Thermal field-flow fractionation of polymeric and particulate materials: applications and fundamental aspects
Mes, E.P.C.
Chapter 5

Sub-Micron Particle Analysis using Thermal Field-Flow Fractionation with Multi-Angle Light Scattering Detection

Abstract

Thermal Field-Flow Fractionation (ThFFF) coupled to Multi-Angle Light Scattering (MALS) detection has been used to analyse sub-micron particles. Polystyrene and styrene-butylmethacrylate latices of various composition were studied as well as different swellable core-shell particles. With ThFFF-MALS thermal diffusion coefficients ($D_T$) of the particles could be calculated directly without the need for additional Dynamic Light Scattering (DLS) measurements. The Soret coefficient was determined from the ThFFF data while MALS provided the particle’s radius of gyration which allowed the calculation of the diffusion coefficient of the particle. Combining both data gave the thermal diffusion coefficient. It was demonstrated that differences in the chemical composition of the particle can lead to differences in thermal diffusion. However, no clear trend was observed, and as thermal diffusion is still a poorly understood phenomenon, it was difficult to correlate chemical composition to $D_T$. Apart from the influence of the chemical composition of the particles, it was found that the pH of the carrier solution also had a strong effect on the thermal diffusion.

Although thermal diffusion will be mainly determined by the surface composition, the study of core-shells showed that swelling of the outer layer of the particle does not significantly influence the thermal diffusion.

In order to calculate the diffusion coefficients for the complex core shells, DLS measurements were required. The combination of DLS and ThFFF-MALS data gave insight in the swelling behaviour of the core-shells and their internal structure.
Introduction

The need for accurate particle-size or particle-size-distribution analysis has greatly increased over the past decade. The development of new materials incorporating small particles, such as water-based coatings, has led to a great demand for flexible and reliable size-analysis methods. However, due to the large variety of materials and the wide span in particle size the development of size-analysis methods remains a difficult and challenging area of research.

The most common method to characterize sub-micron particles in suspension is Dynamic Light Scattering (DLS). Although DLS has been proven to be an invaluable technique to provide absolute values for particle sizes, it only measures average or "bulk" characteristics and does not allow the determination of particle size distributions (PSD).

Particle-size-analysis methods that are able to determine a PSD are the flow-fractionation techniques. These include Field-Flow Fractionation (FFF) and Capillary Hydrodynamic Fractionation (CHDF). By far the most versatile particle separation technique is FFF. FFF comprises a number of subtechniques, all based on the same principle. Depending on the technique used, particles with sizes ranging from a few nm up to about 100 µm can be separated according to size (Flow FFF), size and density (Sedimentation FFF), or the size/charge ratio (Electrical FFF). Only rarely Thermal Field-Flow Fractionation (ThFFF) has been applied for the analysis of particulate matter. Therefore, very little is known about particle behaviour in ThFFF.

In ThFFF the retention is determined by the so-called Soret coefficient of a molecule or particle, defined as the ratio of the thermal diffusion coefficient $D_T$ and the normal diffusion coefficient $D$. To extract the information on the size and chemical composition of polymer molecules or particles from the retention time in ThFFF is not straightforward, as the retention is a function of both parameters ($D$ and $D_T$). So far, only a few studies have been carried out on the relation between the thermal diffusion and the particle composition. Generally, the observed $D_T$ values are a factor of 5 to 10 times lower than polymer thermal diffusion values. It appears that $D_T$ is mainly determined by the chemical composition of the surface of a particle. Unfortunately, straightforward correlations between $D_T$ and the composition of particles, as have been found for random copolymers, have not been shown yet. In contrast to soluble polymers, a size-dependence of $D_T$ has been observed occasionally for particles. Furthermore, recent studies have shown that particle retention in ThFFF is influenced not only by the composition of the particle, but also strongly by the composition of the
carrier solution.\footnote{11-13} It may be concluded that the thermal diffusion of particles is still a poorly understood phenomenon, which makes it difficult to correlate the retention behaviour of particles to size and/or chemical composition characteristics. Therefore, more study is required on the phenomena that determine the thermal diffusion.

