Determination of the compositional heterogeneity of polydisperse polymer samples by the coupling of size-exclusion chromatography and thermal field-flow fractionation

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Determination of the compositional heterogeneity of polydisperse polymer samples by the coupling of size-exclusion chromatography and thermal field-flow fractionation

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Abstract

An off-line coupling of size-exclusion chromatography (SEC) and thermal field-flow fractionation (ThFFF) was used successfully to cross-fractionate copolymers and polymer blends. Various fractions of different molecular mass were obtained from polydisperse polymer samples by SEC. Because the molecular diffusion coefficients were known, the ThFFF analysis of these fractions yielded directly thermal diffusion coefficients. As thermal diffusion is strongly affected by the chemical nature of the polymer, the chemical composition of polymer samples can be studied as function of the molecular mass with this technique. This is illustrated with the SEC-ThFFF cross-fractionation of a polystyrene sample blended with a polybutadiene and a polytetrahydrofuran standard, and of butadiene- and styrene-methylmethacrylate copolymers.

1. Introduction

Depending on the polymerization process used, copolymer samples and polymer blends may possess a chemical composition distribution (CCD) as well as a molecular mass distribution (MMD). Usually, the ratio of the various monomers and the distribution of the chemical composition strongly affect the physical properties of copolymers. Therefore, in copolymer analysis the determination of the CCD is just as important as the determination of the MMD. In order to obtain both distributions a deconvolution of molecular mass and chemical composition is necessary. If a sample is first fractionated according to molecular mass and the various fractions are then analyzed according to chemical composition, the relationship between the CCD and the MMD can be studied.

In size-exclusion chromatography (SEC) fractionation is not completely independent of chemical composition since polymers elute according to size (or molecular diffusion) rather than to molecular mass. Still, SEC is clearly a good option for obtaining mass defined fractions of polymer samples, and, therefore, the coupling of SEC with techniques that produce information on chemical composition is ideally suited for copolymer analysis [1]. Over the last decades many groups have utilized this strategy to determine the compositional heterogeneity of copolymer samples.

When SEC is combined with selective detection of each comonomer, the composition as function of the molecular mass is directly obtained. For the analysis of copolymers containing

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styrene (S) units, SEC fractionation with simultaneous refractive index (RI) and ultraviolet absorption (UV) detection has proven to be useful [2-4]. The UV detector is used to measure the styrene content of the eluate, whereas the RI detector monitors the total polymer concentration. Also SEC multi-detector schemes involving infrared (IR) spectrophotometers have been employed [2,5]. One of the drawbacks encountered with these set-ups was the relatively large error in the determination of the copolymer composition at the outer parts of the size distribution, where the polymer concentration tends to be low [3,6]. In this respect, better results were obtained with the coupling of SEC with pyrolysis-gas chromatography (Py-GC) [3,7,8].

However, all methods described above are only able to produce the mean compositional values for the given SEC fractions. With these methods it is for instance impossible to distinguish copolymers from mixtures of homopolymers. Consequently, for a more rigorous determination of compositional heterogeneity of polymer samples so-called cross-fractionation (CF) methods should be used [6], in which SEC is coupled to a complementary method that fractionates according to chemical composition. With thin-layer chromatography (TLC) it is possible to fractionate polymer samples solely on the basis of differences in composition [9]. Teramachi et al. [10] used a SEC-TLC combination to obtain the methylacrylate (MA) content as function of the molecular mass of a high conversion S-MA copolymer. A strong increase in MA content at higher molecular mass was observed.

However, as TLC remains a laborious method, more attention has been focused on the coupling of SEC with high-performance liquid chromatography (HPLC) techniques. SEC-SEC systems have been used for copolymer analysis [11,12]. The use of solvent/non-solvent gradients for the second SEC column induced non-exclusion mechanisms which made it possible to fractionate S-butylmethacrylate (BMA) copolymers according to chemical composition. However, because fractionation according to size caused by normal exclusion effects can interfere, the use of packing particles with smaller pores has been recommended [13].

