Recent developments in polyolefin fractionations

by

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Abstract
Since the total polyolefin (PO) production exceeds 100,000 kiloton per year, while still showing an exponential growth, the PO research is one of the most important areas for both the academic world as the industrial companies. As a result of the increasing requirements in properties and performance of PO and the broadening of the application field by applying structural changes, using different catalysts within the polymerization process, the analytical requirements for complete characterization of polyolefin structures is challenging. Within this report several techniques for the characterization of the chemical composition of polyolefins are presented and compared.

The two main fractionation techniques available adsorption and crystallization are complementary to each other in terms of separation characteristics. For adsorption based fractionations high temperature high performance liquid chromatography (HT-HPLC) seems to be preferred over temperature gradient interaction chromatography (TGIC) because of the superior efficiency and separation power; however, HT-HPLC is limited to detection by evaporative light scatter detection (ELSD) whereas TGIC is applicable to a wide variety of detectors. Regarding the crystallization techniques, temperature rising elution fractionation (TREF), successive self-nucleation and annealing (SSA) and crystallization elution fractionation (CEF), it can be clearly stated that CEF performed better than TREF. Whether CEF is also preferred over SSA depends on the application, for a rough characterization of molecular properties, SSA might be sufficient, whereas CEF will give a more comprehensive view for somewhat longer analysis times. Also the choice between an interaction based or a crystallization based technique depends on the analytical question that has to be answered.

Another technique for polyolefin fractionations is so called cross-fractionations, where two -preferably orthogonal- separation techniques are applied in a comprehensive way. Regarding 2D separations, high temperature size exclusion chromatography (HT-SEC) coupled to HT-HPLC, in which the added dimension can physically separate the fractions, whereas it is actually applied as a molecular weight sensitive detector, shows to be a very promising technique for the separation of complex molecules especially when compared to TREFxSEC. Nevertheless, there are some inconsistencies between the molecular weight polydispersity determined by SECxHT-HPLC and those determined solely by SE. This shows that the newly developed technique -it was only introduced in 2010- still seems to show some teething problems; which will most likely be resolved in the upcoming years, making this an extremely powerful techniques for complex polyolefin characterizations.

Apart from SEC combined to another technique for either crystallization or adsorption/interaction based fractionation, due to the complementarity TGICxCEF or even SECxCEFxTGIC might be good combinations for a more complete characterization of polyolefin.
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1. Introduction
Some of the most important commodity polymers are polyolefins (PO). Particularly polyethylene (PE) and polypropylene (PP) are globally the major plastic materials. The PO production exceeds 100.000 kiloton per year, while still showing an exponential growth [1]. The importance of PE and PP in the world-market of plastics is related to the diversity of possible structural differences and their influence on the end characteristics of the polymer. One of the main catalyst species in the polymerization of PO is the Ziegler-Natta catalyst, which was discovered in the early 1950s. This catalyst led to a drastic reduction of the production costs, and enabled synthesis of new types of polyolefins. Further optimization of this catalyst throughout the years resulted in very active and stereospecific catalysts, which, in combination with improved processing techniques, led to a broad range of possible applications for PO. As a result, polyolefins can now fulfill the full range of polymeric demands, from hard thermoplastics to soft elastomers, while still using solely ethylene and propylene as building blocks.

In order to tailor the properties of the polymer to the required application, it is vital to correlate end properties of the polymer with molecular characteristics as measured by analytical techniques. Several studies towards the effect of molecular characteristics on polymer properties have been conducted in the past. Especially the effect of copolymerization and stereo- and region-defects, as studied by De Rosa et al. [2-4], on the properties and crystallization of PP increased the understanding.

Just like polymers consisting of a single monomer, like PE or PP, a polymer can also consist of different monomers; in that case it is referred to as a copolymer. A copolymer is built from different monomeric units, resulting in a different composition. If ethene is polymerized with the addition of α-olefins (mono-unsaturated paraffins with the double bond in the first position, e.g. 1-hexene), only two carbons of the α-olefin become part of the backbone, while any additional carbons will be observed as a side chain. This leads to a short chain branching distribution (SCB or SCBD) since the comonomer will be built into the polymer at random locations.

The distribution of the α-olefin along the polymer chain is particularly important, since many copolymers can exhibit highly heterogeneous intra- and/or inter-molecular-co-monomer distributions [5]. The development of reliable techniques to characterize the short chain branching distribution (SCBD) has been the goal of many researchers in the field, especially because both the physical and mechanical properties are highly influenced by the SCBD.

Within polymer characterization, important properties are the molecular weight distribution (MWD), the chemical composition distribution (CCD) consisting of the SCB, comonomer content, etc. and the molecular topology, e.g. long chain branching (LCB). For the characterization of the MWD, first of all there is size exclusion chromatography (SEC), which for decades is the main tool, used for the characterization of MWD, LCB and SCB. In SEC, the sample is passed through a column filled with particles with a range of different pore sizes. The separation in SEC is based on hydrodynamic volume, which determines whether or not a molecule fits in the pores. Large molecules, not able to penetrate
the pores, pass in between particles and elute first, while the smallest molecules fit in all the pores, and thus have a longer pathway, these will elute last.

Another of these techniques is Field Flow Fractionation (FFF), which is a separation technique in which a flow passes through a narrow channel, while, perpendicular to that flow a second field (e.g. thermal gradient) is applied, separating the compounds over the width of the channel. As a result of the laminar flow through the channel, high flow speed in the middle, zero flow at the wall, the elution time, and thus separation, also depends on the position of the compound within the channel, enhancing the separation. This technique was already developed in 1966 by Giddings [6], and can be used as a tool to determine the molecular weight distribution, similar to SEC. Furthermore there are some additional MWD based separation techniques like molecular topology fractionation (MTF), slalom chromatography and hydrodynamic chromatography (HDC); these are however not further discussed within this report.

One of the main techniques for the characterization of the CCD is temperature rising elution fractionation (TREF), introduced by Wild et al. [7], in 1991. This separation technique is based on crystallization of the polymer, which is again linked to the SCBD. After slowly crystallizing a polymer from solution onto an inert support, e.g. glass beads, the polymer is dissolved and eluted at successively rising temperatures. As a result of the slow crystallization, the influence on the molecular weight is limited, since separation is mainly determined by differences in crystallinity dependant on e.g. SCBD differences.

Owing to the long measurement times of TREF, other techniques, similar to TREF have been developed. One of these techniques is so-called crystallization analysis fractionation (CRYSTAF) [8] (1994), which is in principle the same as TREF; however, CRYSTAF monitors the concentration of the polymer in solution during the crystallization stage, whereas TREF monitors the concentration of the polymer in solution during the elution stage. Thus, CRYSTAF simply skips the elution step which is performed in TREF, resulting in shorter analysis times. However, since the crystallization in TREF is the most time-consuming, CRYSTAF still has a significant analysis time. Another method similar to TREF is crystallization elution fractionation (CEF), which is more or less an improved version of TREF with shorter analyses times and higher resolutions. The difference between TREF and CEF is the fact that during crystallization a low flow rate is applied. Subsequently, just like with TREF the temperature is gradually increased for elution of the compounds. The addition of “pre-fractionation” during the precipitation process, leads to an increased resolution.

Apart from TREF, CEF and CRYSTAF which make use of a solvent during fractionation, some other techniques do not require a solvent for the fractionation of polymers by CCD. These techniques, called thermal fractionation techniques, are able to fractionate a polymer as it is, by melting and solidifying the polymer itself. These techniques, e.g. successive self-nucleation and annealing (SSA) and stepwise crystallization (SC), are performed in combination with differential scanning calorimetry (DSC) as analytical tool. A method similar to SSA-DSC was first introduced by Gray et al. [9], in 1964, whereas SC-DSC was first shown by Varga et al. [10] in 1976. SC-DSC, as the name implies, step-wise cools down the polymer, after heating it above the melting temperature, until it completely solidifies. SSA-DSC also
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starts with heating the polymer above the melting temperature, to subsequently cool-down until complete solidification, however, after the cool down the polymer is heated again to a temperature slightly lower than the previous melting temperature, followed by a new cooling step. This process is then repeated several times.

Furthermore there are two, interaction based, CCD separation techniques, being high temperature high performance liquid chromatography (HT-HPLC) and temperature gradient interaction chromatography (TGIC). As the name already implies, HT-HPLC is a HPLC method, ran at higher temperatures, typically above 100°C, and as in most HPLC methods, the elution is performed isothermally using a solvent gradient. For HT-HPLC this concept has not changed, however, TGIC, which was proposed as a method only very recently, uses a temperature gradient, as already implied by the name, which is the opposite of HPLC, since TGIC is performed isocratically. For both HT-HPLC and TGIC, the separations are based, among others, on a combination of the interaction between the stationary phase and the molecules, and the solubility of the molecules in the mobile phase.

In order to further enhance separation capabilities, several groups are publishing work regarding so-called cross-fractionations. These cross-fractions are basically two dimensional separations, e.g. SEC-TREF to get a two dimensional plot of the MWD on the x-axis and the SCBD of copolymers, or the tacticity of PP, on the y-axis.

Increased complexity in polymer composition requires improved analytical techniques for correct characterization. With a technique like SEC, HDC or FFF, a fractionation can be performed which is mainly based on the molecular weight distribution (MWD) of the polymer, however, based on the scope of this research, MWD separation techniques will not be further discussed. Since TREF methods are currently up and running within DSM Resolve, a movement towards CRYSTAF, which offers similar results within a slightly shorter time-span by compromising the resolution, does not seem viable; therefore also CRYSTAF is not further discussed within this report.