Although potentially a calibrated ThFFF system allows the direct calculation of a PSD from a fractogram for particles with a uniform composition, in practice this requires that the $D_T$ of the particles is constant. It has been shown that this is not necessarily the case, which makes the calibration of ThFFF a delicate task. An important aid for the ThFFF analysis of particles can therefore be Multi-Angle Light Scattering (MALS) detection. In a previous study we have shown that ThFFF-MALS is a powerful combination for the characterization of soluble (co)polymers with a non-uniform composition.\footnote{16} Although MALS as detection technique for FFF is gaining popularity, the combination of FFF techniques with MALS detection for particle analysis has been limited to Flow FFF so far.\footnote{2,17-20}

Coupling of ThFFF to MALS would greatly simplify particle sizing, as ThFFF then acts as a fractionation method while the MALS gives the absolute particle size and its distribution. Thus, no FFF calibration would be needed. On the other hand, the size information that MALS provides can also be used for chemical composition analysis of particles by ThFFF. Instead of performing laborious off-line DLS measurements to determine $D$, MALS size data can be converted into diffusion coefficients. Hence, the coupling of ThFFF to MALS can significantly enhance the potential of ThFFF as a particle analysis method.\footnote{12}

Here we report a study on the use of ThFFF-MALS to analyse sub-micron particles. The first part of this study deals with the characteristics of the ThFFF separation, whereas the second part is devoted to the application of MALS detection. ThFFF has been studied as a separation method for the analysis of polystyrene (PS) latices and styrene-butylmethacrylate (Sty-BMA) latices, and of (alkali-swellable) core-shell particles of varying composition. In a previous study, we investigated the influence of the carrier composition on the particle retention behaviour and thermal diffusion.\footnote{13} Here, we focus on the influence of the (chemical) composition of the particle. Furthermore, the core-shells also allowed us to study the effect of swelling of the outer layer on the particle thermal diffusion.

The use of absolute MALS detection coupled to ThFFF to analyse particles is reported in the second part of this study. Possibilities and limitations of the ThFFF-
MALS method are illustrated by the analysis of the above-mentioned samples. The use of MALS to measure the PSD as well as the possibility to calculate thermal diffusion values without the need for additional DLS measurements are investigated. The ThFFF-MALS results obtained are compared with off-line DLS measurements.

Theory

ThFFF
A ThFFF system consists of a flat open channel, through which a liquid is forced to flow under laminar conditions. A thermal gradient is applied perpendicular to the flow, forcing the particles in thin layers against the wall. This leads to differential migration according to:

\[
\frac{t_R}{t_0} \approx \left( 6 \left( \frac{D}{D_r \Delta T} + \frac{r}{w} \right) \right)^{-1}
\]  

where \( t_R \) is the retention time of a particular particle, \( t_0 \) the void time, \( r \) the particle radius, \( w \) the channel height, and \( \Delta T \) the applied temperature difference between the walls of the channel. The theory of ThFFF has already been discussed in many publications and for that we refer to the pertinent literature.\(^{21}\)

Characteristic features of ThFFF are a low efficiency (broad peaks) but a high separation selectivity and versatility. Compared to CHDF, ThFFF is relatively insensitive to secondary effects,\(^{2,4}\) but as a result of the low efficiency, system peak broadening can hamper the analysis and complex deconvolution procedures are often required to calculate an accurate size distribution.\(^{22}\) This drawback is largely circumvented when the technique is combined with MALS detection.