Therefore, the fractionation of polymers according to chemical composition using HPLC columns with solvent/non-solvent gradient elution is a better option. In these techniques separation is caused by two phenomena. If the polymer sample is insoluble in the starting mobile phase composition, fractionation is mainly governed by precipitation and subsequent redissolution during the gradient run. In this case elution volumes are usually independent of the type of packing material used. This mode of operation has been indicated by Glöckner and co-workers [14-16] as high-performance precipitation liquid chromatography (HPPLC). However, for different experimental conditions also adsorption mechanisms can determine the extent of fractionation [17-20]. The combination of SEC with gradient HPLC has been used for the analysis of S-methylmethacrylate (MMA) [6,13,21] and S-acrylonitrile (AN) copolymers [14-16].

Finally, also the cross-fractionation of polyethylene and polypropylene polymers and copolymers by means of temperature rising elution fractionation (TREF) and SEC has been employed in order to study the relationship between branching, tacticity, crystallizability or composition and molecular mass [22-26].

Besides SEC, also thermal field-flow fractionation (ThFFF) can be used for the determination of the MMD of synthetic polymer samples [27-31]. ThFFF is performed in a thin open channel through which a carrier liquid, usually an organic solvent, is pumped. By applying a large temperature gradient across the channel thickness macromolecules are concentrated in the colder regions of the channel due to the so-called thermal diffusion effect. As the flow of the carrier liquid in the channel is laminar, accumulation of polymer zones near the cold wall results in retention and consequently fractionation [32]. Retention in ThFFF is determined by the applied temperature drop and the ratio of the molecular and thermal diffusion coefficient of the polymer. Although no real understanding of the thermal diffusion effect in liquids exists, ThFFF studies have indicated that the thermal diffusion coefficient is indepen-
dent of the molecular mass of the polymers, whereas it is strongly affected by the chemical composition of both the polymer and the solvent [33]. This latter statement indicates that ThFFF also has potentials to fractionate polymer and copolymer samples according to chemical composition. ThFFF has indeed been used to separate chemically different polymer standards of equal size [34–36]. Furthermore, Schimpf and Giddings [37] demonstrated that ThFFF offers possibilities to determine whether a copolymer possesses a block or a random configuration.

However, as also the molecular diffusion coefficient affects retention, the direct use of ThFFF for the measurement of the CCD of a polydisperse polymer sample is impossible [1]. Therefore, in this work a promising new off-line SEC-ThFFF method is described for the cross-fractionation of polydispersity polymer samples. Polymer samples are first fractionated according to size with SEC in order to obtain sample slices in which the polymer size and with that the molecular diffusion coefficient are approximately constant. The individual slices are then analyzed with ThFFF. This approach enables the direct transformation of retention times in the ThFFF fractogram into thermal diffusion coefficients. Since the latter parameter is linked to the chemical composition of the polymer fraction, a SEC-ThFFF system can effectively be used to determine the relationship between composition and molecular mass. This has been demonstrated with the SEC-ThFFF fractionation of a polydisperse polystyrene (PS) sample blended with a polybutadiene (PB) and a polytetrahydrofuran (PTHF) standard of different molecular mass. Furthermore, S-MMA and butadiene (B)-MMA copolymers have been analyzed with the use of this cross-fractionation technique.

2. Theory

2.1. Retention in ThFFF

With a theoretical model describing the fractionation process in FFF, important polymer parameters can be determined by simply measuring the retention ratio. The retention ratio $R$, defined as the void time divided by the retention time of the polymer zone, is related to the dimensionless zone thickness $\lambda$ by [38]

$$R = 6\lambda \left[ \coth \left( \frac{1}{2\lambda} \right) - 2\lambda \right]$$

(1)

The parameter $\lambda$ is the layer thickness of the compressed polymer zone divided by the channel thickness. For ThFFF this parameter can be approximated by

$$\lambda = \frac{D}{D_T \Delta T}$$

(2)

where $\Delta T$ is the applied temperature drop and $D$ and $D_T$ are the molecular and thermal diffusion coefficient of the polymer, respectively.

