Comprehensive characterization of branched polymers

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Chapter 1: General introduction

Abstract

In this chapter the objective of the PhD study is introduced. Theory, concepts, instruments and technologies for the analysis of branched polymers are presented. Also different ways to achieve branching in the polymer structure and the impact on the polymer properties are reviewed.
1.1 An introduction to polymers

The ability to characterize polymers has been of critical importance for progress in the field of macromolecular chemistry. It allows one to understand how a material behaves, how it was made and how to make it better. Continuous development of polymers has resulted in materials that are highly optimized and in the rapid proliferation of polymers into everyday life of the 21st century. Polymers with a very wide range of physical properties can now be produced, often at low cost. They cover an incredible application space that continues to expand. The traditional applications, such as simple molded items, fibers and disposable items, are still present today. More recent is the introduction of functionalized and smart materials. Modification of the polymers can be used to increase durability, conduct electricity or even provide self-healing properties. These specialty materials provide higher added value and are, therefore, of great interest for production in a commercial setting. An overview of common synthetic polymers and their applications is presented in Table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Application example</th>
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<tbody>
<tr>
<td>Polystyrene</td>
<td>Coffee cups</td>
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<td></td>
<td>Envelope window film</td>
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<td></td>
<td>Insulation foam</td>
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<td>Polyvinylchloride</td>
<td>Piping</td>
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<td></td>
<td>Window lining</td>
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<td></td>
<td>Wire &amp; cable insulation</td>
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<tr>
<td>Polyethylene</td>
<td>Bags</td>
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<td></td>
<td>Garbage containers</td>
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<td></td>
<td>Artificial ice-skating floors</td>
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<td>Polypropylene</td>
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<td>Heat-resistant food packaging</td>
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<tr>
<td>Polyester</td>
<td>Soda bottles (polyethylene terephthalate)</td>
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<td></td>
<td>Clothing / fibers</td>
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<tr>
<td>Polyamide</td>
<td>Nylon stockings</td>
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</table>
1.1.1 Macromolecules

A landmark in history has been the discovery of covalent bonding between smaller molecules (monomers) [1] to form polymers or ‘macromolecules’ of high molar mass [2]. These concepts were introduced in the 1920’s by Hermann Staudinger, for which he was awarded the Nobel Prize in 1953 [3]. The term ‘polymerization’ was introduced already in 1863 by Berthelot, who recognized the ability of unsaturated compounds to react with themselves and yield high-boiling oligomers [4]. His work did not comprise the formation of higher polymers. The idea of higher polymers was opposed by the ruling misconception from crystallography that molecules had to fit in a single unit cell. It was not until the late 1920’s that the concept of higher polymers became accepted. Before this time the mechanism of polymerization was not well understood and was attributed to self-assembly of small molecules by colloidal interactions [5]. Poor understanding of molecular structure did not withhold Baekeland from producing the first fully synthetic polymer already in 1907 [6,7].

1.1.2 Early characterization of polymers

The difficulty in obtaining experimental proof for higher polymers was one of the reasons that it took a long time for macromolecules to become accepted. Many methods for determining the molar mass of macromolecules were published in the years following the introduction of the macromolecular concept [8]. This is not strange, considering that the interpretation of most measurement techniques depends on (assumptions about) the structure of the analyte.

Colligative properties of polymers in dilute solution can be used to determine molar mass. The response of such properties corresponds to the mole fraction in solution as pointed by Johannes van ‘t Hoff (Nobel Prize in Chemistry, 1901) and may be used to obtain number-averaged molar-mass ($M_n$) data. Membrane osmometry has historically been favored over other techniques, such as freezing-point-depression and vapor-pressure measurements, because it is more practical to measure and offers better accuracy. End-group determination may also yield $M_n$, provided that a selective detection of terminal groups is possible and the polymer molecules are known to be linear. Other techniques available for molar-mass determination are light scattering and
ultracentrifugation [9]. Both techniques may be used to provide accurate ("absolute") molar masses, as is the case for the colligative properties described before.

Viscosity of polymer solutions has been recognized as a readily accessible and sensitive property for molar-mass determination by so-called viscometry. It is due to the expanded nature of the molecules in solution that viscosity is increased by most polymers. The empirical relation between intrinsic viscosity ([η]) and relative molar mass \( M_r \) was introduced by Staudinger [10] (Eq. 1).

\[
[\eta] = KM_r^a
\]  
(1)

This equation has become known as the Mark-Houwink relation after their efforts to improve the theory of this relation and their documentation of constants \( K \) and \( a \) for different polymer-solvent systems at given temperatures [11,12,13]. The simplicity of capillary viscometry for determining molar mass resulted in a high popularity of this method and documentation of Mark-Houwink constants for many polymer-solvent systems [14]. Viscometric methods are relative measurements, because the relation between molar mass and viscosity needs to be determined for each different polymer at each set of conditions (solvent and temperature). Relations between polymer melt viscosity and molar mass were also investigated. Determination of molar mass with much better precision was possible due to the higher viscosity of the pure polymer than of a polymer-containing solution, but the empirical relations were found only to hold for relatively low molar masses [15,16,17].

The macromolecular structure of polymers was supported by published work on the application of these techniques for polymers. Polymer science and related analytical capabilities expanded rapidly once the scientific community accepted the existence of macromolecules. Research into polymerization reactions and mechanisms thereof increased throughout the 1930’s. This revolutionized polymer synthesis and quickly resulted in the first commercial production of polystyrene, polyesters, polyvinylchloride, polyethylene and polyamides. Development of polymer-characterization techniques was driven by the need to support polymer production and studies into new synthesis routes and application fields. In 1953 Flory wrote ‘Principles of polymer chemistry’, an overview of both polymer chemistry, as well as
characterization methods for polymers, which is still considered an important reference work [8]. Flory’s contributions to the theory of polymers in solution (Flory-Huggins solution theory and excluded volume) earned him the Nobel Prize in Chemistry in 1974.