MALS detection
MALS is a static light scattering technique that provides absolute size determination. The radius of gyration \( R_g \) is, according to the Rayleigh-Gans-Debye (RGD) theory, directly related to the excess Rayleigh ratio, \( R(\theta) \), as follows:\(^{23}\)

\[
R(\theta) = K c M \left( 1 - \frac{16 \pi^2}{3 \lambda_i^2} R_g^2 \sin^2(\theta/2) \right)
\]  

[2]
where \( c \) is the particle concentration, \( M \) the (weight-average) molecular mass, \( \lambda \) the vacuum wavelength of the light, and \( \theta \) the scattering angle. \( K \) is an optical constant given by:

\[
K = \frac{4\pi^2 \left( \frac{dn}{dc} \right)^2 n^2}{N_A \lambda_i^4} \tag{3}
\]

where \( n \) is the refractive index of the solvent, \( \frac{dn}{dc} \) is the refractive index increment, and \( N_A \) is Avogadro's number. From the angular dependence of the Rayleigh ratio, \( R_g \) can be calculated.

Irrespective of the shape of the analyte, MALS allows the direct determination of the radius of gyration as long as the RGD approximation is valid.\(^2\) For sub-micron particles these requirements are not completely met. Especially for larger particles, the RGD approximation is becoming less applicable. Nevertheless, Shortt et al.\(^{24}\) showed that MALS analysis of particles with diameters as large as 700 nm yielded errors of only 5\%. Analysis of larger particles requires the use of the more complicated Lorenz-Mie scattering theory.

Until recently, virtually all FFF particle analysis applications have made use of UV detection. However, often the UV detector acts as a forward-scattered light detector for particles, and correction for the so-called Lorenz-Mie effects is required but often overlooked.\(^2\)

**DLS**

DLS measures the time-dependent fluctuations in the intensity of laser light scattered from a sample. The apparently random fluctuations of the scattering intensity result in a noise-like pattern. By using time-dependent correlation functions for the signal it is possible to obtain quantitative information about motion within the sample. The autocorrelation function \( C(\tau) \) is related to the diffusion coefficient of the scattering particles by:\(^{25}\)

\[
C(\tau) = e^{-Dq^2\tau} \tag{4}
\]

where \( \tau \) is the delay time. The scattering vector \( q \) is defined as:

\[
q = \frac{4\pi n}{\lambda_i} \sin (\theta/2) \tag{5}
\]
The autocorrelation function of DLS provides direct information on the (average) diffusion coefficients of scatterers in a sample. The hydrodynamic radius $R_h$ of the particles can be calculated with the Stokes-Einstein Equation: \[ R_h = \frac{kT}{6\pi \eta D_0} \] \[ [6] \]

where $k$ is Boltzmann's constant, $\eta$ is the viscosity of the solvent, and $D_0$ is the diffusion coefficient at infinite dilution.

**Experimental**

**Instrumentation**

All ThFFF experiments were performed with a laboratory-made channel ($0.0125 \times 1.5 \times 46$ cm). A Gynkotek (model 300; Germering, Germany) HPLC pump delivered a flow rate of 0.25 mL/min. The injection volume was 30 $\mu$L. A 7-$\mu$m in-line filter was inserted between the injection valve and the ThFFF channel. A stop-flow period of 6 minutes was employed after injection to allow relaxation. Unless stated otherwise, the temperature drop $\Delta T$ was 40 K and the cold wall temperature $T_{\text{cold}}$ was 298 K. The temperature drop was controlled by the FFF software, which was obtained from FFractionation (Salt Lake City, USA).

A UV detector (model 757; Applied Biosystems, Ramsey, USA) set at 254 nm and a Dawn-DSP MALS detector equipped with a 30-mW argon-ion laser at 488 nm (Wyatt, Santa Barbara, USA) connected in series were used as the detection devices.