In the upcoming chapter, some general information about polymers is presented. Chapter 3 contains the crystallization based fractionation techniques like TREF and CEF; furthermore SSA and SC as thermal fractionation techniques will be compared and discussed. In the subsequent chapter more details will be given about the interaction based separation techniques TGIC and HT-HPLC. Chapter 5 will discuss developments regarding cross-fractionations followed by an outlook for polyolefin fractionations in chapter 6. In chapter 7 the findings will be concluded and recommendations will be made.
2. General information
In this chapter some general information regarding the discussed topics is.

2.1. What Are Polymers
A polymer, also referred to as macromolecule, consists of a repetition of a single type, or a few different types, of building blocks, the so-called monomers. These polymers are synthesized through the process of polymerization, the reaction of monomer molecules in a chemical reaction forming polymer chains. Butane and hexane could already be seen as a polymer consisting of two or three ethene monomer building blocks respectively, although these molecules are not produced through a polymerization process.

Regarding the origin of polymers, they can be divided in three different groups:
- natural polymers, e.g. cotton
- semi-synthetic polymers (produced from natural polymers), e.g. cellulose
- synthetic polymers (polymerization reaction of monomers), e.g. polyethylene

The chain of a polymer can be built from a single type of monomer, resulting in a so-called homo-polymer, or from a combination of different types of monomers, resulting in a so-called co-polymer. For copolymers there are several different categories: random, alternating, block and graft copolymers, as shown in Table 1. Whereas for random and alternated copolymers the name already implies its distribution, block copolymers have a linear chain in which different units at different length of the same monomer, while graft copolymers have a branched chain with a different monomer in the branch than in the backbone.

<table>
<thead>
<tr>
<th>Type of copolymer</th>
<th>Skeletal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graft</td>
<td>B-B-B-B</td>
</tr>
<tr>
<td></td>
<td>B-B-B-B</td>
</tr>
</tbody>
</table>

Apart from the skeletal structures, polymers can also be classified in three groups based on properties:
- Elastomers
  - Elastic, stretchable, rubberlike polymers with high amount of crosslinking; cannot be reshaped after curing.
- Thermosets
  - Network structure resulting in rigid material; cannot be reshaped after curing.
Thermoplastics (either crystalline [ordered structure] or amorphous [unorganized])

- Linear of branched structured polymers which are solid when cooling and melt while heating, enabling the possibility to reshape the polymer.

Crystalline polymers show an ordered structure, having parallel chains in the solid phase, whereas amorphous polymers are incapable of creating this organization, leading to uncontrolled folding of the chain. Since the crystallization of thermoplastics is not a straight forward process the polymers become semi-crystalline materials, as shown in Figure 1. Since crystalline materials are hard and rigid and amorphous materials are hard and elastic, the semi-crystalline materials result in strong and ductile polymers.

![Figure 1: Semi-crystalline polymer with crystalline and amorphous regions.](image)

2.2. What Are Polyolefins

Examples of thermoplastics are polyolefins (PO), which are among the most important commodity polymers. Particularly polyethylene (PE) and polypropylene (PP) are major global plastic materials. Polyolefins are produced using olefins (unsaturated paraffins) as monomer building blocks. Some product examples in which PO’s are used are shampoo bottles, plastic foil, films, gas pipes and garden furniture.

For polyethylene several different polymerization methodologies are used in order to obtain different structures and densities. Some examples of polyethylene are high density poly ethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and very low density polyethylene (VLDPE), as illustrated in Figure 2. Whereas HDPE is unbranched resulting in a high crystallinity, LDPE is strongly branched which results in a more amorphous character. In LDPE the crystallinity is hindered by long chain branching (LCD) whereas LLDPE is more hindered by short chain branching (SCB), as a result of the branched chain not fitting into the crystals.
2.3. Properties of Polyolefins

Properties of polyolefins can be divided into two categories. The material properties which are the properties at the macroscopic level; the properties observed and utilized in normal day life; within the scope of the research the material properties like the tensile strength or Young’s modulus are not further discussed. Additionally the polyolefins have specific molecular properties which are influenced by the used catalyst, co-monomer, process parameters, additives, etc. These molecular properties require complex analytical techniques, however, even with all available analytical techniques; full characterization and full understanding of the functioning of a polymer might still remain vague.

2.3.1. Material Properties of Polyolefins

The material properties can be divided into mechanical properties and phase properties. Within the material properties of polyolefins solely the phase properties melting point and glass transition temperature are briefly described within this report, since these are the characteristics determined by DSC. For other material properties like the tensile strength or the Young’s modulus (mechanical properties) other literature should be consulted.

Regarding the phase behaviour, an important aspect is the melting point of the polymer ($T_m$). For polyolefins the melting point, which refers to a transition from (semi-)crystalline towards amorphous, is taken into account as a characterization parameter as a result of the broad melting point range of polyolefins, approx. 165°C for PP and approx. 130°C – 105°C for PE depending on crystallinity; higher crystallinity results in a higher melting temperature.

Another property of phase behaviour is the glass transition temperature ($T_g$), which is the temperature at which the polymer changes from a glassy state into a liquid and/or rubbery state. At low temperature the polymer exists in the glassy / solid state. After reaching the glass transition temperature, the polymer chains gain movement and change conformation. By increasing the temperature above the glass transition temperature, some polymers will melt and the polymer chains can move freely. The glass transition temperature can be influenced by altering the degree of branching or crosslinking. Another method of influencing the $T_g$ is the addition of plasticizers into the polymer.

Figure 2: Different types of PE and their density and crystallinity.
2.3.2. Molecular Properties of Polyolefins
Polyolefins can be generally divided into homopolymers, consisting of a single type of monomer and copolymers, consisting of several different types of monomers. Based on this division, the molecular properties can be divided into properties applicable to all polyolefins, or those only applicable to copolymers.

2.3.2.1. Applicable To All Polyolefins
The molar mass distribution, crystallinity and additives are molecular properties that are applicable to all polymers.

2.3.2.1.1. Molar Mass Distribution
A very important property of polyolefins or even polymers in general, is the molar mass distribution. This value quantifies the average molecular mass of a polymer. With respect to the average molecular mass, it can be calculated in different ways, one being the number average molecular mass (\(M_n\)), in which the molecular mass is simply calculated by dividing the sum of the different molecular masses (per molecule) by the number of molecules, as shown in Equation 1.

\[
M_n = \frac{\sum M_i N_i}{\sum N_i}
\]

Another method is the calculation of the weight average molecular mass (\(M_w\)), which corresponds to the average weight of a monomer which is present within the polymer. The average molecular mass (\(M_w\)) is calculated as shown in Equation 2.

\[
M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i}
\]

The third method for the calculation of the molar mass is the Z average molar mass (\(M_z\)), which correlates more to the higher molecular weight parts of the molecular weight distribution. In general the \(M_n\) corresponds to the lower molecular mass fraction, the \(M_w\) gives information about the middle of the molecular mass distribution and the \(M_z\) represents a value of the higher molar mass range. The Z-average molecular mass (\(M_z\)) is calculated as shown in Equation 3.

\[
M_z = \frac{\sum M_i^3 N_i}{\sum M_i^2 N_i}
\]
The correlation between the weight average molecular mass ($M_w$) and the number average molecular mass ($M_n$) is called the polydispersity. The polydispersity is a method for distinguishing between a narrow and a broad molecular weight distribution within a polymer. The polydispersity index (PDI) can simply be calculated by Equation 4, and represents the width of the molar mass distribution.

Equation 4

$$PDI = \frac{M_w}{M_n}$$

2.3.2.1.2. Crystallinity

Furthermore, crystallinity as discussed in chapter 2.1 is an important factor in the characterization of polyolefins. The crystallinity refers to the structural order, which has an influence on for instance the hardness, density, transparency.

2.3.2.1.3. Additives

Another molecular property of polymers, which have an influence on the material properties are the additives added to the polymer. Some examples of additives added to a polymer are:

- Plasticizers, which are used to influence the $T_g$.
- Stabilizers, used to make the polymers more resistant to temperature-driven oxidation.
- Talc is added to influence crystallinity and thus the modulus of the polymer.

2.3.2.2. Applicable To Copolymers Only

The molecular properties as described below require the use of different monomer types, and are therefore only applicable to copolymers.

A copolymer is built from different monomeric units, resulting in a different composition. If ethene is polymerized with the addition of $\alpha$-olefins (mono-unsaturated paraffins with the double bond in the first position, e.g. 1-hexene), only two carbons of the $\alpha$-olefin become part of the backbone, while any additional carbons will be observed as a side chain. This leads to a short chain branching distribution (SCB or SCBD) since the comonomer will be built into the polymer at random locations or in more blocky sequences.

If during the polymerization process a low concentration of diolefine (e.g. butadiene) is dosed into the reaction of ethylene, the butadiene can react with two ethylene molecules, one being part of the polymer backbone and the other leading to a side chain formed on the additional in-saturation from the butadiene, this results in the so-called long chain branching distribution (LCBD) and/or network formation, e.g. polybutadiene rubber.

Another aspect is the chemical composition distribution (CCD) or the sequence distribution (SD) which is the order of the different monomers within the polymer. When performing a block polymerization, this is called the block length distribution (BLD), which corresponds to the block lengths of the different
monomeric units within the polymer backbone. These distributions are of course also related to the SCBD, since the different units will give different branches and thus influence the SCBD.