According to IUPAC the modern definition for macromolecule or polymer is: "A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass” [18]. Different types of polymer may be identified depending on their origin. Most common are synthetic polymers and natural- or biopolymers. Examples of natural polymers include proteins, starch, cellulose and DNA. The emphasis throughout the work presented in this thesis will be on synthetic polymers.

<table>
<thead>
<tr>
<th>Table 2. Different levels of polymer structure</th>
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<tr>
<td><strong>Polymer</strong></td>
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<td><strong>Micro-level (molecular)</strong></td>
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<tr>
<td>Relative molar mass (MMD)</td>
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<tr>
<td>(Relative) Monomer content (CCD)</td>
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<tr>
<td>Functionality (end groups)</td>
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<tr>
<td>Branching / Topology</td>
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<tr>
<td><strong>Meso-level (morphology)</strong></td>
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<tr>
<td>Crystallinity</td>
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<td>Self-assembly</td>
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<td>Particle size distribution</td>
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<td>Mixing and compatibilization</td>
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<tr>
<td>Orientation</td>
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<tr>
<td><strong>Macro-level (polymer properties)</strong></td>
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<tr>
<td>Density</td>
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<td>Glass transition temperature</td>
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<td>Melting point</td>
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<tr>
<td>Optical properties</td>
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<tr>
<td>Solubility</td>
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<tr>
<td>Strength</td>
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<tr>
<td>Viscosity (melt)</td>
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</table>

1.1.3 Polymer structure

The characteristics of polymeric materials are the results of many structural features (Table 2). It is for this reason that characterization is not straightforward and that understanding of the material properties requires information on more than a single structural feature. The basic structure of a polymer is determined by the chemistry of the repeat units and how they are linked together (micro-level). Structural features at the
meso- and macro-level depend on the molecular features, but also on the processing conditions of the material. Polymers are heterogeneous materials and so the distribution of micro-structural features is important as well.

A very important parameter is the number of repeat units in a chain, which is also known as the degree of polymerization. It has a large impact on polymer properties (macro-level) and is typically expressed as the relative molar mass ($M_r$). A molar-mass distribution (MMD) is invariably present in synthetic polymers due to the stochastic nature of polymerization reactions. This does result in molecules with different $M_r$ being formed even when reaction conditions are kept identical. A common metric for the MMD in polymers is the polydispersity index (Eq. 2), which is defined as the ratio of weight averaged to number-averaged molar mass ($M_w$ and $M_n$ respectively).

$$PDI = \frac{M_w}{M_n}$$  \hspace{1cm} (2)

Optimization of polymerization conditions makes it possible to control $M_r$ and MMD and obtain polymers with targeted properties. Reversely, measuring $M_r$ and MMD may provide information on the polymerization conditions, in particular the termination reactions [19]. Details on various types of polymerization reactions can be found in textbooks on polymer chemistry [e.g. 8,20].

Chemistry is the broadest variable in polymer structure. Polymers with different monomer chemistries have vastly different properties and application areas. Co-polymers can be created with monomers of different chemistry, which are appropriately referred to as co-monomers. The chemical-composition distribution (CCD) may deal with overall composition (inter-chain composition), as well as distribution within chains (intra-chain distribution). Examples include randomness and block-length distribution. Tacticity is an intra-molecular form of stereochemistry and may therefore also be considered part of the CCD. When the chemistry of individual repeat units has affects reactivity or structure this is classified as “functionality”. Typical examples are reactive end groups and pendant groups on the backbone.
Branching and topology are other important aspects of the polymer structure. Polymers with branching may be obtained through the addition of (multi-functional) co-monomers, post-reaction processing or ‘back-biting’ side-reactions taking place during polymerization [21]. There are many variations possible to the linear structure, resulting in branched polymers with many different forms (Fig. 1). The most common applications of branched polymers take advantage of the melt rheology and solid-state material properties that are unique for these materials. These macro-level effects can be explained by the characteristics at the meso- and micro-structural level. Especially the level of (inter-molecular) chain entanglement and crystallinity are affected by branching properties, which affects material properties related to stretching, deformation or flow of the polymer.

Changes on the molecular level as a result of branching include a higher number of end groups, shorter back-bone length and a more compact structure relative to linear polymers. Branched polymer with chemically different or modified end groups can be used as highly effective functional materials. The compact molecular structure of branched molecules gives rise to the melt and material properties corresponding to a
combination of shorter chain length but higher molar mass. It is also an important handle in the characterization of branched polymers using dilute-solution techniques, which will be explained later. The main classes of branched polymers are presented in Table 3.

Table 3. Different types of branched polymers and the properties

<table>
<thead>
<tr>
<th>Type</th>
<th>Effects and applications</th>
<th>Chemical pathways</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Long-chain branching</strong></td>
<td>Melt rheology modification, Increased toughness</td>
<td>Back-biting in ethylene and acrylate polymerization, Co-polymerization, Light Cross-linking [22]</td>
<td>LDPE, polypropylene, polycarbonate [23], polystyrene, nylon, PMMA [24]</td>
</tr>
<tr>
<td><strong>Short-chain branching</strong></td>
<td>Reduction in crystallinity, Improved material properties</td>
<td>Back-biting in ethylene polymerization, Co-polymerization</td>
<td>Polyolefins, LLDPE</td>
</tr>
<tr>
<td><strong>Star</strong></td>
<td>Model component in rheology research, Multi-functional macro-monomers, Functional materials</td>
<td>Core-first, Multi-functional initiator</td>
<td>Thermo-responsive polymer [25], Low-viscosity inkjet ink [26], Light-switchable coatings [27]</td>
</tr>
<tr>
<td><strong>Combs/brush</strong></td>
<td>Model component in rheology research, Functional materials</td>
<td>Macro-monomer polymerization [28]</td>
<td>Polyelectrolites [29], Biomimetic materials [30]</td>
</tr>
<tr>
<td><strong>Dendrimers / Hyperbranched polymers</strong></td>
<td>Multi-functional macro-monomers, Functional materials [31]</td>
<td></td>
<td>Drug delivery [32], OLEDs [33]</td>
</tr>
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</table>