The DLS experiments were performed on a Malvern 4700c light scattering instrument (Malvern Instruments, Malvern, UK). The instrument was equipped with a 200-mW argon-ion laser (488 nm). The temperature was set at 303 K. Measurements were performed at an angle of 90°. For every sample the normal diffusion coefficient and the hydrodynamic radius were calculated as an average from 5 successive measurements. Because of the high dilution (see the chemicals and solutions section) of the dispersions the concentration dependence of the diffusion coefficient could be neglected ($D = D_0$).
The normal diffusion coefficients, either measured by DLS or calculated from the known particle diameter, were recalculated for the temperature in the centre of gravity \(T_{cg}\) of the particle zones. \(D_r\) values were obtained by multiplying the Soret coefficients obtained with ThFFF, with the above-mentioned normal diffusion coefficients. Corrections for the temperature dependence of the thermal conductivity and viscosity of the carrier, as well as for steric particle-wall effects were included in the calculations. A home-written Turbo Pascal software program was used for the calculation of the thermal diffusion values.

**Chemicals and solutions**

Polystyrene (PS) latex standards with diameters of 107, 202, and 356 nm were studied. The standards were obtained from Polysciences GmbH (Eppelheim, Germany). A latex sample composed of 20 % (m/m) styrene (Sty) and 80 % (m/m) butylmethacrylate (BMA) with a diameter of 165 nm was also used.

**Table I:** Composition of the particles studied.

<table>
<thead>
<tr>
<th>Particle</th>
<th>Diameter (nm)</th>
<th>Core % (m/m)</th>
<th>Shell % (m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>BMA</td>
<td>Sty</td>
</tr>
<tr>
<td>PS 107</td>
<td>107*</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>PS 202</td>
<td>202*</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>PS 356</td>
<td>356*</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Sty/BMA</td>
<td>165</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>Core-shell 1</td>
<td>192* (173)</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>Core-shell 2</td>
<td>181* (165)</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

Number between brackets represents the core diameter.

* Values specified by the supplier.

* Values measured by DLS (pH 5.1).

In addition, two core-shell latices based on the aforementioned Sty/BMA latex sample with the shell composed of different ratios of butacrylate (BA), methylmethacrylate (MMA), and methacrylic acid (MAA) were studied. Akzo Nobel (Arnhem, The Netherlands) provided the Sty/BMA sample and core-shell samples. The composition of the particles studied are summarized in Table I. Scanning Electron Microscope (SEM) experiments showed that the particles were spherical and of uniform size.
Original concentrations of the PS latex standards were in the order of 2.5 mg/mL and of the Sty/BMA and core-shell samples 15 – 25 mg/mL, respectively. All samples were, prior to analysis, diluted to a concentration of 1.25 µg/mL and vortexed thoroughly. A 2.5-mM phosphate buffer at different pH values was used. Polyoxyethylene laurylether (Brij 35) (Acros; Geel, Belgium) at a concentration of 0.2 mM was added to all samples and carrier solutions.

Results and Discussion

Influence of particle composition
In previous studies it has been established that the chemical composition of the particles can have a profound effect on the thermal diffusion, although no systematic trends have been observed. In Table II the calculated thermal diffusion values together with the normal diffusion values of all samples from Table I are given.

Table II: Normal diffusion and thermal diffusion coefficients of particles measured at pH 5.1.

<table>
<thead>
<tr>
<th>Particle</th>
<th>D ( \times 10^{-12} \text{ m}^2/\text{s} )</th>
<th>( D_T \times 10^{-12} \text{ m}^2/\text{sK} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS 107</td>
<td>4.7 (299.5)</td>
<td>5.9</td>
</tr>
<tr>
<td>PS 202</td>
<td>2.5 (298.9)</td>
<td>5.9</td>
</tr>
<tr>
<td>PS 356</td>
<td>1.4 (298.7)</td>
<td>6.1</td>
</tr>
<tr>
<td>Sty/BMA</td>
<td>3.0 (299.2)</td>
<td>4.5</td>
</tr>
<tr>
<td>Core-shell 1</td>
<td>2.6 (299.1)</td>
<td>4.7</td>
</tr>
<tr>
<td>Core-shell 2</td>
<td>2.8 (299.1)</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Values between brackets indicate the temperature in the centre of gravity \( T_{cg} \) (K) of the particle zone.