Furthermore there are some other monomeric distributions, like the grafting distribution (monomer A in the backbone with different side chain lengths of monomer B) and the functional type distribution (end-group distribution); a schematic overview is given in Figure 3.

**Figure 3:** Schematic view of different distributions in polyolefins; A and B are monomeric units, C and D are end groups; reprinted from [11].

### 2.3.2.3. Applicable To Homopolymers Only

The tacticity distribution is an example of a molecular property which is only applicable to homopolymers. In case of a polyethylene, the monomer, ethylene, is completely built into the polymer backbone, as shown in Figure 4. In case of polypropylene the additional methyl-group of the monomer can be located on both sides of the backbone, which leads to stereo chemical distributions, referred to as tacticity. There are three different types of tacticity sequences, being syndiotactic, all methyl groups on the same side, isotactic, the methyl groups on alternating sides, and atactic which corresponds to a random arrangement, as shown in Figure 5.

**Figure 4:** Ethylene built into polymer backbone.

**Figure 5:** Tacticity of polypropylene, a) syndiotactic, b) isotactic and c) atactic distribution.
2.4. Characterization of Polyolefins

Looking at the different molecular and material properties as discussed in the previous chapter, it can be expected that a complete characterization of polyolefins is a complex science, especially, since the list of the properties as discussed can be further extended by for instance morphological properties and molecular topology. For the characterization of the molecular properties as discussed above, a short overview is presented in Figure 6 below, in which different characterization techniques are connected to the different aspects of the polymer properties. Out of these properties, the main focus within this report is the characterization of the chemical composition distribution or the short chain branching distribution.

![Diagram showing characterization techniques for polyolefins](image)

Figure 6: Overview of some of the properties of a polyolefin including characterization techniques. TGIC=Temperature Gradient Interaction Chromatography; HT-HPLC: High Temperature High Performance Liquid Chromatography; NMR: Nuclear Magnetic Resonance Spectroscopy; CRYSTAF: CRYSTAlisation Fractionation; CEF: Crystallization Elution Fractionation; TREF: Temperature Rising Elution Fractionation; DSC: Differential Scanning Calorimetry; SSA: Successive Self-nucleation and Annealing; SC: Step-wise Crystallization; SEC: Size Exclusion Chromatography; FFF: Field Flow Fractionation and HDC: HydroDynamic Chromatography.
2.5. Detection & Quantification

In this paragraph a few details are given about some of the detectors commonly used for the macromolecular detection and quantification. With most of the fractionation techniques discussed in the upcoming chapters one or more of these detectors can be coupled in order to acquire specific information. In general the detectors can be divided in three categories:

- Concentration detectors (e.g. infrared, evaporative light scattering detector and refractive index detector), used for quantification.
- Mass sensitive detectors (e.g. light scattering detector and viscometer), used for the molar mass determination.
- Chemical composition detectors (e.g. infrared detector).

2.5.1. Infrared Detector

The infrared detector, as the name already states, is a detector sensitive to infrared radiation of the passing effluent. Infrared radiation (700nm – 1mm) is similar to visible light (380nm – 700 nm), although, due to the longer wavelengths in infrared they are not visible for the human eye. The advantage of infrared is that the absorbed wavelength is dependent of the chemical neighbourhood of the atom. Therefore, apart from solely quantitation, this detector can also be used for identification purposes. A disadvantage is the fact that this detector is sensitive to the background, e.g. the used solvent; furthermore the infrared region has lower intensity photons leading to lower sensitivities.

2.5.2. Viscometer

The viscometer is a detector which measures the intrinsic viscosity of the passing effluent, which can be used for the determination of the molecular size, conformation and structure. Since different solvents have different viscosities, the viscometer can only be used in setups using a single solvent.

2.5.3. Evaporative Light Scattering Detector

The idea behind the evaporative light scattering detector (ELSD) is the possibility to evaporate the solvent, whereas the polymers do not evaporate. The not-evaporated polymers are then transported as a smoke into a lamp or a laser beam, with a light sensitive detector measuring the scatter of the laser beam. This detector, however, is not linear with concentration and furthermore, while using different solvents, e.g. a gradient during a HT-HPLC run, the sensitivity during the run might vary slightly.

2.5.4. Refractive Index Detector

The refractive index (RI) is a measure for the propagation of radiation through a medium. The RI detector measures the change in RI of the column effluent passing through the flow cell. The sensitivity of the RI is highly dependent of the RI difference between the reference and the effluent passing through the cell. Furthermore, since different solvents have different RI’s the RI detector cannot only be applied for single solvent chromatographic setups.
2.5.5. Light Scattering Detector

With the light scattering detector, the Rayleigh scatter of the polymer in the effluent is measured under one or more angles. This is a measure for both the molecular weight and the concentration, which can be deducted by using the Zimm equation, as shown in Equation 5.

\[
\frac{KC}{R_\phi} = \frac{1}{MP_\phi} + 2A_2C
\]

In which \( C \) = concentration; \( A_2 \) = second virial coefficient of solution; \( R_\phi \) = excess of Rayleigh scatter; \( M \) = molecular weight; \( P_\phi \) = particle scattering factor and \( K \) = composite of optical and fundamental constants.
3. Crystallization Based Fractionation Methods

In this chapter the theoretical aspects of the crystallization based fractionation methods temperature rising elution fractionation (TREF), crystallization elution fractionation (CEF), stepwise crystallization (SC) and successive self-nucleation and annealing (SSA), are discussed.

3.1. Temperature Rising Elution Fractionation

Temperature Rising Elution Fractionation (TREF) is an often applied method for polyolefin fractionations. The separation within TREF is based on the crystallizability of the polymer chains. Since most polyolefins are crystallizable, TREF is a well suited technique for the fractionation of these polymers.

TREF consists of several steps; initially the sample is dissolved in a high boiling point solvent, e.g. xylene or trichlorobenzene (TCB). This step can be performed at normal heating rates, since the speed is not critical for the end result. The polymer solution is mixed with an inert support, e.g. glass beads; this procedure takes place within a column, of which the temperature is controlled. In the next step the temperature is slowly decreased. Typical cool down rates are around 0.1°C per minute, resulting in very long cool down times.

The effect of cooling is crystallization of polymer as function of crystallinity. At a lower temperature, the less crystalline part remains dissolved whereas the more crystalline part will precipitate. If the cooling process is too fast, co-crystallization of fractions which have different crystallinities can occur. During this cool down process, layers of different crystalline fractions, almost independent of the molecular weight [12], are deposited on the inert support. As schematically illustrated in in Figure 7 (reprinted from [12]), the most crystalline fraction forms the inner layer and the least crystalline fraction the outer layer.

Figure 7: Schematic view of an inert support coating with different crystalline fractions of a polymer, after the TREF cooling process, reprinted from [12].

Subsequently to the cooling process a temperature increasing program is started in combination with a solvent flow, in order to elute the fractions, as illustrated in Figure 8. Initially the least crystalline (or most amorphous fraction) will elute, whereas the highest crystalline fraction will only dissolve at high temperatures and thus elute last.
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TREF can be performed on an analytical scale (a-TREF) or preparative scale (p-TREF). For a-TREF [13-22], online detection is performed during the fractionation, this typically results in a TREF curve, as shown in Figure 9. On-line detection of analytical TREF can be performed by e.g. an infrared detector, a light scatter detector, a viscometer or a refractive index detector (see paragraph 0). With p-TREF [15, 23-33] no detectors are used. The aim is to separate larger amounts of fractions as a function of temperature.

This allows to subsequently performing additional analytical techniques like NMR or DSC. In literature, initially TREF was performed as analytical technique, however, over the years the use of analytical scale TREF seems to stabilize, whereas the preparative scale TREF shows an upwards trend. This trend is an indication for the increased complexity of the samples, and therefore the increased demands on the analytical techniques, and for that purpose preparative TREF is a very powerful technique in order to strengthen the power of other techniques like NMR.

TREF is an effective method for blend and copolymer separation [7, 15, 34]. The crystallinity of ethylene copolymers is mainly based on the short chain branching content, TREF chromatograms shows a separation based on the short chain branching distribution (SCBD), which provides information about the polymerization mechanism and nature of the catalyst.

For polypropylene (PP), the crystallinity is mainly based on the stereoisomerism. Analysing PP by means of TREF will therefore give information about the tacticity distribution of the PP. However, due to a lack
of reliable calibration curves isotacticity determinations are usually performed by preparative TREF in combination with NMR [12, 26-28].

As proven by Tso et al. [16], TREF coupled to a series of detectors, offers insight into the heterogeneity of resin blends by infrared detection, in combination with some molecular weight information from the viscometer and light scattering detector. With these three detectors coupled in series, the so-called 3D-TREF is a rather powerful technique for the characterization of polyolefins. However, the main disadvantages of TREF are the inability to fractionate amorphous samples, the appearance of co-crystallization and the time consumption.

In an article of Gabriel et al. [21], the comparison of TREF, CRYSTAF and DSC (upcoming chapter), and showed similar results regarding the SCBD of LLDPE. The main advantage of TREF is the high resolution and the excellent separation of differently branched components in PO, as shown in Figure 10 [35], however, Figure 11, originating from [21], shows a superior resolution and separation power for DSC, compared to TREF. Furthermore it should be noted that the cooling time for TREF was as low as 0.03 K/min, whereas the DSC was cooled at a rate of 0.1K/min. Thus the work of Gabriel et al. seems to show superior performance of DSC over TREF, unlike what is shown in Figure 10, originating from Vela Estrada et al. [35], while being less time consuming. This was demonstrated for respect to the comonomer distribution of LLDPE; however, for the investigation of polyolefin blends the combination of the three methods is found to be recommendable. Additionally it should also be noted that the principle of separation in TREF and DSC are different, whereas TREF uses a solvent, DSC does not, while crystallinity of the polymer can differ based on the presence of solvent.