Short-chain branching (SCB) is a property that is almost exclusively associated with polyolefins. This is because in other polymers the functionality of pendant groups is different from the backbone and it is reflected in the CCD. Unlike other forms of branching, the impact of short-chain branches on polymer properties is mainly a result of interference with crystallinity at the microscopic level (meso scale). The most common application of SCB is in the modification of linear high-density polyethylene. With Ziegler-Natta catalysts linear low-density polyethylene may be produced by co-polymerization of ethylene with alpha-olefins, ranging from propylene to 1-hexadecene,
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to introduce SCB. With contemporary single-site and metallocene catalysts it is possible to precisely control the degree and distribution of SCB in LLDPE polymers and, thus, to produce materials with highly optimized properties. An increase in SCB density results in lower crystallinity and lower density of the material. These are important characteristics of linear low-density polyethylene, where ‘linear’ in the name refers merely to the absence of long-chain branching (LCB). It is generally accepted that very short branching introduces rubber-like behavior (e.g. ethylene-propylene rubbers), whereas longer chains as obtained by copolymerizing 1-hexene or 1-octene provides elasticity and other properties beneficial for LLDPE films [34]. Low-density polyethylene (LDPE) is produced by free-radical polymerization at high pressure and contains both SCB and LCB as a result of back-biting. This is a side-reaction where in a propagation step the free radical at a terminal methylene group is transferred to a methylene group somewhere in the chain by hydrogen abstraction. Branches of random length and at random position are created in this way. LDPE combines the distinct advantages of LCB polymers with a lower density than linear high-density polyethylene (HDPE).

Advantages of LCB polymers are higher zero-shear viscosity, improved melt strength, reduced melt fracture, reduced melt viscosity at high shear rates (i.e. shear thinning) and extensional thickening. Polymers with LCB have superior processing properties and they can be used for demanding applications such as blow molding, blown-film formation and closed-cell foam production. Long-chain branching has an effect on viscosity through entanglement of the polymer molecules. Above the critical molecular weight $M_c$, which marks the onset of chain entanglement, the melt viscosity of polymers increases no longer linearly with mass but with $M_c^{3.4}$ [35,36]. The average length of the chain segments between entanglements $M_e$ can be determined using experimental techniques [37,38]. An overview of $M_e$ values for many polymers has been established based on rheology and small-angle neutron scattering (SANS) measurements on linear and short-chain-branched model compounds [39]. For amorphous polymers the critical molecular weight $M_c \approx 2M_e$. The chemical composition of the polymer backbone has a large effect on the onset of entanglement. Therefore, the effects of LCB may differ for polymers with different chemistries through the effect on $M_e$. Branches in LCB-polymers should be longer than $M_e$ to affect
the rheology of the material. In practice long-chain branches will have a significant chain length relative to the backbone of the polymer. Polyolefins with LCB are created using free-radical polymerization, but may also be obtained in metallocene catalyzed polymerization. Using constraint geometry catalysts (CGC) it is possible to produce and incorporate chains with vinyl terminal groups into the final polymer [40,41,42]. The typical branching frequency for CGC and other metallocene polyethylenes is less than 1 long chain branch per polymer [43], while in LDPE between 3 and 7 long chain branches are common. LCB in CGC polyethylene will be longer (1300 – 1600 carbon atoms) than LCB in LDPE, which has branches with 200 – 300 carbon atoms in the backbone [44,45,46,47,48]. Other pathways for the introduction of LCB are the use of multi-functional co-monomers [24] or multi-functional initiators. Cross-linking after reaction can also be used to introduce LCB, for instance by addition of peroxides or irradiation. Treatment of HDPE and LLDPE with gamma-irradiation has been performed to induce LCB successfully [22]. A too high degree of cross-linking will result in network or gel formation, which will compromise the melt behavior of the material.

LCB is introduced in most commercially produced polymers by chemistry that adds branches at random locations on the backbone. The polymerization processes for polymers with controlled and regular LCB (star, comb and brush polymers) are usually not cost effective for the production of commodity plastics, because of the need for high-purity monomers or expensive reactants. These materials are typically produced using multi-step reactions, in which macro-monomers or multi-functional cores are coupled using anionic polymerization or controlled polymerization reactions, such as atom-transfer radical-polymerization (ATRP) [49], nitroxide mediated polymerization (NMP) [50] or reversible addition-fragmentation chain-transfer polymerization (RAFT) [51]. Only the use for specialty applications or functional materials justifies the cost involved in producing these materials (Table 3). The ability to create polymers with well-defined branching topologies and branch lengths is important for studies into the rheological behavior of polymers [37,38,52]. In this way the effect of increased branching frequency and branch length on various rheological and material properties can be determined. Results from this type of research are used to design new materials with optimized properties.
In dendrimers and hyperbranched polymers the branching functionality is included in the main polymerization process, rather than a variation to linear polymerization. Most often such polymers are produced using condensation polymerizations. The emphasis is on chemical functionality of the material and most dendrimers are used as functional materials [31].