The normal diffusion coefficients were calculated from the diameters given in Table I by using the Stokes-Einstein equation or were directly measured by DLS. In order to be sure that possible swelling effects of the core-shell particles did not influence the retention, the ThFFF and DLS analyses were performed at pH 5.1.
It is seen that the $D_T$ values of PS particles are higher than those of the BMA/Sty particles, thus showing the compositional dependence of the thermal diffusion. No significant size-dependence for the PS particles was found.
A second observation is that the $D_T$ values found for core-shells 1 and 2 were very close to the value found for Sty/BMA particle (having the same composition as the core of the core-shells). Therefore, either the $D_T$ values of the Sty/BMA particle and the core-shells accidentally happen to be nearly equal, or the influence of the shell on the thermal diffusion is less than expected. However, the latter explanation is in contrast with findings by Shiundu et al.$^{10}$ It is more likely that in the present study the thermal diffusion values of the individual components of the particles are too close to actually correlate $D_T$ to the composition. If so, this illustrates that in order to distinguish particles by composition, significant differences in $D_T$ with composition are needed.

As is shown in Figure 1, the pH of the carrier solution has a strong influence on the retention of the Sty/BMA and core-shell particles in ThFFF. While at pH 5.1 the three particle types show almost equal retention, at pH 11.3 large differences in retention times are observed. Apparently, the carrier pH has a strong effect on the Soret coefficients ($D_T/D$), especially on those of the core-shell latices, as is shown in Figure 2A. However, the Soret coefficient of the solid Sty/BMA particles is also a function of the pH.

In first instance one would expect for the core-shells that mainly the normal diffusion coefficients are affected by the pH, as a result of the swelling observed for these particles at high pH. To study this swelling effect, independent measurements on the diffusion coefficients of the particles as a function of the pH have been performed by DLS. The results of these measurements are shown in Figure 2B. It can be seen that the diffusion coefficients of the core-shell particles decrease significantly with increasing pH. Swelling up to almost twice the original size for core-shell 2 is observed at pH 11.3. On the other hand, the diffusion coefficient, and therefore the size of the Sty/BMA particles remains virtually unchanged. From the Soret coefficients (obtained by ThFFF) and the diffusion coefficients (obtained by DLS) thermal diffusion coefficients were calculated. The results are given in Figure 2C. For comparison, $D_T$ data on the 202 nm PS latex particles are included in this figure. A decrease of the $D_T$ values with pH is seen for all particles. As $D_T$ must be determined by the outer layer of a particle, it is certainly possible that the swelling of the core-shells also influences $D_T$. However, the pH-dependency of $D_T$ is almost identical for all types of particles, including the PS latices. Moreover, the largest changes of $D_T$ are found between
Figure 2: Plots of (A) Soret coefficients $D_r/D$, (B) diffusion coefficients $D$, and (C) thermal diffusion coefficients $D_T$ at different pH values; (●) PS 202, (○) Sty/BMA, (▲) core-shell 1, and (×) core-shell 2.
pH 5.1 and 7.4, where swelling still does not occur. Therefore it must be concluded that the swelling itself has only a minor, if any, effect on $D_T$ for the core-shell particles, and that there is a more general effect of the carrier pH on the thermal diffusion of the various particles studied.

As the differences in the calculated $D_T$ values for PS and Sty/BMA particles show, ThFFF can in principle be used to extract information on the surface composition of particles. In practice however, it remains difficult to actually correlate thermal diffusion to composition, as particle thermal diffusion is still a largely unexplored area. More study is required to fully exploit the compositional dependence of the retention.