Figure 10: Overlay of TREF, CRYSTAF and DSC for the SCBD of a Ziegler-Natta-LLDPE, reprinted from [35].
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Overall analytical scale TREF seems to be a well-established but rather slow method for the determination of short chain branching distribution or tacticity, based on a separation as function of the crystallization. The separation power and resolution seems to be rather low, but the advantage is the use of a single solvent, making use of more detectors easier, resulting in more characteristic information from a single analysis (3D-TREF). Furthermore, the calculation of the composition of a polyolefin blend by use of a model is more easy for TREF. As a result of the relatively low resolution in combination with the long analysis time, a more recent technique, crystallization elution fractionation (CEF) will be preferred over TREF, and therefore it can be expected that the use of analytical scale TREF will slowly decrease.

Preparative scale TREF on the other hand is a very useful, but also time-consuming and labour intensive, technique for generating relatively large fractions of the polyolefin, rendering it capable of performing less sensitive techniques like $^{13}$C-NMR, although, with the enhanced sensitivity of cryo-probes used for NMR, the sample requirements have decreased, which might results in CEF offering sufficient sample loading and fractionation capabilities. Even the use of on-line CEF-NMR might be introduced; however, as long a p-TREF will be used, a-TREF will be required for the determination of the elution profile in order to select the correct fractions.

Overall it can be concluded that TREF is a powerful fractionation technique, but it has a few disadvantages being:
- Inability to fractionate amorphous samples (>8-10% comonomer); this can also be seen as an advantage in order to easily quantify the amount of amorphous structure within a polymer
- Co-crystallization can occur
- Long analysis time

Figure 11: left, mLLDPE/mHDPE/PP blend analysed by TREF and DSC; right, metalloocene mLLDPE by means of TREF and DSC, reprinted from [21].
3.2. Crystallization Elution Fractionation

One of the most recent developments in crystallization based separation techniques is crystallization elution fractionation (CEF), introduced by Monrabal et al. [36, 37]. CEF is a method similar to TREF. While comparing CEF to TREF the difference is the use of a small flow over the system during the crystallization phase which results in an initial separation based on the crystallinity. Afterwards for both CEF and TREF the elution phase is initiated, in case of TREF the sample is still not fractionation whereas with CEF a “pre-fractionation” has taken place, which is further improved during the elution step where the system is slowly heated, as explained in the previous chapter discussing TREF. The total process is illustrated in Figure 12.

![Separation principle within TREF (top) and CEF (bottom); CEF adds separation during the crystallization stage, resulting in improved separation in the end, reprinted from [36].](image)

One of the advantages of CEF over TREF and CRYSTAF is the increased analysis speed (as low as 30 minutes per sample), furthermore CEF can be performed on a typical TREF instrument and can thus be used in combination with viscometry, light scattering, composition and molar mass sensitive detectors. Another advantage is that the separation can be improved by tuning the experimental conditions according to the crystallization range of the sample. And since the increased separation of CEF over TREF is originating from the separation during crystallization, optimizing these parameters has a significant effect on the end result.

Monrabal et al. [37] also discussed a solution for the reduction of co-crystallization with CEF, by performing multiple cycles of crystallization and elution, which also led to an increase in resolution apart from the decrease of co-crystallization.

Suriya et al. [38] compared the performance of CRYSTAF and CEF, and concluded that CEF is more robust and has less co-crystallization than CRYSTAF. Furthermore CEF requires shorter analysis times for similar resolutions as achieved within CRYSTAF.
Overall CEF proves to be a good “upgrade” from the existing TREF methods, resulting in similar or improved resolution achieved in a shorter analysis time with less co-crystallization. The incapability of separation of more amorphous samples will still be present, although this can be seen as an advantage since the quantification of an amorphous phase within a polymer can be performed with ease.
3.3. Successive Self-Nucleation and Annealing & Stepwise Crystallization

Both stepwise crystallization and successive self-nucleation and annealing (SSA) are techniques usually performed prior to a Differential Scanning Calorimetry (DSC) measurement resulting in SC-DSC or SSA-DSC. DSC is a thermal analysis technique in which the difference in heat flow rate to the sample and to a reference sample is measured, while they are subjected to a controlled temperature program. DSC can be applied for e.g. the characterization of materials, the analysis of the thermal transitions within a sample, the determination of oxidative stability, the determination of the purity of substances and to analyse the influence of a catalyst on a reaction.

There are basically two ways to perform DSC, heat flux DSC and power compensation DSC. Heat flux DSC uses a single oven to heat both the reference material and the sample material by means of thermal conduction, as illustrated in Figure 13. During this process the heat delivered towards the sample and the reference, the heat capacity, is measured.

![Figure 13: The furnace of a (disk-type) heat flux DSC; S is sample, R is reference, reprinted from [39.]](image)

Unlike heat flux DSC, power compensation DSC consists of two separate furnaces, as illustrated in Figure 14. Both are constantly kept at the same temperature, thus during a change in the sample, the heat requirement in order to maintain a stable temperature changes. These changes are appearing as deviations of the DSC curve.

![Figure 14: The furnace of a power compensation DSC; S is sample, R is reference, reprinted from [39.]](image)

For simple samples the DSC will result in thermograms, the visualization of the analysis result of a DSC run, with a single peak (Figure 15 a), whereas for (semi-)crystalline polymers multiple melting peaks are frequently observed.
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The influence of the thermal history of polyethylene on the melting curves has been reported back in the 60’s by Gray et al. [9]. Based on these findings, the use of a thermal fractionation (temperature based fractionation performed within the polymer itself) prior to DSC might be a possible alternative to temperature rising elution fractionation (TREF) [7] or crystallization analyses fractionation (CRYSTAF) [8]. In order to “introduce” thermal history into the polyethylene, several methods have been developed out of which stepwise crystallization (SC) [14, 41-48] and successive self-nucleation/annealing (SSA) [5, 26, 47, 49-58] are the most common. SSA is widely used for characterization of the microstructure of polymers, mainly for the VLDPE (very low density polyethylene) and LLDPE (linear low density polyethylene), nevertheless, in some articles also the characterization of HDPE (high density polyethylene) [59, 60] and iPP (isotactic polypropylene) [26, 27] are performed by SSA-DSC.

Both stepwise crystallization and successive self-nucleation/annealing are methods for the thermal fractionation of polymers prior to the recording of a DSC thermogram. Stepwise crystallization is a method in which the sample is heated above the melting point to subsequently, in steps of

Figure 15: a) Single peak thermogram of HDPE, reprinted from internal document; b) overlay of several more complex DSC thermograms, b) reprinted from [40].
approximately 5°C, slowly cool down (up to a few hours per step) the sample. This results in structured crystallization.

The effect of performing stepwise crystallization on the polymer, prior to the DSC analyses, is illustrated in Figure 16 (DSC thermogram without SC) and Figure 17 (DSC thermograms after performing SC). It can be concluded that the SC does significantly enhance the resolution of the m-VLDPE, whereas the effect for the m-LLDPE is visible, but it seems to be less effective. Furthermore, the stepwise crystallization method used by Razavi-Nouri et al. was performed with 10 steps (385-340K) for the m-LLDPE and 14 steps (385-320K) for the m-VLDPE, each step consisting of 2 hours of crystallization time. Including sample handling, warming and cooling periods, it took approximately 24-36 hours per sample to perform the stepwise crystallization.

The resulting thermogram is a measure for the required melting energy. This can be either a positive (Figure 15) or a negative (Figure 16 & Figure 17) value. The energy required for melting the sample is an indication for the quantity of sample that melts at a certain temperature. After performing thermal fractionation like SC or SSA the sample starts showing several melting peaks. These peaks represent the different fractions of the sample with their own melting temperature. The intensities represent the quantities of the fractions within the sample. And the melting temperatures can be calculated back towards characteristics of that fraction, which is discussed at a later stage in this chapter.

![Figure 16: m-VLDPE and m-LLDPE DSC thermograms without step-wise crystallization, reprinted from [42].](image-url)
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Successive Self-Nucleation and Annealing is a method which is comparable to stepwise crystallization. Instead of stepwise cooling down the sample after heating, the sample is cooled down to a low temperature, resulting in self-nucleation of the polymer. Subsequently it is heated to a lower temperature, resulting in annealing of the not-melted crystals at the reduced temperature. The main advantages of applying a SSA fractionation include reduced measurement time, molecular segregation, enhanced resolution and improved molecular structural information [5]. A comparison graph of the temperature ramps is shown in Figure 18 (these values are fictive), from which it becomes clear that in the time SC passed a few cycles SSA performs more than four times as many cycles, resulting in a faster process. According to Zhang et al. [18] and Arnal et al. [60], SSA is a method designed to fractionate semi-crystalline polymers by lamellar thicknesses of the crystals and/or by methylene sequence length. Furthermore, SSA enhances the sensitivity of DSC, by minimizing the extent of co-crystallization between dissimilar chain segments [59].

Figure 17: m-VLDPE (left) and m-LLDPE (right) DSC thermograms after performing step-wise crystallization, reprinted from [42].