1.2 Characterization and separation of branched polymers

Nowadays several techniques are available for the characterization of branched polymers. The effectiveness generally depends on the type of branching, as well as the impact on the measurement by other structural properties of the polymer and the distribution thereof. In certain cases it is therefore desirable or even necessary to add a separation step before measurements are performed on the polymer.

1.2.1 TREF, Crystaf and DSC

Measurements on crystallization behavior and rheological properties of polymers are common in quality control, production and application-related testing. These tests are highly sensitive towards the impact of branching on the macro level properties. The impact of branching on crystallinity and melt-behavior was described in the section on polymer structure above. Techniques that are often applied are differential scanning calorimetry (DSC), temperature-rising elution fractionation (TREF) and crystallization analysis fractionation (Crystaf). In TREF the polymer is first loaded on a stationary phase and subsequently eluted as temperature is increased [53]. The loading step is performed by having the polymer crystallize slowly out of solution. The polymer eluting from the stationary phase upon temperature increase may either be fractionated or subject to concentration detection for characterization of the redissolution behavior. TREF was developed in the early 1980’s and has been widely applied to characterize the short-chain-branching distribution (SCBD) and tacticity, but it may also be used to fractionate by chemical composition for certain polyolefins. In more recent applications the analysis of TREF fractions by, for instance, size-exclusion chromatography (SEC) has been automated [54]. Crystaf was developed in the 1990’s and is used to monitor the crystallization of polymer in solution when the temperature is decreased [55]. Crystaf is preferred over TREF, because the analysis can generally be performed at higher cooling rates, provided the desired information on polymer composition can still
be obtained. The suitability of either technique depends on specific crystallization behavior. It is known that the crystallization and dissolution delays for ethylene and propylene polymers are different, which implies that the separation of polyethylene and polypropylene is only possible with TREF. Another complication is the “supercooling” of crystallizable materials in solution when the solution is cooled down faster than nucleation in solution occurs [56, 57]. Crystallization steps should be performed at sufficiently slow so as to prevent co-crystallization. These effects have been illustrated in a comparison between TREF, Crystaf and DSC for the analysis of LLDPE and blends with polypropylene [58].

Results for Crystaf analysis of an LDPE and an LLDPE resin are compared in Fig. 2 [59]. Crystaf and TREF results are typically presented in the same way with differential polymer concentrations in solution on the y-axis and temperature on the x-axis. For Crystaf analysis the results have been measured starting at 95°C down to 30°C in 1,2,4-trichlorobenzene (TCB). For LLDPE a typical bi-modal distribution is observed. The mode near 80°C corresponds to crystalline polyethylene segments in the polymer, whereas the broad mode below 75°C represents the amorphous material. Only one single mode is observed for LDPE in the amorphous region as a result of both SCB and LCB. Crystallization behavior is influenced not only by the amount of co-monomer (i.e. degree of branching), but also by the distribution and block-length of segments with different crystalline properties. Therefore, crystallization techniques are the method of choice for characterizing modern LLDPE polymers. These may be prepared using multiple metallocene catalysts or in a multi-stage reactions, resulting in complex distribution of SCB. Crystaf and related techniques are the first choice for monitoring catalyst efficiency in production processes or for investigating unexpected changes in polymer performance.

1.2.2 Rheology

Measurements of viscosity and the behavior of polymer melts are among the most sensitive methods known for characterizing LCB in polymers. Rheological experiments allow for direct characterization of macro-level properties. Different types of measurements are performed, depending on the shear-rate regime of interest [60].
Dynamic-mechanical analysis (DMA) can be performed to obtain detailed information on stress-strain relations typically in the range between 0.1 and 100 s$^{-1}$ using rotational viscometers. Zero-shear viscosity is obtained from the viscosity value at an arbitrary low shear value, typically 0.1 s$^{-1}$. Elastic properties (e.g. shear storage- and loss modulus) and dampening ($\tan \delta$) may be investigated by oscillatory viscometry in frequency-sweep experiments. All these parameters have been compared against structural properties for polyethylene and were found to be affected by SCB and LCB in distinct ways [37,61]. Measurements with an extensional rheometer are used to test for strain-hardening behavior, and uniaxial and biaxial elongation [62]. Branching often improves strain-hardening and biaxial-elongational properties of polymers. Therefore, extensional rheology can be used for quality control of LLDPE and other branched polymers. DMA at shear rates $< 0.1$ s$^{-1}$ is rarely used for purposes other than studies on creep behavior of polymers. Capillary viscometers are used for measurement at shear rates $> 100$ s$^{-1}$. Applications include the measurement of polymer melt-flow-rate (MFR, also referred to as melt flow index in case of polyethylenes) and determination of intrinsic viscosity of polymers in dilute solution. Solution measurements using capillary viscometry will be described in more detail later (see section Size-exclusion chromatography with selective detection).
The effect of long-chain branching on viscosity is demonstrated in a comparison of rheology curves for polyethylenes with different LCB frequency (Fig. 3) [45]. These materials were prepared using a constrained-geometry catalyst, which is a metallocene-type catalyst that allows for accurate control of LCB in the polymer [61,63]. An increased zero-shear viscosity and a shear-thinning effect at high shear rate are observed for polymers with higher branching frequencies. A metric that is used to express shear-rate sensitivity is the ratio of melt-flow indices obtained with two different loads. The measurement of melt-flow indices is performed at standardized conditions (ASTM D-1238), where the melt flow through a capillary is measured with either 2.18 or 10 kg of load on the piston driving the polymer. For polyethylene this measurement is typically performed at 190°C.