![Graph showing data](image)

**Figure 3:** Influence of the order of detectors; (a) UV (254 nm) signal, detector order: UV-MALS; (b) UV (254 nm) signal, detector order: MALS-UV; (c) MALS (90°) signal, detector order: UV-MALS; (d) MALS (90°) signal, detector order: MALS-UV. Elution order is PS 107 nm, PS 202 nm, and PS 356 nm; $\Delta T = 50$ K; $T_{\text{cold}} = 300$ K; carrier solution: phosphate buffer (2.5 mM, pH 7.4).

**ThFFF-MALS analysis**

As stated in the introductory section, a key factor in the future applicability of ThFFF for particle analysis is the ability to measure particle size distributions and possibly chemical composition distributions. Therefore, we tried to measure the PSD on-line.
with MALS detection. Furthermore, we studied the possibility to use this data for the calculation of the thermal diffusion coefficients as an indication for the chemical composition of the particles.

During our initial ThFFF-UV-MALS experiments it was unexpectedly found that the order of the (UV and MALS) detectors significantly influences the sensitivity of the MALS detector. In Figure 3, fractograms of a mixture of PS latices, measured with ThFFF-UV-MALS and ThFFF-MALS-UV, are depicted. It is clear that the UV signal is not influenced by the order of detectors, while the MALS signal is strongly reduced if the UV detector is placed after the MALS. This effect might be explained by insufficient mixing of the carrier solution eluting from the ThFFF channel. The MALS cell itself has a total volume (including connecting pieces) of approximately 70 µL. The actual detection volume is, however, determined by the laser beam width and is much smaller. It can be argued that particles with low diffusion coefficients can, upon reaching the MALS detector, still be compressed in a layer of a few micrometers thick as formed on the accumulation wall of the channel. If no sufficient mixing occurs, it is conceivable that the laser only partly detects them. In our case, the UV detector obviously acts as a mixing chamber. This slow mixing effect can probably also be of influence for the detection limit of ultra-high-molecular-mass polymers.

We tested the ThFFF-MALS method with a mixture of well-defined PS latex standards. It can be seen from Figure 4 that the latex particles are nearly monodisperse. Nevertheless, as a result of the low efficiency, relatively broad peaks elute. When conventional calibration without deconvolution had been used, a considerable (apparent) size distribution would have been found. It was calculated that the use of conventional calibration without deconvolution for a 200 nm particle eluting at $t_p/t_0 = 10$ leads to an apparent distribution with a relative standard deviation of 10 %. Furthermore, due to the potentially combined chemical-composition and size dependencies of the thermal diffusion, conventional ThFFF calibration is only possible if the samples and standards are of exactly the same composition and if the composition of the carrier is kept perfectly constant.

Since the PS latex particles can be regarded as hard spheres, the hydrodynamic diameters could be calculated from the radius of gyration with:

$$d = \sqrt{\frac{20}{3}} R_g$$

[7]
The particle diameters as found by MALS detection (peak top values of 109 nm (± 2.9 %), 206 nm (± 1.1 %), and 348 nm (± 0.4 %)) were in good accordance with the values given by the manufacturer. The errors indicated are the relative standard deviations of the results of four measurements.

![Graph](image)

**Figure 4:** ThFFF-MALS analysis of PS latex particles; (a) PS 107 nm; (b) PS 202 nm; (c) PS 356 nm. (⊙): diameter measured by MALS; ΔT = 50 K; Tcold = 300 K; carrier solution: phosphate buffer (2.5 mM, pH 7.4).

Obviously, by calculating the normal diffusion coefficients via the Stokes-Einstein equation, the thermal diffusion coefficients can be estimated without the use of additional measurements. The coupling of MALS to ThFFF can, therefore, considerably enhance the applicability of ThFFF.

