Thermal field-flow fractionation of polymeric and particulate materials: applications and fundamental aspects
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Summary and future prospects

This thesis concerns the Thermal Field-Flow Fractionation (ThFFF) technique. ThFFF is a one-phase separation technique that relies on a temperature gradient to fractionate polymer, colloid, or particle samples. The driving force of ThFFF is the so-called thermal diffusion. The thermal diffusion phenomenon is, however, not well understood, which hampers the development of ThFFF. The main topics of the study described in this thesis are the thermal diffusion effect and the development of new applications of ThFFF.

Chapter 1 is a general introduction about Field-Flow Fractionation dealing with the basic principles, the different retention modes, and often used sub-techniques. Emphasis is put on ThFFF.

Because normal diffusion coefficients are required to calculate thermal diffusion coefficients from ThFFF retention data, several methods to determine the normal diffusion coefficient have been studied in Chapter 2. By analysing a number of styrene acrylonitrile copolymer samples it was found that Taylor Dispersion Analysis (TDA), Dynamic Light Scattering (DLS), Hydrodynamic Chromatography (HDC), and Size-Exclusion Chromatography (SEC) could all be used to accurately determine diffusion coefficients of samples having low polydispersities. However, a relatively high polydispersity or the presence of low-molecular-mass material can cause considerable differences between the methods.

The driving force of ThFFF, thermal diffusion, is influenced by the chemical composition of the polymer, giving it an extra dimension not shared by SEC or other FFF techniques. In Chapter 3 the applicability of ThFFF to detect composition drift in heterogeneous copolymers has been explored. To this end, ThFFF was coupled to a Multi-Angle Light Scattering (MALs) detector. The thermal diffusion coefficient was calculated from the ThFFF retention data and the MALs data. It was shown that the thermal diffusion coefficient distribution could serve as a measure for the chemical composition distribution.

Apart from being able to analyse lipophilic polymers, ThFFF can also be used to separate particulate matter in aqueous suspensions. Unfortunately, not much is known about the thermal diffusion behaviour of particles. In Chapter 4 the influence of the
carrier composition on the retention and thermal diffusion of sub-micron polystyrene latex particles is described. It was found that the particle retention is highly sensitive to small changes in the carrier composition. Furthermore, it appeared that the thermal diffusion is mainly influenced by the interaction between the particle surface and the carrier liquid.

In Chapter 5 ThFFF-MALS is applied to analyse sub-micron particles. The method allowed the direct calculation of the thermal diffusion coefficients. The influence of the chemical composition of the particles, the pH of the carrier, and the swelling of the particles on the retention and thermal diffusion was studied.

Chapter 6 describes a model that allows the qualitative prediction of thermal diffusion coefficients of polymers from polymer-solvent interaction parameters. This highly simplified model, which was based on the Flory-Huggins lattice theory, was in good qualitative agreement with experimental data. Quantitative comparison between predicted and experimental thermal diffusion data of polystyrene in a number of solvents was less successful. This was, however, in view of the simplicity of the model to be expected and a more sophisticated polymer-solvent theory is needed and requires further study.

Future prospects. Despite the fact that ThFFF was already developed in the 1970's, it has still not found wide applicability in industry. This is certainly the result of a combination of factors. One of the reasons is likely the fact that it took a long time before commercial instruments became available. Furthermore, to practice FFF successfully requires a certain amount of experience and knowledge of the underlying mechanism of separation. Another important factor may be that the initial focus of FFF researchers (in the 1970's and 1980's) was mainly on polymers having molecular masses between $10^4$ and $10^6$ Da, that could just as well - or better - be analysed with the well-established SEC technique.

During the past five to ten years there has been a shift in FFF research towards the analysis of (ultra)high-molecular-mass polymers, colloids, and particulate matter. In this area SEC clearly falls short and FFF is a powerful technique. This development resulted in an increased interest in FFF.

The greatest potential for ThFFF is in the area of ultra-high-molecular-mass lipophilic polymers, such as the analysis of gels in rubbers. However, it must be noted that new
instrumental developments in Flow FFF might lead to a successful alternative to ThFFF. Other interesting applications are high-temperature separations of polyolefins and size-based/chemical-composition-based separations of particles. The latter application requires a more thorough understanding of the thermal diffusion phenomenon. Coupling of ThFFF to other separation techniques or detection techniques is also an important development. Especially the combination of ThFFF with MALS gives a versatile and powerful technique and should be pursued.