Investigation of LCB using rheology curves is complicated, because the viscosity and the shear-rate dependence thereof are also influenced by other properties of the polymer. Comparing polymers with different MMDs is difficult. An increase in the molar mass will result in a higher viscosity, irrespective of the shear rate. Changes in the polydispersity will affect shear-rate-dependent viscosity, with an increase in PDI resulting in changes comparable to those observed for polymers with increased LCB frequency. The presence of additives (Table 2) will also affect rheology curves. It is known that additives can have an unexpected impact on rheology that interferes with the
measurement. Rheological measurements, therefore, are most useful when performed on pure polymers with comparable characteristics. Access to a number of comparable pure reference materials with known architecture is highly desirable for interpretation of the results in terms of relative differences. Comparison of molar-mass data and zero-shear viscosity for such a set of data provides very sensitive detection of LCB in the polymer [43].

1.2.3 Spectroscopy

Information obtained from spectroscopic techniques can be used to elucidate the micro-level structure of polymers. Infrared detection is traditionally used for monitoring the chemical composition and it can be used to discriminate between repeat units and branch points. It was used already in 1940 by Fox and Martin to prove branching in polyethylene polymers [64]. The only common application for branching-selective detection with IR today, however, is for the determination of SCB in polyolefins by selective detection of C-H bonds on secondary and primary carbon atoms [65]. Short-chain-branching frequency is reported as the number of methyl groups per 1000 carbon atoms. Most often information on the SCB distribution of a polymer rather than an average SCB frequency is desired. Such information can be obtained by infrared analysis of the fractionated polymer or by using a hyphenated technique, such as SEC-FTIR. Deslauriers et al. demonstrated SEC-FTIR with a precision of ±0.5 Methyl/1000C under optimized conditions for ethylene 1-olefin copolymers with ethyl and butyl branches [65]. Partial least squares regression was used to build a calibration between a selected spectral region and reference data on SCB frequency. Precision of FTIR detection depends on the training set used to build a model. Either levels of ethyl and butyl branches beyond that of the training set or inclusion of different functionality will reduce the accuracy of the model. On-line coupling with chromatographic techniques reduces the sensitivity of FTIR, because of the dilute solutions inherent to most forms of chromatography [66,67]. An alternative to dilute-solution detection in flow cells is available in the form of on-line polymer deposition on a germanium disk using an LC-transform interface [68]. Polymer composition may be detected more sensitively in this way without interference by the solvent, but the precision and accuracy of the method leave to be desired [69].
Both SCB and LCB may be studied by NMR spectroscopy. In case of $^{13}$C NMR quantitative results well below 1 in $10^4$ carbon atoms have been reported for polyolefins with good precision using modern techniques [61]. It is possible to distinguish between branches of different length up to hexyl side-groups and report their frequency independently [48,70]. Branching frequency may be reported per molecule or an arbitrary number of carbon atoms, provided molar-mass information is available. Most quantitative results have been obtained by measurement of polymer solutions, but melt analysis by magic-angle spinning NMR has also been reported [66]. Unfortunately, measurement of the backbone atoms near or at low-abundance branch points requires very long measurement times in $^{13}$C NMR. Fractionation and even on-line coupling with HPLC or SEC is possible, but this is only practical for $^1$H NMR for reasons of sensitivity and speed [71]. LC-NMR is used more often for screening of chemical composition [72] than for characterizing LCB.

Mass-spectrometric characterization of branched polymers is limited to a specific number of applications, despite its proliferation for polymer characterization in general [73]. Soft ionization techniques, such as matrix-assisted laser/desorption ionization (MALDI) and electrospray ionization (ESI), in combination with high-resolution mass spectrometry (e.g. time-of-flight mass spectrometry, ToF-MS) are most useful for the analysis of dendrimers [74]. These techniques are not applicable for polyolefins and traditional random LCB polymers, because their molar mass is too high and branching does not induce distinct mass differences of fragments. Mass spectrometry can be applied successfully for branched polymers with moderate molecular weight and sufficient ionizability. Products of condensation polymerization, including dendrimers and hyperbranched polymers, are often amenable for characterization using mass spectrometry [75,76]. Most mass-spectrometry applications for polymers deal with the analysis of chemical-composition distributions, which includes the use of multifunctional initiators and repeat units ultimately resulting in branched polymers. Hyphenation of various types of liquid chromatography with ESI-ToF-MS provides a strong combination for these polymers [77].
1.3 Size-exclusion chromatography with selective detection

Separations are important in many techniques for the characterization of polymer microstructure and are essential when studying the distribution in polymer properties. Size-exclusion chromatography (SEC) is one of the most-common techniques in the characterization of polymers. Since its introduction the 1960’s [78,79] SEC has been used for the characterization of molar mass and MMD of polymers. In combination with selective-detection techniques, such as on-line laser-light scattering and viscometry, the degree of branching may be studied as a function of molar mass. The sensitivity of these techniques is highest for LCB polymers, but other types of branching may be investigated as well. A general requirement is that the polymers under consideration are well dissolved and do not significantly differ from random-coil behavior in solution. Different configurations of SEC with selective detection may be applied to obtain comparable information of branched polymers. Preference for any separation or detector configuration depends on specific strengths and tolerances. Separation and different forms of detection are presented in the following sections to introduce the considerations for common configurations of SEC with selective detection.

1.3.1 SEC separation of branched polymers

Separation in SEC is achieved through size-selective migration of polymers in dilute solution through a column packed with porous particles [80]. The separation is entropic in nature and interactions between the polymer and the column packing should be negligible. Large polymer molecules are selectively excluded from pore space in the SEC column. Their reduced access to the stagnant mobile phase in the pores results in elution before materials that can enter the pore volume driven by random diffusion. The relevant size parameter is that of the free molecule in solution and is referred to as the hydrodynamic size or volume of the polymer [81].