As the $\Delta T$ value and the void time are known, Eqs. 1 and 2 can be used to convert ThFFF retention times directly into $D/D_T$ values. However, because of the use of a large temperature gradient in ThFFF, the equations given above are only an approximate description. In this study a more refined model, which takes the temperature dependence of both the solvent viscosity and thermal conductivity into account, has been used for the calculation of the $D/D_T$ values from the retention measurements [39].

SEC can be used to obtain fractions containing macromolecules of a known size. As polymer size is related to molecular diffusion and the thermal diffusion effect is strongly affected by the chemical composition of the polymer, the ThFFF analysis of such fractions will directly yield information on the chemical composition as function of the molecular mass.

2.2. The sampling process

In the operation of a two-dimensional separation system the ideal from the point of view of selectivity is obtained when the resolving power in each dimension is preserved in the coupling [40]. For an off-line system, where fractions from the first technique have to be transferred to the second technique, this means that the fractions should be sufficiently small (and as a result numerous), so that the resolution in the first dimension is not affected. Thus, the fraction
width has to be chosen smaller than the standard deviation in the first dimension.

In the present work, where high-resolution SEC is applied as the first dimension, the adherence to this principle would lead to a rather large number of fractions of small volume, with resulting long total analysis time and cumbersome ThFFF analysis. Therefore, a more modest approach, where fraction widths are chosen in relation to the maximum information that can be produced by the second technique (ThFFF), has been adopted in this study.

For meaningful use of the second, ThFFF, separation system, it is essential that the interpretation of the ThFFF retention in terms of $D_T$ values (chemical composition) is reliable. In other words, the dependency of the ThFFF retention (determined by $D_T/D$) on the diffusion coefficient $D$ has to be eliminated, by assuring that each fraction contains only a small variation of $D$ values (or molecular sizes). If this is the main restriction for the sampling process, the fraction width is then determined by the standard deviation in the ThFFF fractogram, and the dependency of ThFFF retention on $D$.

As a result of this strategy, part of the separation obtained in the SEC dimension is lost in the fraction collection. However, we think that this is still a sensible approach, as much time is saved in this way, while the polymers can still be divided into a reasonable number of size fractions. In the following the maximum fraction width, for which still no information in the ThFFF fractogram is lost, is calculated.

### 2.2.1. Calculation of maximum fraction width

For a well designed ThFFF system operated under normal working conditions, zone broadening is mainly determined by the so-called non-equilibrium contribution, which corresponds to slow lateral mass transfer in the presence of a velocity gradient [41]. Under these circumstances the ThFFF standard deviation, expressed in time units, $\sigma_{(sd, ThFFF)}$, can be expressed as

$$\sigma_{(sd, ThFFF)} = w \sqrt{t_0 \cdot \frac{\chi}{R} \cdot \frac{1}{\sqrt{D}}} \quad (3)$$

where $sd$ indicates system dispersion, $w$ is the channel thickness, $t_0$ is the void time, and $\chi$ is a complicated function of $\lambda$, which readily increases with $\lambda$ [42].

However, due to the high mass selectivity of ThFFF [43] the molecular mass distribution of the sample that is analyzed will usually also contribute significantly to the peak width of the observed signal. If each SEC fraction can be represented by a block function with a width corresponding to a change in the molecular diffusion coefficient of $\Delta D$ (this is only a simplification as polymer concentration can change within the time needed to collect a fraction), the standard deviation caused by the sampling process, expressed in units of molecular diffusion, is equal to [44]

$$\sigma_{D(sp)} = \frac{\Delta D}{\sqrt{12}} \quad (4)$$

where $sp$ refers to the sampling process.