Figure 18: Comparison between SSA and SC temperature ramp; starting temperature 160°C, first $T_s$ (self-seeding temperature) 140°C, step size 50°C, isothermal SC 120 minutes, isothermal SSA 5 minutes, ramp SSA heating/cooling 10°C/min; these values are solely for illustrative purposes and not based on experimental results.
SSA is a method to subject a polymer to a series of annealing steps. During these steps, the polymer is fractionated based on the crystallization behaviour, which is dependent on e.g. the type of polymer (for blends), the short chain branching and the molecular mass. This technique involves partial melting of the existing crystals followed by recrystallization, while using not-molten crystals as self-nuclei. Subsequent to the annealing steps, the sample is cooled and a DSC measurement is performed. The resulting endotherm will show peaks corresponding to the different annealing steps. Figure 19 shows a DSC thermogram of two polymers before and after performing SSA. The SSA method as applied by Lorenzo et al. [61], consisted of 13 steps (124°C – 59°C) for the 11U4 and 7 steps (102°C – 72°C) for the HPB, with heating rates of 5°C/min to -20°C and self-seeding times of 5 minutes, it took on average 30 minutes per step, resulting in approximately 8 hours for the 11U4 and 6 hours for the HPB polymer to perform the SSA.

![DSC thermograms of polymers](image)

Figure 19: DSC heating scans (10 °C/min) for different polymers, (a) before and (b) after SSA fractionation, reprinted from [61].

In order to actually compare the SC and SSA method, the same samples should be used for the different methods, which has been performed by Starck et al. in 2002 [46]. In Figure 20, an overlay is given of the thermograms of two Ziegler-Natta-catalysed ethylene-1-butene copolymers. Both have been fractionated with SC and SSA, rendering this overlay ideal for the comparison of these two methods.
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While interpreting the data of the EB 5-V (the short thermograms), it is clear that the SSA fractionation shows a better separation between the peaks. Additionally the SSA-DSC shows up to 11 peaks, whereas the SC-DSC only shows 7 peaks. Similar results are obtained from the EB1-ZN polymer, for which the SSA-DSC shows up to 11 peaks, compared to the 7 peaks as detected for the SC-DSC thermogram. The amount of peaks perfectly corresponds to the number of steps that were performed during the thermal fractionation. From these results it can be concluded that the use of SSA seems to be a more efficient thermal fractionation method, resulting in higher resolution thermograms. These results, as achieved by Starck et al. [46], are in agreement with those of Müller et al. [62]. Additionally, the stepwise crystallization of the polymers took on average about 18 hours, whereas the successive self-nucleation and annealing was performed in only 4 hours on average. Thus SSA is significantly faster than SC, while achieving better resolution [5, 18, 46, 60, 62], as shown in Figure 20.

After performing SSA-DSC, the resulting thermogram could be de-convoluted by using peak fitting software, as shown in Figure 21. Whereas Figure 21 shows a perfect fit between the experimental and the peak fit data for both the HPB and 11U4, for the 11U4 a different peak shape is calculated for the second last peak (right figure; generated peaks (bottom)). Compared to the other peak shapes, it is unlikely that the peak at 120°C will have such a wide base, especially since the step size during fractionation was constant, it is expected that the peak width at the base are similar. Performing these peak fittings should therefore be done with caution.

Figure 20: DSC thermograms of two ZN-catalysed ethylene-1-butene copolymers, obtained after performed either SC or SSA, reprinted from [46].
Hosoda suggested a relationship between the melting temperature of a m-LLDPE copolymer, of ethylene with 1-hexene or 1-butene, and the degree of short chain branching [63]. Based on the equation by Hosoda [63], Razavi-Nouri [42] calculated the short chain branching content of a m-VLDPE and a m-LLDPE. They found a good agreement with the calculations based on the theory of the rubber elasticity. However, since the melting point of a polymer depends not only on the branching but also on the composition and the molecular weight, the resulting short chain branching should be interpreted in a semi-quantitative way. Furthermore quantitative analysis by means of DSC is difficult since the intensity originates from the combination of the amount of material and the enthalpy of fusion at a particular temperature [64]. Although, Torabi achieved comparable results between DSC and $^{13}$C NMR for the short chain branching content of 6 different LLDPE’s [65].

Performing successive self-nucleation and annealing, will form lamellae within the polymer, of which a transmission electron microscopy (TEM) image is shown in Figure 22. The lamellae thickness and distribution depends on the composition of the polymer, and is related to e.g. the methylene sequence lengths (MSL).

The Thomson-Gibbs equation is used to calculate the relation between the lamellae (crystal) thickness and the melting point, as shown in Equation 6, in which $T_m^0 =$ equilibrium melting temperature [K]; $T_m =$ melting point [K]; $\sigma =$ surface energy [J/m$^2$]; $\rho =$ density [g/m$^3$]; $\Delta H_f =$ fusion heat for fully crystalline

$T_m = T_m^0 - \frac{\sigma}{\rho \Delta H_f}$
polymer \([\text{g}/\text{g}]\) and \(L_c = \text{lamellae thickness} \text{ [m]}\). When applying the Thomson-Gibbs equation, after calculating the amount of material melting at a particular temperature, the temperature axis can be converted into lamellar thickness or into MSL. This is however subject to controversy within the literature [61]. First of all the equilibrium melting point, the melting point of a 100% crystalline polymer, which can be calculated by either the Gibbs-Thomson plot or the Hoffman-Weeks method is an important factor within the Thomson-Gibbs equation. The Gibbs-Thomson plot is a plot of the melting temperature, acquired by DSC, versus the inverse of crystalline lamellae thickness, acquired by Small-Angle X-ray Scattering. The Hoffman-Weeks plot is a plot of the relationship between the melting point and crystallization temperature, as shown in Equation 7, in which \(T_m^0 = \text{equilibrium melting temperature} \text{ [K]}\); \(T_m = \text{melting point} \text{ [K]}\); \(\gamma = \text{Thickening coefficient and} \ T_c = \text{Crystallization temperature}\). Creating a Gibbs-Thomson plot is very time consuming. While the Hoffman-Weeks method seems to face some difficulties [66, 67]; within literature several values, between 141-145.5 °C [5, 60, 62], have been used as equilibrium melting point. From which 145.5°C corresponds to infinitely thick linear polyethylene, and that it is depressed by the introduction of branches in the polyethylene chains [61].

\[
Equation\ 6
\]

\[
T_m^0 - T_m = \frac{2\sigma T_m^0}{\rho \Delta H_f L_c}
\]

\[
Equation\ 7
\]

\[
T_m = T_m^0 \left(1 - \frac{1}{\gamma}\right) + \frac{T_c}{\gamma}
\]

Furthermore, for copolymers of ethylene and \(\alpha\)-olefins the lamellae thickness calculated via the Thomson-Gibbs equation do not correspond to the values as measured by TEM. This seems to be related to the broader melting temperature range of the random copolymers [61, 68]. Although SSA-DSC is a much faster technique than TREF (previous chapter), it only gives a qualitative description of branching structure and is unable to determine the average content of branches in VLDPE/LLDPE samples [65], nevertheless, recent developments regarding chip based DSC led to quantitative results [69]. For isotactic polypropylene, SSA-DSC does enable an accurate characterization of the tacticity distribution. As proven by Virkkunen et al. [26, 27], the same results are obtained as by \(^{13}\text{C}\) NMR and TREF. The results showed that a correlation exists between the lamellar structure generated in SSA and the crystallizable isotactic sequence length. This however is not applicable to all fractions; octane soluble at 80°C fraction did not show this correlation [26]. Virkkunen also stated that the quantitative aspect of SSA-DSC is not significantly affected by changes in the sample composition, while measuring isotactic polypropylene.
4. Interaction Based Fractionation Methods

In the upcoming chapters more details will be given about the interaction based separation techniques temperature gradient interaction chromatography (TGIC) and high temperature high performance liquid chromatography (HT-HPLC).

4.1. High Temperature High Performance Liquid Chromatography

High-performance liquid chromatography (HPLC) is a solvent separation technique which applies high pressures in packed columns in order to optimize the resolution while reducing the analysis time. HPLC is used to separate compounds in a mixture on basis of polarity (e.g. the electron affinity between atoms within a molecule). The chromatographic setup consists of a mobile phase (a solvent that is constantly pumped through the system), a stationary phase (present within in column) and a detector. The principle behind HPLC is the interaction of the compound of interest with the stationary phase present inside the column and the solubility of the compound in the mobile phase which is passed through the column. In the past, HPLC was solely performed at ambient temperature (uncontrolled) or slightly elevated temperatures (typically around 40°C). Especially in the last decade, strong progress was made in the development, both instrumentation and methodology, of this method for polyolefin characterization.

Performing polyolefin separations around ambient temperatures does not seem to be a viable principle as a result of the crystalline nature of the polyolefins. Most polyolefins can only be dissolved at high temperatures (>100°C). High boiling point solvents are thus required. The choice of solvent is therefore limited.

Since the separation is based on the interaction between the analytes with the stationary phase, within the column, in combination with the mobility through (diffusion), and solubility of, the analyte in the mobile phase, many variables can be changed in order to alter the selectivity of the system or optimize the separation of the different analytes. Furthermore, within HPLC several separation mechanisms can be applied, e.g. steric exclusion (size based separation), adsorption (chemical interaction based separation), partitioning (phase separation), solubility (precipitation chromatography) and ion-effects (adjust interaction with stationary phase by ionizing analytes), in order to achieve optimal separation. One of the main advantages of using HT-HPLC over the other techniques is the great flexibility of the technique.