Separation in SEC is an indirect result of molar mass and branching through their impact on hydrodynamic size. It is therefore important to understand how experimental and molecular properties affect the relation between size and mass. The theory for solution behavior of flexible-chain linear polymers has been described in detail by Flory and Casassa [8, 82]. They found that random-coil statistics could be used to describe the relation between molar mass and ‘coil dimensions in solution’ (simply referred to as
polymer size from here on) for ideal polymers. Application of random-coil statistics can be used to describe many other structure-property relations of real polymers appropriately using scaling laws [83]. The relation between polymer size $r$ and molar mass may be described using the general scaling law shown as Eq. 3, with empirical constants $a$ and $b$ correcting for polymer-solvent specific behavior (with $b = 0.5$ for a random coil).

$$r = a M^b$$  \hspace{1cm} (3)

Scaling laws can be used, for instance, to describe mass dependency of intrinsic viscosity using the Mark-Houwink relation (Eq. 1) over a molar-mass range of several orders in magnitude [84]. Branching in polymers will interfere with the scaling behavior between hydrodynamic size $r_h$ and molar mass $M$ (Fig. 4) [85,86].

An increasing level of (long-chain) branching will result in a reduced freedom of the chain and therefore a smaller size in solution. Another effect is the increase in segment density, which generally results in a lower intrinsic viscosity. The differences in scaling behavior between linear and branched polymers *i.e.* different relation between molar mass and polymer size, may result in co-elution of polymers with different molar mass when linear and branched molecules are present. Branched polymers will generally elute from the SEC column together with linear polymers with lower molar mass (but identical hydrodynamic size) due to their more compact coil structure. Local polydispersity in SEC [87,88,89] as a result of branching has been studied by several experts. Its presence was proven experimentally by careful consideration of the results from on-line detection techniques that provide either number- or weight-average molar mass at each elution increment. The calculation of local polydispersity is typically not
included in the workflow of multi-detector SEC techniques and only possible with the additional effort of setting up a universal calibration. This highlights one of the fundamental limitations of multi-detector SEC and supports the need for better separation techniques that can resolve linear and branched materials.

1.3.2 SEC with on-line (micro-)viscometry

Capillary viscometry has been used for calculation of molar mass since the early discovery of the Mark-Houwink relation for polymers. Before the advent of on-line detectors in the 1980’s, Mark-Houwink relations had to be established by measurement of solution viscosity using, for instance, Ubbelohde viscometers. With the introduction of differential viscometry it became possible to hyphenate viscometers with separation techniques [80]. Viscometers based on the Wheatstone-bridge design have been commercialized and have become widely available for viscosity measurement in SEC [90]. Most commercial detectors use a Wheatstone bridge constructed made with four steel capillaries with matched restriction. For the work presented in the rest of this section a novel micro-sized viscometer has been used. This detector was made available by Polymer Laboratories and Micronit in an effort to address the challenges experienced with traditional commercial viscometers [91]. The Wheatstone bridge of this detector has a total volume of only 8 µL and has been created on a glass chip, which allows for tight engineering specifications and a perfectly balanced bridge. At a flow rate of 100 µL/min the viscometer operates at a shear rate of 3000 s⁻¹, which is the standard for commercial capillary viscometers. With the reduced detector bridge volume this detector can match cell volumes encountered in contemporary light scattering and concentration detectors. A complete set of miniaturized detectors allows also for “miniaturized” separations. Therefore, SEC columns with dimensions of 4.6 mm ID × 250 mm were used.

With differential viscometry the specific viscosity can be measured on-line. In combination with on-line concentration detection it will allow calculation of intrinsic viscosity at each elution volume (Fig. 5). For polymers with known Mark-Houwink constants the molar mass can also be calculated at each elution volume. This approach is not practical for the analysis of branched polymers, because the Mark-Houwink parameters change with branching properties and frequency. However, other approaches
that do not require Mark-Houwink parameters may be used to characterize branched polymers using SEC with viscometry.

![Fig. 5. Instrument configuration for SEC with on-line viscometry as used for universal calibration.](image)

1.3.2.1 Universal calibration

Regular molar-mass calibrations, prepared using narrow standards, have limited applicability. Corrections for other polymer systems can only be made when Mark-Houwink constants are known for both calibrant and analyte. A universal calibration method was introduced by Grubistic [92]. Knowledge on Mark-Houwink parameters of the analyte is no longer required for molar-mass calculation when an on-line viscometer is used. Intrinsic viscosity may be used to calculate molar mass directly when a column calibration is available in terms of hydrodynamic volume ($V_h$). This is possible because of the direct proportionality between $V_h$ and the product of intrinsic viscosity [$\eta$] and molar mass ($M$) (Eq. 4).

$$V_h \propto [\eta]M$$  \hspace{1cm} (4)

Validity of the universal calibration for polymers of different architecture and composition has been demonstration by the good correlation for all polymers in a plot of [$\eta$]M against elution volume [84,92]. Accuracy of the results obtained by universal calibration is challenged by the sensitivity of this calibration principle to experimental imperfections. For samples with narrow MMD the incomplete separation is incorrectly interpreted, resulting in a higher PDI and “anomalies” in Mark-Houwink plots. Better results are obtained using the concentration and viscometer signals from the setup in Fig. 6. For samples with broad MMD acceptable results could be obtained. Also these results were extremely sensitive to changes in absolute retention time (correction using flow-marker possible) and inter-detector delay volume. Changes in the room
temperature suffice to compromise the accuracy of universal calibration for systems that are not fully thermostatted, such as the setup used in this study. Good results with acceptable accuracy may be obtained using universal calibration performed under well-controlled conditions.