Analysis of the core-shell particles at different pH values revealed that swelling of the shell did not lead to a significant increase of the radius of gyration of the particles. In Table III, the \( R_g \) values measured with MALS are compared with \( R_h \) values obtained by DLS. For PS 202 and Sty/BMA \( R_g/R_h \) values close to the theoretical value of 0.775 (\( \sqrt{3/5} \)) for a hard sphere were found.\(^{29}\) Approximately the same ratios were found for the (non-swollen) core-shells measured at pH 5.1. For both core-shells, a decrease of \( R_g/R_h \) was found with increasing pH. The highest decrease was for the particle con-
taining the largest amount of methacrylic acid (core-shell 2). The change in $R_g/R_h$ can be explained as follows: As core-shell particles swell, they can be regarded as a spherical core being made of pure polymer, surrounded by a shell being a mixture of polymer and solvent, with all polymer chains having at least one end anchored at the core surface.

**Table III:** Radius of gyration ($R_g$) obtained from MALS and hydrodynamic radius ($R_h$) obtained from DLS at pH 5.1, 7.4, and 11.3.

<table>
<thead>
<tr>
<th>Particle</th>
<th>pH 5.1</th>
<th>pH 7.4</th>
<th>pH 11.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_g$</td>
<td>$R_h$</td>
<td>$R_g/R_h$</td>
</tr>
<tr>
<td>PS 202</td>
<td>79.3</td>
<td>101*</td>
<td>0.785</td>
</tr>
<tr>
<td>Sty/BMA</td>
<td>62.0</td>
<td>82.3</td>
<td>0.753</td>
</tr>
<tr>
<td>Core-shell 1</td>
<td>69.8</td>
<td>95.9</td>
<td>0.728</td>
</tr>
<tr>
<td>Core-shell 2</td>
<td>65.6</td>
<td>90.3</td>
<td>0.726</td>
</tr>
</tbody>
</table>

* Specified by the supplier.

The solvent molecules are thus immobilised and the hydrodynamic radius can be regarded as the geometric radius. The radius of gyration, however, is determined by the internal mass distribution of a particle: \(^{23}\)

$$R_g^2 = \frac{\sum r_i^2 m_i}{\sum m_i} = \frac{1}{M} \int r^2 \, d\mu$$  \[8\]

where $r_i$ is the distance between the particle's centre of mass and the mass element $m_i$. The radius of gyration of a particle does not describe the external geometry and is, therefore, fundamentally different from the hydrodynamic radius.

With the core-shell particles studied here, most of the mass resides in the (non-swelling) core. The increase of the thickness of the shell with swelling is accompanied with a proportional decrease of the polymer density, and therewith with a decrease of the scattering power of this shell. Therefore, swelling of the shell will only contribute to a limited extent to an increase of the radius of gyration of the particles. \(^{30,31}\) The ratio of the radius of gyration to the hydrodynamic radius ($R_g/R_h$) for a swollen core-shell particle will therefore be lower than the value predicted for solid
spherical particles (0.775). The experimental results depicted in Table III are in accordance with the above explanation. For (homogenous) PS and (heterogeneous) Sty/BMA lattices, values close to 0.775 were found. Furthermore, it can be concluded that the presence of a shell at low pH (non-swollen, thickness of 8 – 9 nm) contributes only very little to the \( \frac{R_g}{R_h} \) value. The slightly lower \( \frac{R_g}{R_h} \) values found compared to the value found for Sty/BMA indicate that the scattering power of the shell is somewhat less than that of the core. At high pH values, however, the core-shell particles are swollen to almost twice the original size and low \( \frac{R_g}{R_h} \) values, are found. The \( \frac{R_g}{R_h} \) ratio can be used as an indication of the extent of swelling. Obviously, to study these complex particle structures, combined DLS and MALS measurements are necessary. DLS provides the geometric radius of the particle and the combination of MALS and DLS gives information about the internal mass distribution and particle structure. Furthermore, due to the complex structure of core-shells it is not possible to use MALS data for the calculation of the thermal diffusion coefficient and additional DLS measurements are in this case still required to study the chemical composition (distributions).