As one of the pioneers, Macko et al. [70] performed a study towards the elution behaviour of polyethylene in isocratic HT-HPLC while using different polar mobile phases on a non-polar stationary phase. Based on the used mobile phases, different elution behaviours were observed, from SEC separation (elution without any (enthalpathic) interaction or adsorption) to fully retained peaks. Using ethylene glycol monobutylether as mobile phase enabled the separation of PE (retained) from PP (eluted in SEC mode). However, the resulting chromatogram, as shown in Figure 23, did not look satisfying due to a lack of resolution. Furthermore it was not always possible (dependent on the polymer/stationary phase combination) to desorb the adsorbed PE and PP from the stationary phase.
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Up to the year 2005 solvent gradients had not been used for the separation of polyolefin by means of HT-HPLC, simply because of a lack of knowledge and equipment. Heinz et al. [71] were the first to publish experimental results based on gradient HT-HPLC of a polyethylene-polypropylene blend. Their experiments led to a successful separation of PE (normal retention) and PP (eluted in SEC mode) by using a mobile phase gradient of ethylene glycol monobutylether (EGMBE) and 1,2,4-trichlorobenzene (TCB) in combination with a silica gel (nucleosil 500) stationary phase. Compared to the chromatograms in Figure 23, as achieved by Macko et al. [70], the results of Heinz et al., using a gradient, showed a significantly improved resolution for the separation of PE from PP, as shown in Figure 24. For PE a small influence of the molar mass on the retention has been observed. It should be noted however that very low molar mass PE (e.g. 1.1 kg/mol) is soluble in EGMBE and thus elutes in the SEC mode together with the PP, showing no retention.

Macko et al. [72] achieved a separation of linear-PE and PP from PE-PP-blends by using selective adsorption of PE and PP on zeolites in isocratic HT-HPLC, nevertheless, the retained compound was difficult, or even impossible to desorb. A few years later Macko et al. [73] were the first to publish a
polyolefin separation based on tacticity, by means of HT-HPLC, using porous carbon-based material as stationary phase. With 1-decanol as a mobile phase (start of gradient), linear-PE, syndiotactic-PP and atactic-PP are adsorbed, while isotactic-PP is fully eluted without adsorption. After the isocratic elution of isotactic-PP the retained polymer fractions are eluted by a gradient from 1-decanol to TCB, which is illustrated in Figure 25.

Figure 25: Separation according to tacticity, by Macko et al., reprinted from [73]; four peaks detected, isotactic-PP $M_w=200\text{kg/mol}$, atactic-PP $M_w=315\text{kg/mol}$, syndiotactic-PP $mw=196\text{kg/mol}$, linear-PE 5 samples from 14-260kg/mol (seen as one peak), respectively.

In 2009, Macko et al. [74] were also the first to publish the separation of polyolefin chains based on the short chain branches (SCBD), they succeeded in the separation of propene/\(\alpha\)-olefin and ethylene/\(\alpha\)-olefin copolymers, by means of solvent-gradient HT-HPLC. Whereas isotactic-\(\alpha\)-olefin (\(\leq C_{10}\) in side chain) eluted in SEC mode, isotactic-\(\alpha\)-olefin (\(\geq C_{11}\) in side chain) showed (slightly) increased retention with (significantly) increasing concentration of co-monomer, rendering the system (slightly) suitable for separation of these copolymers according to the chemical composition, as illustrated in Figure 26. However, the opposite was observed for ethylene/1-hexene copolymer, in that case the retention reduced with increased co-monomer concentration, as shown in Figure 27, most-likely caused by a reduction in length of the continuous methylene sequences which is expected to adsorb to the graphite. Furthermore isotactic-PP was separated from syndiotactic-PP, using this setup of a Hypercarb® packed column with porous graphite, while using a linear gradient from 1-decanol to TCB, as already presented in [73].
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Chitta et al. [75] studied the elution behaviour of polyethylene and polypropylene standards on different carbon sorbents using several solvents. These combinations led to new sorbent/solvent systems which have different selectivity compared to the setups of Macko et al. [70, 73] and Heinz et al. [71]. Chitta et al. managed to separate PP from PE, by eluting PP (isotactic-PP, atactic-PP and syndiotactic-PP) in SEC mode and adsorb PE (including the <20kg/mol fraction) to subsequently elute the PE during a gradient. The used chromatographic system contained ZirChrom-CARB sorbent, with a gradient from 2-ethyl-1-hexanol to TCB at an isothermal temperature of 160°C; the resulting chromatogram is shown in Figure 28.
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Whereas the setup of Macko et al. [74], Figure 25, is capable of separating PP based on tacticity, the setup of Chitta et al. [75], Figure 28, showed a slight influence of the molecular mass on the separation of PE, up to 60kD. A combination of these two systems would be a good setup for complete characterization of PE, PP and PE-PP blends, although this is not viable since both the mobile phase and the stationary phase was different between the two experiments.

With the same setup as used for the separation of PP and PE in Figure 28, Chitta et al. [75] also managed to separate ethylene/1-hexene copolymers according to their chemical composition, as previously performed by Macko et al. [74] (Figure 27). The resulting chromatogram is shown in Figure 29. Whereas Macko et al. [74] (Figure 27) suffered from split peaks, Chitta et al. [75] (Figure 29) do not seem to have to cope with that problem. Furthermore, the chromatogram of Chitta et al. seems to show full adsorption of the high co-monomer content copolymers.

At this moment HT-HPLC starts to become a good alternative for conventional methods like TREF and CRYSFAT, since HT-HPLC is performed in a shorter time span. In the chromatograms as shown above, all fractions eluted within 13 minutes, which is, compared to the time required for TREF, a significant gain.
in efficiency. Furthermore, it can separate amorphous fractions >8% co-monomer, unlike TREF. On the other hand the separation within CEF and TREF is mainly based on crystallinity rendering the techniques complementary to HT-HPLC. The main disadvantage of HT-HPLC is the use of a solvent gradient, which limits the selection of possible detectors; only the ELSD is a viable detector in combination with HT-HPLC. Furthermore the reliability of the hardware is currently below industry standards. Apart from that it is difficult to perform method development, because the solvent combinations are limited. And since HT-HPLC works well for polymers that show adsorption at a stationary phase in a good solvent and elute in another good solvent, finding the right solvents with completely different behaviour towards adsorption of the polymers on stationary phases also requires some more research in order to simplify the method development.
4.2. Temperature Gradient Interaction Chromatography

Temperature Gradient Interaction Chromatography (TGIC) is a liquid chromatography method which is performed under isocratic mobile phase conditions whereas separation is controlled by the use of a temperature gradient. The basic principle of TGIC is the compound-dependent temperature influence on the interaction between the analyte and the stationary phase. Partition coefficients, the affinity between the compound of interest and the stationary phase versus mobile phase, of the analyte are controlled by the variation of the temperature during the elution. For most compounds, the retention factor, which quantifies the degree of interaction between the compound and the stationary phase, decreases at an increased temperature, resulting in adsorbed analytes to be desorbed and eluted, although some compounds show the opposite effect [76]; illustrated in Figure 30.

![Figure 30: influence of temperature (K⁻¹) on the retention factor (ln k), left the retention is reduced at increased temperatures, reprinted from [77], right the retention increases with the temperature, reprinted from [78].](image)

The main advantage of TGIC over (HT-)HPLC is the use of a single solvent, which not only enlarges the selection of possible detectors, e.g. the use of a refractive index detector, viscometer and IR detector, but also improves the performance of for instance the ELSD detector. Furthermore, TGIC offers an increased loading capacity compared to HT-HPLC, rendering it more capable of performing polymer fractionations on a preparative scale for off-line analysis by means of other methods, e.g. infrared or NMR. A downside of the use of TGIC is the narrow optimum separation conditions for a specific polymer, requiring more optimization of these settings [79-81].

Initial TGIC experiments, as performed by Lee, et al. [80], showed molecular weight separation of polystyrene which outperformed the resolution as achieved by SEC. These TGIC experiments were afterwards performed again on polystyrene, Poly(methyl methacrylate), polyisoprene and poly(vinyl chloride) by the same group at the Pohang University of Science and Technology, between 1998 and 2006 [79, 81-88]. However, these experiments were all conducted at temperatures up to 60°C [79], which is not sufficient for the characterization of polyolefins.

Further developments of TGIC led to methods which achieved separation based on chemical composition. For these methods, just like with HT-HPLC as discussed previously, one fraction elutes in SEC mode, whereas the other fraction is initially adsorbed, to subsequently elute during the temperature gradient. An example is given in Figure 31, in which the work of Lee, et al. [89], the SEC
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separation of PI (polyisoprene) and the TGIC separation of PS (polystyrene) in a PI-PS mixture (a), and vice versa (b), is presented.

Figure 31: TGIC chromatograms of PI-PS mixtures; (a) NP-TGIC, PI separated in SEC mode, PS separated in TGIC mode; (b) RP-TGIC, elution reverses since PI is adsorbed in reversed phase, reprinted from [89].

As shown by Teramachi et al. [90], TGIC can be used for analytes that have decreased retention at increased temperature and analytes that have increased retention at increased temperatures by adjusting the direction of the gradient, increasing versus decreasing temperature in time. A positive (increasing) temperature gradient was effective in systems consisting of NH₂ modified silica with tetrahydrofuran (THF) and n-hexane as eluent-mixture, whereas a negative temperature gradient was effective for a system in which the THF is replaced by chloroform. However, poly(ethylene oxide) (PEO) is one of the only polymers which show increased retention at increased temperatures.