**Fig. 6.** Instrument configuration for triple-detection SEC.

### 1.3.2.2 Triple detection SEC

With on-line light-scattering detection the molar mass of polymers can be measured directly. For polymers in dilute solution the weight-average molar mass may be calculated from the intensity of the scattered light using the Rayleigh-Gans-Debye approximation [80,86]. A practical complication is the angular dependence of scattering as a result of destructive interference of scattered light from molecules in solution larger than roughly 1/20 times the wavelength of the light. The applicable size is the root-mean-square radius of the polymer, also referred to as radius of gyration ($r_g$). A correction is generally applied to obtain corrected values for $M$ and $r_g$ through iterative calculations [93].

In triple-detection SEC both a light scattering and viscometer are added to the detector array. In the original configuration of triple detection SEC a right-angle laser-light-scattering detector is used [93]. With measurement of light scattering at 90° the traditional problems with signal noise at low angles are avoided, but a correction for angular dependence is required. This is achieved using an estimate of $r_g$ calculated using the viscometer data, estimated $M$ and the Flory-Fox equation. The detector
configuration allows for calculation of both $M$ and $[\eta]$ at every elution volume without the need for column calibration. This prevents issues and limitations inherent to the universal calibration with respect to absolute elution-volume differences. The sensitivity to errors in inter-detector delay or band broadening remains. In Fig. 7 the effect of inter-detector band broadening in a non-optimized setup is demonstrated for the analysis of six-arm star polystyrenes with narrow MMD [94]. Broadening in the detector signals for the RALLS and viscochip was caused by splitting of the flow towards the differential refractive index (dRI) detector before the RALLS detector (in contrast to the configuration in Fig. 6). This resulted in an unrealistic increase in both $M$ and $[\eta]$ at higher elution volumes. The RALLS signal was found to be broadened by 2 seconds for a narrow-standard peak with a width at half height of 36 seconds on the dRI signal.

With the appropriate detector configuration as displayed in Fig. 6 good results have been obtained without artifacts resulting from inter-detector band broadening. Z-RAFT six-arm star polystyrenes were analyzed using triple-detection SEC with UV absorption for concentration detection (Fig. 8 and Fig. 9). The extent of inter-detector band broadening was minimal due to the small UV detector-cell volume of only 2.5 µL. Most of the polystyrene polymers were found to have an extremely narrow MMD (i.e. PDI < 1.1), with the exception of polymerization products obtained at very high levels of conversion. Absolute molar-mass results obtained using triple detection were used for confirmation in studies into the molar-mass offset in conventionally calibrated SEC by polymers with known branching topology [94,95]. The results of this work are treated in more detail in Chapter 5.

The traditional strength of triple-detection SEC lies in the possibility of absolute molar-mass detection for polymers with relatively low molar mass. A RALLS detector is simpler by design (less expensive) and can be built with a smaller detector-cell volume relative to the more complex forms of light-scattering detection. In modern applications the uncertainties introduced by angular correction and estimation of $r_g$ using the Flory-Fox equation may be alleviated by using a dual-angle detector. Above an arbitrary mass or estimate of $r_g$ the low-angle signal is used, which is much less sensitive to angular dependence.
**Fig. 7.** Mark-Houwink plot; example of triple-detector data subject to inter-detector band broadening. (a) linear PS1683, (b) 6-arm star polystyrene polymers with different molar mass but uniform arm length.

**Fig. 8.** Chromatograms of narrow-MMD six-arm star polymers and a broad-MMD reference; (a) linear PS1683, (b) 6-arm star PS polymers, (c) 6-arm star PS polymer obtained at high monomer conversion.

**Fig. 9.** Mark-Houwink plot for narrow-MMD six-arm star polymers and a broad-MMD reference.
1.3.3 SEC with multi-angle laser-light-scattering detection

The different relation between molar-mass and intrinsic viscosity of branched polymers is clearly observable in the Mark-Houwink plot. Six-arm star polymers have higher molar mass and lower intrinsic viscosity than linear polystyrene with an identical hydrodynamic size. The difference in solution properties of branched polymers relative to those of linear polymers can be detected using SEC with selective detectors. Multi-angle laser-light scattering (MALLS) is another selective detector that was not introduced yet, but is commonly used in the characterization of branched polymers. Due to the added information of scattering at multiple angles relative to the incident light the angular dependence may be solved to obtain $r_g$ directly at every elution volume, provided that the particle is large enough to yield appreciable angular dependence. Calculation of $r_g$ does not require any other detector signal and is therefore not affected by the experimental imperfections of multi-detector arrays, such as inter-detector volumes and inter-detector band-broadening.

Relative differences in solution behavior of polymers are often expressed as contraction ratios based on either MALLS detection (Eq. 5) or viscometry (Eq. 6). The subscripts $B$ and $L$ indicate data for branched and linear reference polymer respectively, comparing data of identical molar mass as indicated as the subscript $M$.

$$g = \left[ \frac{\left( r_g \right)_B^2}{\left( r_g \right)_L^2} \right]_M$$

$$g' = \left[ \frac{[\eta]_B}{[\eta]_L} \right]_M$$

Differences in $r_g$ and $[\eta]$ between linear and branched polymers may be small and hard to observe in log-plots in comparison with plots of contraction ratio vs. molar mass. Theoretical models for long-chain-branching frequency based on the relative changes compared to linear polymers were derived for random-coil polymers even before SEC with on-line detection became available [96]. Nowadays contraction ratios have been tabulated for many branched polymers under different solvent conditions [86]. Plots of contraction factors, $r_g$ or $[\eta]$ as a function of molar mass provide important information on the branching distribution and are often indicative of the polymerization mechanism.
related to the inclusion of branching. The relation between the parameters $g$ and $g'$ has been of great interest, because the models for branching frequency are based on $g$. The relation between both parameters is not straightforward and varies within polymers as a function of molar mass. SEC-MALLS and triple-detection SEC with a MALLS detector may be used to investigate this relation on-line [97,98].

