CRYSTAF), GPC, DSC, ^{13}C-NMR and fourier transform infrared spectroscopy (FT-IR). In this study, preparative TREF was used to obtain fractions of narrow short chain branching distribution. Polymer samples, 2 g, were dissolved in 200 mL of ODCB at 140°C for 1 h in the presence of an antioxidant (BHT). The polymer solution was transferred to a steel column which was placed in a temperature-programmable oil bath (100 X 20 mm inside diameter) packed with silica. The crystallization step was carried out at a rate of 2°C/h from 140°C to 25°C. The elution step was carried out under ODCB flow by increasing the temperature discontinuously at a rate of 20°C/h in steps of 5°C, from 25°C to 140°C. It was found that the obtained results can be well understood with simple mathematical models that describe the number of active site types present on the catalyst used to produce these

polyolefins. Deconvolution of MWD measured by GPC and chemical composition distribution (CCD) measured by either analytical TREF or CRYSTAF leads to consistent results that indicated the presence of multiple site types on the catalyst. Analysis of preparative TREF fractions of these polymers by complementary techniques further support the modeling approach proposed herein.

In 2000, Hussein et al. [42] studied the thermomechanical degradation in the preparation of polyethylene blends. The rheological and GPC analyses were complemented by NMR, TREF, and DSC testing. In the TREF analysis, polymer sample (5 mg) was dissolved by immersion in o-xylene at 125°C for 4 h, followed by slow cooling rate to -8°C at a cooling rate of 1.5°C/h. The crystallized sample was then filtered into a TREF column containing 100 mesh glass beads. The TREF process was then initiated with passage of another solvent (ODCB) through the column as the column temperature was raised in order to extract the branched species from linear species according to their different solubilities as temperature changed. The temperature of the packed column was ramped at a rate of 1°C/h up to 125°C with a solvent flow at 1 mL/min. It was found that TREF profile of LLDPE shown the narrow peak at high temperature and a broad peak at lower tempetrature. This observation could be used to support the rheology and NMR data that suggested long chain branching cross-linked gels in LLDPE resins conditioned extra conditioned antioxidant.

In 2001, Viville et al. [43] characterized the molecular structure of two highly isotactic polypropylenes produced with different heterogenous Ziegler-Natta catalytic systems by preparative TREF, 13C-NMR, SEC and DSC. The polymer samples, 6 g, were introduced in a 1000 mL flask containing 300 mL of xylene stabilized with 1100 ppm Irganox 1010. The polymer was dissolved at 130°C for about 30 min. The hot polymer solution was then loaded into the inner part of the glass column. The solution was allowed to cool to room temperature at a rate of 2.4°C/h from 130 to 30°C. Extraction took place over temperatures ranging from 30 to 130°C/h, divided into 17 steps (30, 40, 50, 60, 70, 80, 90, 100, 103, 106, 109, 112, 115, 118, 121, 124 and 130°C). Polymer was eluted during 120 min at every step after the temperature had stabilized for 30 min. It was

found that TREF does not strictly fractionate PP according to tacticity, but according to the longest crystallizable sequence in a chain. ^{13}C-NMR, SEC and DSC analyses of the fraction demonstrated that the inter-chain tacticity distributions of the polypropylene were affected by the change of the polymer conditions.

In 2001, Quijada *et al.* [44] studied structure evaluation of copolymers of ethylene and 1-octadecene by using the temperature rising elution fractionation technique. The sample of ethylene-octadecene dissolved in ODCB crystallize by lowering the temperature at a rate of $2^{\circ}C/h$. The crystallize fractions are eluted according to a temperature gradient, i.e., as the temperature increases, the fractions having a higher crystalline content are eluted. The fractions eluted at predetermined temperatures are collected and analyzed separately. It was found that the branching content of polymer sample ranged from 26-39 branch/1000 carbons.

In 2002, Galland *et al.* [45] studied the influence of the reaction parameters on the composition of the metallocene-catalyzed ethylene copolymers. Samples not only C_6-LLDPE (A) and C_6-LLDPE (B) being different in molecular weight (21,700 and 85,900) but also C_8-LLDPE copolymers prepared using the metallocene catalyst *rac*-Et[Ind]$_2$ZrCl$_2$ were fractionated by preparative TREF and characterized by ^{13}C-NMR, DSC and GPC. The preparative TREF was used to obtain fractions of narrow short chain branching distribution for further analysis. A 2 g polymer sample was dissolved in 200 mL of ODCB at $140^{\circ}C$ during 1 h. BHT was added as stabilizer. The polymer solution was transferred to a steel column (100 X 20 mm ID) packed with inert material (silica) through which ODCB could be pumped. The crystallization step was carried out at a rate of $2^{\circ}C$ down to $25^{\circ}C$. The temperature was increased discontinuously at a rate of $20^{\circ}C/h$ in steps of 5 up to $140^{\circ}C$. For each fraction, 300 mL of solvent were pumped through the column, at 10 mL/min after allowing 20 min for equilibrium at the elution temperature. It was found that mol% of C_6-LLDPE (A) and C_6-LLDPE (B) ranged from 3.6-4.6 and 4.1-16.8, respectively. And mol% of C_8-LLDPE ranged from 3.6-4.1.

In 2002, Shan and his co-worker *et al.* [46] studied the mechanical properties of LLDPE-1-hexene copolymer prepared by using Ziegler- Natta and metallocene catalyst as a catalyst during polymerization. TREF was applied for this study. It exhibited that the polydispersity index of polymer prepared by metallocene catalyst was narrower than the conventional one. Moreover, the tensile strength of copolymer was controlled by the ratio of crystalline in the polymer sample.

In 2003, Zhang *et al.* [47] studied a terpolymer of propylene with low amounts of ethylene and 1-butene co-monomers. The polymers were fractionated by TREF. The preparative TREF system consisted of a jacketed column thermostated to $0.1^{o}C$ by calculating hot oil and a fractionation column with a free volume of 1250 mL made of a large double-walled glass condenser packed with fine glass beads. A 15 g sample were dissolved in 400 cm^3 of TCB at $140^{o}C$ and stabilized with antioxidant DBPC. The solution was transfused to the fractionation column from the top at $140^{o}C$. To make polymer molecule deposit around glass beads in layers step by step crystallizability, it took nearly 100 h for the column to cool from $140^{o}C$ to room temperature. The most easily crystallizable macromolecules precipitated first around the glass beads in the inner most layers. Molecular with least crystallinity precipitated last around the outermost layer. As the column was heated gradually, polymer fractions were eluted continuously from outermost layer to inmost layer, and collected in batches as temperature increased gradually stepwise from room temperature to $140^{o}C$. Some key fractions were analyzed by NMR, GPC, and DSC. It was found that the polymer fractions had narrow crystallization temperature distribution than the original sample, suggesting the results of TREF were excellented and polymer fractions uniform.

In 2003, Lugao *et al.* [48] characterized the gamma-irradiated high melt-strength polypropylene. The polymer sample, 2 g, was dissolved in 180 mL of ODCB over 1 h at $140^{o}C$. Sample was passed through a fractionating column heated to $140^{o}C$ then began the cooling rate at $12^{o}C/h$ to $25^{o}C$ when the first fraction was recovered. Heating commenced at $15^{o}C/h$ and fractions were taken at 40, 80, 100 and $140^{o}C$. It was found that TREF analyses showed very similar elution profiles, even where huge differences in

melt strength exist. High melt strength properties can be achieved only by increasing molecular weight or by the addition of long chain branching. Therefore, such modified molecules are likely to be partially cross-linked and partially branched.