Whereas the development of TGIC capabilities was being further studied for years, it took until 2011 for the first publication on High Temperature Thermal Gradient Interaction Chromatography (HT-TGIC) on the separation of polyolefins to appear in Macromolecules. In this paper of Cong et al. [91] described HT-TGIC as a new characterization technique to quantify co-monomer distributions of which the performance was proven by the characterization of a series of ethylene octene copolymers with octene co-monomer contents between 0% and 50.7%.

As a result of the lack of solubility of polyolefins at ambient temperature, elevated temperatures are required for dissolving these polymers. The HT-TGIC experimental setup, using HYPERCARB stationary phase in combination with 600PPM butylated hydroxytoluene (BHT) in ortho-dichlorobenzene (ODCB) as mobile phase, used is shown in Figure 32, reprinted from [91], in which, $T_\text{s}$ = stabilization temperature; $F_C$ = flow rate of pump during cooling; $F_E$ = flow rate of pump during elution; $F_F$ = flow rate of pump during flushing; $t_{\text{loop}}$ = stabilization time; $t_{\text{column}}$ = precooling time; $R_C$ = cooling rate; $T_C$ = final temperature of cooling process; $t_C$ = post-cooling time; $t_E$ = soluble fraction elution time; $R_E$ = elution rate and $T_E$ = final elution temperature.
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In Figure 33 an overlay of a series of chromatograms for the different copolymers (ethene + 0% - 50.7% octene) is presented. Whereas TREF or CRYSTAF are normally incapable of fractionating copolymers with >10% co-monomer, as a result of the increased amorphousness, the TGIC method clearly shows interaction up to 32.5% mol% of octene in a ethene-octene copolymer.

The peak at a temperature of 0°C, 50.7mol% octene, eluted isothermally as a sharp peak, whereas the polyethylene and the 1.33mol% octene eluted at high temperatures as sharp peaks. The signals in between seem to show more broadening, although, it looks like the broadening does decrease with increasing elution temperatures. Observing the shape, a clear tail behind the apex, might point towards a molecular weight distribution of the different fractions, or secondary interactions between the analyte and the stationary phase; nevertheless, the actual cause remains unknown.
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Figure 33: Chromatographic overlay of different ethene/octene copolymers, varying from 0% to 50.7% octene, showing a clear co-monomer based separation; reprinted from [91].

Furthermore, the TGIC method seems to show a linear relationship between the elution temperature and the copolymer concentration, as shown in Figure 34. Apart from some random error in the measurement points, the 32.5 mol% and 50.7 mol% octene seem to deviate from the line. For the 32.5 mol% that might be caused by the asymmetric peak shape, resulting in the top of the peak eluting at a lower temperature, whereas the 50.7 mol% shows no retention, which can already be expected starting from approximately 48.8 mol%, based on the calibration line.

Figure 34: Linear relationship between octene content in ethene/octene copolymers and elution temperature for HT-TGIC, reprinted from [91].

This dependence of the elution temperature on the copolymer content has been shown by performing preparative HT-TGIC in combination with $^{13}$C-NMR, which is presented in Figure 35. These NMR results are, however, a bit low regarding the octene mol%. The 96°C-102°C fraction contains between 8.5 and 10 mol% of octene, whereas in the chromatogram, as presented in Figure 33, from 96°C-102°C the tailing of 19 mol% and 21.7 mol% octene copolymer elute, together with the fronting of the 13.88 mol%.
This would mean that either the mol% octene should be between 13.88 mol% and 19 mol% instead of 8.5%-10%, or that the NMR results are not properly calculated. This does not count for the 126°C-132°C fraction, whereas it contains between de 5.5 and 6.5 mol% according to the NMR results, the chromatogram shows the tailing of the 8.52 mol% and the fronting of the 3.99 mol%. Therefore, it might also point towards broad copolymer distributions for the different copolymers analysed, which would also explain the wide peaks as observed in the chromatogram.

Another aspect shown by Cong et al. is the interaction between the graphite of the HYPERCARB column and the polyolefin. Whereas TREF or CRYSTAF show elution temperatures for the polyethylene around 100°C and DSC show a melting temperature around 135°C, the elution temperature on the HYPERCARB column using the TGIC method, is around 150°C. With some simple experiments in which the elution and stabilization (starting) temperatures have been varied, Cong et al. proved a clear interaction between the HYPERCARB and the polyethylene for temperatures below 140°C [91], which is illustrated in Figure 36. With a starting temperature of 140°C no interaction occurred, and the polymer eluted directly (red sharp peak). When decreasing the temperature to 135°C, partial interaction is observed, a small fraction still eluted instantly (green line, first peak) whereas the main part shows interaction and eluted around 145°C. Decreasing the temperature further, to 130°C or below, full interaction is observed and the whole sample elutes after the 140°C which was previously enough to elute the sample. This points towards the presence of interaction.
Figure 36: Influence of stabilization temperature on the final elution temperature and thus the interaction with the stationary phase, reprinted from [91]. At a temperature of 140°C no interaction occurs between the polyethylene and column is observed, whereas temperature below 130°C show a clear interaction, that even requires increased temperatures for elution. The additional peak in the green chromatogram is related from a low molecular weight fraction of the polyethylene.

An important advantage of TGIC is the use of a single solvent, compared to a solvent gradient in HT-HPLC, enlarging the selection of possible detectors and enabling multiple detection modes in series, e.g. a coupled infrared - viscometer – light scattering, for the comprehensive determination of microstructures [91]. Furthermore, TGIC is applicable towards a larger range of co-monomer content, compared to e.g. TREF, and due to the absence of crystallization, co-crystallization is no longer an issue.

Overall it can be concluded that (HT-)TGIC might become a very promising technique for the characterization of polyolefins based on the chemical composition distribution. However, since only a few publications are available about TGIC and only a single publication about HT-TGIC, which is required for the analysis of polyolefins, developments are still in an early stage. The results, as presented by Cong et al., are promising, although optimizations have to be performed on for instance peak shapes and separation efficiencies. Additionally, the technique should be applied to other copolymers and blends, and different solvent/column setups should be tested, in order to verify the finds.
5. **Two dimensional fractionations**

Molecular characterization of synthetic polymers used to be dominated by SEC. However, the downside of SEC is that several molecular characteristics determine the behaviour of the analyte, since the sizes of polymers in solution highly depends on e.g. molar mass, chemical structure and physical architecture. An alternative would therefore be the use of liquid chromatography (LC) in which the separation is based on a single molecular characteristic, which is strongly enhanced, while suppressing the other characteristics in order to neglect the influences [92]. Such suppression or enhancement can be achieved within LC separation by applying different separation mechanisms such as exclusion, adsorption, partitioning, solubility or ion-effects. As Giddings [93] stated, for each dimension present within a sample, an analytical separation dimension is required within the separation system employed, in order to achieve optimal separation efficiency. Combining these statements, quickly leads to the choice for multiple dimension fractionations, as first applied by Balke [94].

In literature, many articles about 2D (polymer) separations can be found [11, 92, 95-102], including some reviews [11, 92, 100, 102]; nevertheless, the amount of articles discussing 2D separations of polyolefins is rather limited. Whereas TREFxSEC was already performing during the late 20th and early 21st century [103], and off-line TREFxSSA is discussed in the review of Müller et al. [5], 2D LC separations of polyolefin were not reported until 2010, by Roy et al. [104, 105].

An example of the 2D separation, is the work by Ginzburg et al. [105]. They used HT-HPLCxSEC as analytical setup, to separate polyolefins independent of their crystallizability. As an example, the separation of a blend of PE, ethylene-vinyl acetate (EVA) and poly(vinyl acetate) (PVAc), by HT-HPLCxSEC and TREFxSEC is shown in Figure 37.

![Figure 37: HT-HPLC x SEC contour plot (left) of a blend of PE, EVA (20 mol% and 57 mol% VA) and PVAc, compared to TREFxSEC (right) on the same sample; it can be concluded that the separation with HPLC is significantly better than TREF although TREF might give different information since it is complementary; reprinted from [105].](image_url)

Unlike 2D separations in gas chromatography, in which the additional separation power is solely used to physically separate peaks, 2D separations in polymer analyses can be performed for different purposes. As shown in Figure 37, the added dimension is not used for the actual separation of the compounds, but
solely for the determination of the MWD by means of a SEC separation. Therefore this additional separation dimension seems to be used as a method of identification, rather than separation.

The method as applied by Ginzburg et al. separates the polymers regarding polarity in the first dimension, whereas in the second dimension a molecular mass separation was performed, in approximately 5 hours. Apart from the improved separation compared to TREFxSEC, as shown in Figure 37, another advantage of HT-HPLCxSEC versus TREFxSEC is the absence of the co-crystallization effects, which might be present in TREF. Furthermore HT-HPLCxSEC is capable of separating semi-crystalline and amorphous polyolefins, whereas TREFxSEC is not capable of separating amorphous (>8mol% co-monomer) polyolefins and thus ideal for determining the amorphous content.

Roy et al. [104] analysed polyolefins by means of HT-HPLCxSEC resulting in a two dimensional contour plot of the composition versus the molecular weight. In Figure 38 the influence of the octene content in ethylene octene copolymers is represented in 2D contour plots. From these plots it is clearly visible that the elution volume of the LC decreases with an increasing octene content. Even the quantification was proven to be quite accurate, with a 50/50 weight% blend sample showing two peaks of 1975 and 2067 area respectively, an error of <5%, which might be related to integration errors, as a result of the poor peak shape, shown in Figure 39.