1.3.4 Application and challenges of existing methodology

Measurement of differences in $r_g$ and intrinsic viscosity with SEC in combination with selective detection techniques is particularly useful for polymers with a low degree of long-chain branching. Branched polystyrenes that have been used throughout this thesis were analysed using triple-detection SEC (Fig. 10 and Fig. 11) and SEC-MALLS-dRI (Fig. 12). Both techniques demonstrate good signal quality for high-molar-mass polymers, because of the high light-scattering intensity. Contraction is observed in $r_g$ and intrinsic viscosity measurements of the branched materials and increases towards increasing molar mass, which indicates an increase in long-chain branching. At the low molar-mass end the data quality is not so good, in particular for the MALLS data. Data for the low-LCB polymer is of similar quality as the linear reference and the scatter in $r_g$ is caused by the small angular dependence of the light scattered by the smaller molecules.

Anomalous results are observed for the polystyrene with high LCB. The material that is eluting later from the SEC columns is responsible for the upward curvature in the conformation plot (Fig. 12). A change of the curve for LCBps in the Mark-Houwink plot towards higher molar mass is observed at the low-mass end, which is indicative of SCB in case of a good SEC separation [99]. This phenomenon is known as anomalous late elution or late elution in SEC and occurs specifically for branched materials. Detailed investigation of the experimental parameters in the SEC separation and comparison with field-flow fractionation (FFF) was performed for polystyrenes and acrylates [100] as well as for LDPE [101]. It was concluded that the high molar-mass tail of branched polymers is retained in the SEC column and slowly elutes together with the molecules of low molar mass.
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Fig. 10. Chromatograms of broad-MMD linear and branched polystyrene samples. (a) linear PS1683, (b) low-LCB PS1500-10, (c) LCB PS PA2258-123 / PSbranch

Fig. 11. Mark-Houwink plot for broad-MMD linear and branched polystyrene samples

Fig. 12. Conformation plot of linear and branched polystyrene samples
The separation of this high-LCB polystyrene was performed using FFF, which separates also the large molecules in solution very well [102] (Fig. 13). In the same figure an overlay is provided of the SEC and asymmetrical flow field-flow fractionation (AF4) results. It is clear that the material on the high molar-mass end is not separated by SEC. As a result of the incomplete separation in SEC the eluent fractions will be polydisperse. Overestimation of $r_g$ is promoted by the higher sensitivity of the MALLS for larger polymers, as the calculated value over the average population is a z-average.

Polymers with very-high molar mass fractions that are not well separated using SEC are preferably separated using FFF or another technique that does not suffer from problems with late-elution of branched or high-molar-mass materials. Separation techniques that do include light scattering will provide the end user with data that makes it possible to recognize problems with late elution, whereas in universal calibration this is not observed unless significant material is observed to elute after the column void volume using the concentration detector. In practice the amount of late-eluting material is very small and it is unlikely that this is detected using a concentration detector. A broader overview of complications in SEC with on-line light scattering and viscometry has been provided by Mourey [103].

![Fig. 13. SEC-MALS and AF4-MALS of the same highly branched polystyrene](image-url)
1.4 Scope of the thesis

The aim of this work is to explore new technology for the characterization of branched polymers, not limited by the traditional boundaries of common applied analytical techniques. Initial results on molecular topology fractionation [104] served as an inspiration to explore this separation further. The mechanism behind this fractionation was still open for multiple explanations, because separation conditions could often not be defined or studied systematically. Monolithic columns were prepared specifically to address this issue. Columns for MTF were applied in a two-dimensional separation with a size-based separation to study and optimize a true separation by topological properties of the polymer.

Chapter 2 deals with the preparation of monolithic columns and their optimization for polymer separations. Monolithic stationary phases have received much attention as an alternative for packed beds for interaction chromatography. The highly interconnected network of channels in polymeric monoliths provides an excellent environment for hydrodynamic separations. Monoliths with different macropore sizes were prepared and the materials were studied in an effort to understand the porous structure. It was concluded that hydrodynamic chromatography was the prevailing separation mechanism based on the confirmation of a unimodal pore-size distribution and a continuous flow-through nature of the pores.

Chapter 3 details the application of multi-dimensional separations with selectivity based on topology. The idea to separate a polymer based on its hydrodynamic size and topology in a comprehensive two-dimensional separation is demonstrated for the first time. A star polymer was used for the branching-selective separation. This serves as a model compound for LCB polymers.

In Chapter 4 the application of MTF is considered in more detail and the mechanism of separation is discussed. A systematic study on the selectivity is conducted using columns with different channel sizes. Knowledge obtained in Chapter 2 on the pore structure and separation characteristics of the columns was taken into account. Columns used in this study provided better efficiency compared to previously used MTF columns, which were short in length and were packed with polydisperse silica. The
flow-rate effect on migration has been investigated thoroughly for both linear and branched polymers.

In Chapter 5 the synthesis and analysis of branched polymers with well-defined topology is presented. It is demonstrated that for polymers prepared with well-defined topology the molar mass can be calculated from conventional SEC experiments. The application is compared with results from theoretical studies for correction factors and experimental results from other researchers. Absolute molar-masses were calculated for the star-branched polymers for validation of the predicted molar mass using both correction factors and theoretical molar mass for specific monomer conversion in the polymer synthesis.

References

Chapter 1

Introduction

[59] H.J. de Jonge, R. Dingemanse, unpublished Crystaf results on research samples of LDPE and LLDPE provided by Dow Chemical.