Conclusions

This work has demonstrated that differences in particle composition can lead to differences in the thermal diffusion coefficient. It was found that the thermal diffusion coefficients of PS particles and Sty/BMA particles (containing 20 % styrene) differed considerably. However, for two core-shell particles studied, the differences in composition did not lead to significantly different \( D_T \) values. Therefore, to correlate \( D_T \) with particle composition strong differences between the particles are needed. For all particles studied, a decreasing trend in \( D_T \) with increasing pH (up to pH 7) was found, and an almost constant \( D_T \) value at higher pH values. Furthermore, the analysis of core-shells showed that swelling of the particles did not significantly influence the thermal diffusion. Still, swelling of the particles could be detected by an increase in retention as a result of a decrease in the normal diffusion coefficient.

The results of the second part of this study show that ThFFF-MALS can be perfectly used to determine particle size distributions of homogeneous particles. By assuming a hard-sphere model, geometric radii and corresponding diffusion coefficients can be
calculated from the radii of gyration of the particles obtained by MALS. In this way thermal diffusion coefficient distributions of particles can generally be calculated without using additional DLS measurements. However, complex particles such as swollen core-shells cannot be regarded as hard spheres and thus still require additional DLS measurements to estimate the diffusion coefficients. Combination of DLS and MALS data provides additional information on the particle geometry and on the internal structure.

Acknowledgement

Dr. A. van Asten of Akzo Nobel (Arnhem, The Netherlands) is gratefully acknowledged for the donation of the core-shell lattices. The DLS measurements were performed at Shell Research and Technology Center Amsterdam (Amsterdam, The Netherlands) under the kind supervision of Dr. R. Haswell.

Symbols

\[
\begin{align*}
    c & \quad \text{concentration} \\
    D & \quad \text{diffusion coefficient} \\
    D_0 & \quad \text{diffusion coefficient at infinite dilution} \\
    D_T & \quad \text{thermal diffusion coefficient} \\
    d & \quad \text{particle diameter} \\
    dn/dc & \quad \text{refractive index increment} \\
    K & \quad \text{optical constant} \\
    k & \quad \text{Boltzmann's constant} \\
    M & \quad \text{molecular mass} \\
    m_i & \quad \text{mass of element } i \\
    N_A & \quad \text{Avogadro's number} \\
    n & \quad \text{refractive index} \\
    q & \quad \text{scattering vector} \\
    R(\theta) & \quad \text{excess Rayleigh ratio} \\
    R_g & \quad \text{radius of gyration} \\
    R_h & \quad \text{hydrodynamic radius} \\
    r & \quad \text{particle radius}
\end{align*}
\]

SI units

\[
\begin{align*}
    \text{kg m}^{-3} \\
    \text{m}^2 \text{s}^{-1} \\
    \text{m}^2 \text{s}^{-1} \\
    \text{m}^2 \text{s}^{-1} \text{K}^{-1} \\
    \text{m} \\
    \text{m}^3 \text{kg}^{-1} \\
    \text{J K}^{-1} \\
    \text{kg mol}^{-1} \\
    \text{kg mol}^{-1} \\
    \text{mol}^{-1} \\
    \text{m}^{-1} \\
    \text{m}^{-1} \\
    \text{m} \\
    \text{m}
\end{align*}
\]


$\rho_i$  
distance between the particle’s centre of mass and element $i$  

$T$  
temperature  

$T_{\text{cold}}$  
cold wall temperature  

$T_{\text{cg}}$  
temperature in the centre of gravity of the particle zone  

$\Delta T$  
temperature drop  

$t_R$  
retention time  

$t_0$  
void time  

$w$  
channel height  

$\theta$  
scattering angle  

$\lambda_r$  
wavelength  

$\tau$  
delay time  

$\eta$  
viscosity  


References

Particle Analysis using ThFFF-MALS

25. V.A. Bloomfield, in *Dynamic Light Scattering*, R. Pecora (Ed), Plenum Press, New York, 1985, Ch. 10