Figure 38: 2D contour plot of a series of ethylene octene copolymers with varying octene concentrations, reprinted from [104]. In the plots it is clearly visible how the peak shifts towards the left, at increased octene content.
In 2010, Ginzburg et al. [106] presented a method for the characterization of polyolefins by means of so-called comprehensive high-temperature two-dimensional liquid chromatogram (HT 2D-LC), consisting of HT-HPLC×SEC. With the system operating at 160°C, using a gradient from 1-decanol to 1,2,4-TCB on a Hypercarb® column enabled the separation of polyolefins according to their chemical composition, followed by a molecular mass separation performed on the SEC column. Analysing a blend of iPP (1.1 and 60 kg/mol), aPP (211 kg/mol), sPP (196 kg/mol) and PE (1.18 and 22 kg/mol) showed an influence of the molecular mass of the iPP 60kg/mol fraction on the solubility in decanol, since a higher molecular mass fraction of the iPP 60kg/mol only eluted after the gradient towards TCB was initiated. This partial adsorption of the higher molecular mass fraction of the iPP 60kg/mol might be related to the quality difference of the 1-decanol, since Macko et al. [73, 74], did not see this adsorption or possible differences in tacticity, which might be confirmed by TREF×SEC. The resulting chromatogram is presented in Figure 40.

Furthermore, Figure 41, shown below demonstrates the real power of HT 2D-LC (HT-HPLC×SEC), since a model mixture of 7 components, being PE (2x), iPP (2x), sPP, aPP and an E/P copolymer show full...
separation. This means that a copolymer of interest can be physically separated from a blend of different polymers. Comparison of these results to TREF-SEC [106], showed that the HT-HPLC-SEC setup is independent of the sample crystallinity.

The separation of iPP, PE and E/P copolymer, was repeated by Lee et al. in 2011 [107]. Nevertheless, the results as presented by Ginzburg et al. [106] in 2010, seemed to be more impressive.

Cheruthazhekatt et al. [108] published a multidimensional analysis of the composition of an impact PP ethylene-propylene copolymer (EPC), by using a combination of TREF, SEC-FTIR-HPer DSC, HT-HPLC and HT 2D-LC. After performing a preparative TREF fractionation, HT-SEC-FTIR proves information regarding the chemical composition and crystallinity, as a function of the molar mass and HT-SEC-DSC yields the melting and crystallization behaviour related to the chemical heterogeneity of the copolymer, from the different fractions. HT-HPLC shows a separation between the homopolymers (e.g. PE) and the copolymer. Furthermore, HT 2D-LC (HT-HPLC-SEC) was used to analyse the TREF fractions according to chemical composition versus the molar mass. Analysis of the bulk sample (non-stabilized impact polypropylene copolymer with 10.5 mol% ethylene) by these techniques does not provide in-depth information regarding the chemical composition and thermal behaviour; therefore a preparative TREF fractionation was performed prior to the analyses. The results pointed out that the techniques used, show some overlap, but overall they are complementary to each other, however, performing such an extended research is of course highly time and resource consuming.

Overall it can be concluded that 2D methods show to be very promising for the separation of complex molecules. Although, as stated by Lee et al. [107], there are some inconsistencies between the molecular weight poly-dispersities determined by SECxHT-HPLC and those determined solely by SEC. This shows that the newly developed technique, it was only introduced in 2010 [104, 105], still seems to show some teething problems.
6. Outlook

SSA-DSC seems to be superior to SC-DSC regarding both the analysis time and the achieved efficiency, it can therefore be expected that SSA might become the main thermal fractionation prior to DSC analyses. This growth might be even strengthened by the development of autonomous equipment being capable of performing these techniques without requiring human interaction. Especially for the characterization of polypropylene regarding its tacticity distribution, SSA-DSC seems to be a reliable technique, for most fractions, as shown by Virkkunen et al. [26, 27]. However, for LDPE SSA-DSC only seems to give qualitative results for the branching structure, and is thus not able to determine the average branching content [65].

Furthermore on the side of SSA, the DSC analysis is currently being improved, regarding sample requirements and ramping speeds. A recent publication of Mathot et al. [69], shows scan speeds up to 20000°C/s for heating and cooling empty cells, whereas speeds of 1000°C/s have been applied on actual samples, of which the results were even reported as quantitative.

Currently analytical scale TREF seems to be a well-established but rather slow method for the determination of short chain branching distribution or tacticity, based on a separation as function of the crystallization. The separation power and resolution seems to be a rather low, in combination with the long analysis time, therefore other techniques seem to be preferred. CEF, which is an improved version of TREF (faster, higher resolution and less co-crystallization), seems to be a viable replacement for TREF since it gives improved separation in a reduced timespan. Furthermore, techniques like TGIC or HT-HPLC might be used for some of the applications on which TREF is currently performed, although TGIC and HT-HPLC can also be complementary to each other [108]. Therefore it can be expected that the use TREF for analytical scale characterization will slowly decrease.

Preparative scale TREF on the other hand is a very useful, but also time-consuming and labour intensive, technique for generating relatively large fractions of the polyolefin, rendering it capable of performing less sensitive techniques like 13C-NMR, however, with the enhanced sensitivity of cryo-probes used for NMR, the sample requirements have decreased, and therefore CEF, which will most likely become capable of fractionating a sample at analytical scale, seems to become a serious threat for preparative TREF. Nevertheless, preparative TREF will still play an important role in the characterization of complex polyolefins for the coming years.

On the other hand the interaction based techniques like HT-HPLC and TGIC are expected to become commonly implemented techniques. The main advantage of TGIC is the use of a single solvent, compared to a solvent gradient in HT-HPLC, enlarging the selection of possible detectors and enabling multiple detection modes in series, e.g. a coupled infrared - viscometer – light scattering, for the comprehensive determination of microstructures [91]. Furthermore, TGIC is, just like HT-HPLC, applicable towards a larger range of co-monomer content, compared to e.g. CEF, and as a result of the high temperature, co-crystallization is no longer an issue. The main disadvantage of HT-HPLC is the use of a solvent gradient, which limits the selection of possible detectors. Eventhough HT-HPLC might be
preferred at the stage, for both techniques, developments are still in a rather early stage. Regarding TGIC some optimizations have to be performed on for instance peak shapes and separation efficiencies; furthermore it should be applied to a broader range of polyolefins.

Whether a choice will be made between HT-HPLC (multiple solvents, single temperature) or TGIC (single solvent, multiple temperatures) mainly depends on the selection of detectors and the application for which it will be used, in combination with future developments in the analytical world.

Regarding 2D separations, HT-SECxHT-HPLC shows to be a very promising technique for the separation of complex molecules, as demonstrated by Ginzburg et al. [105, 106], especially when compared to TREFxSEC. However, as stated by Lee et al. [107], there are some inconsistence between the molecular weight polydispersity determined by SECxHT-HPLC and those determined solely by SEC. This shows that the newly developed technique, it was only introduced in 2010 [104, 105], still seems to show some teething problems; which will most likely be resolved in the upcoming years, making this an extremely powerful techniques for the complex polyolefin characterizations.

Another option would be the combination of HT-TGIC and HT-HPLC by simply combining a solvent and temperature gradient in a single run, this might even further enhance the separation capability, and it does not require additional hardware.

Based on the complementarity of CEF and TGIC or HT-HPLC, 2D setups will arise. Especially CEFxTGIC might become a very strong 2D technique in the future, due to the possibility of simultaneously utilizing a series of detectors.

Overall the developments of the techniques will go into miniaturizing, e.g. chip based separation [69, 109, 110], enabling the use of parallel characterizations, in a way comparable to the loop storage method of LC-NMR. In this technique, the fast LC separation is automatically fractionated into different sample loops, which can subsequently be analysed by the relatively slow NMR technique. However, the downside to miniaturisation is peak broadening.

Towards the polymer fractionation it might be an option to connect a solvent based technique, e.g. HT-HPLC or HT-TGIC, to a series of chips, on which fractions are collected. These chips can subsequently run a SSA-DSC in parallel, resulting in highly valuable information in a rather short time span.
7. Conclusion & Recommendation

Based on the current developments, SSA-DSC, HT-HPLC and CEF are the most promising techniques. Even though HT-HPLC, as interaction based technique, seems to be limited regarding detection; it is still preferred over the TGIC method, which requires further development.

SSA-DSC is can be seen as a fast technique in order to gain a first impression on the molecular structure of the polymer. It can therefore be a method which is used for deciding whether HT-HPLC is used, or even complementary, performing SSA-DSC on fractions collected from the HT-HPLC, as a result of the low sample requirements of the HT-HPLC.

Analytical TREF and CRYSTAF can be seen as techniques sliding towards extinction, as a result of the introduction of CEF. Based on the different separation techniques, crystallization versus interaction, HT-HPLC and CEF are complementary to each other [108], which can be utilized by 2D setups. Whereas preparative TREF will still be performed in the near future order to fractionate co-polymers prior to e.g. $^{13}$C-NMR characterizations.

Whether CEF, HT-HPLC, SSA-DSC or (on-line coupled) combinations of these techniques will be used, depends mainly on the analytical questions that have to be answered.

Table 2, shown on page - 51 -, gives a summary of the techniques as discussed within this report.
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**Table 2: Overview of different techniques discussed within this report.**

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Literature references


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