As is shown in Eqs. 1 and 2, retention in ThFFF is strongly influenced by the molecular diffusion coefficient of the polymer. Therefore, a substantial $\Delta D$ for a given SEC fraction will result in broad peaks in the corresponding ThFFF fractogram. This will cause a decrease in resolution for the fractionation purely according to thermal diffusion or chemical composition.

The standard deviation, expressed in time units, observed in ThFFF due to the diffusion distribution of a given SEC fraction is related to $\sigma_{D(sp)}$ by

$$\sigma_{(sp, ThFFF)} = \left| \frac{d_r}{dD} \right| \cdot \sigma_{D(sp)} \quad (5)$$

where $t_r$ is the ThFFF retention time.

As was stated earlier on in this section, the retention ratio is defined as the void time divided by the retention time. Furthermore, $R$ is only a function of the dimensionless parameter $\lambda$, whereas this latter parameter is an explicit function of $D$. Therefore, Eq. 5 can be converted to

$$\sigma_{(sp, ThFFF)} = \frac{t_0}{R^2} \left| \frac{dR}{d\lambda} \cdot \frac{d\lambda}{dD} \right| \cdot \sigma_{D(sp)} \quad (6)$$

The two derivatives can be evaluated with the
use of Eqs. 1 and 2. Subsequently, if Eqs. 2 and 4 are inserted in Eq. 6 the following result is obtained

\[ \sigma_r(\text{sp, ThFFF}) = \frac{t_v}{\sqrt{12}} \cdot \left[ \frac{\lambda}{R^2} \cdot \frac{dR}{d\lambda} \right] \cdot \frac{\Delta D}{D} \]  

(7)

The term in brackets on the right-hand side of Eq. 7 is only a function of \( \lambda \). Since for small \( \lambda \) values \( R \) can be approximated by \( 6 \lambda \) [42], \( dR/d\lambda \) will increase to the asymptotic value of 6 with increasing retention.

Ultimately, the system dispersion occurring in the ThFFF channel will limit the resolution of the fractionation according to chemical composition. In order to perform the cross-fractionation at this specified limit, the zone broadening due to the diffusion range in the SEC fractions should be small compared to system dispersion. If arbitrarily an increase of 10% in \( \sigma(\text{ThFFF}) \) caused by the \( \Delta D \) values of the fractions is accepted, the maximum \( \sigma_r(\text{sp, ThFFF}) \) is given by

\[ \sigma_r(\text{sp, ThFFF}) = f \cdot \sigma_r(\text{sd, ThFFF}) \]  

(8)

where \( f \) is a constant equal to 0.46.

With the use of Eqs. 3, 7 and 8 the maximum value of \( \Delta D \) can be expressed as

\[ \Delta D = \frac{t_v}{\sqrt{12}} \cdot \frac{w}{\sqrt{6}} \cdot \left[ \frac{R \sqrt{\chi}}{\lambda (dR/d\lambda)} \right] \cdot \sqrt{D} \]  

(9)

Again the term in brackets in this equation is only a function of \( \lambda \). As for high retention \( R \) is equal to \( 6 \lambda \) and \( \chi \) can be approximated by \( 24 \lambda^3 \) [42], it can easily be seen that this term increases with \( \lambda \). It should be noted that Eq. 2 demonstrates that \( \lambda \) is influenced by \( D \). However, the instrumental parameter \( \Delta T \) can be adjusted in order to achieve a given \( \lambda \) value.

One is of course free to collect SEC fractions with lower \( \Delta D \) values if this is technically feasible. This leads in principle to a higher peak capacity, as long as the fraction width is large compared to the system dispersion in the SEC column. However, it would not lead to a ThFFF retention that is more reliable in terms of chemical composition (\( D_f \)), as the ThFFF performance is determined by the zone broadening in the channel, and not by the variation in \( D \). As mentioned before, we were satisfied with a somewhat smaller peak capacity and have focused on the maximum \( \Delta D \) value as determined by the ThFFF apparatus.

In Fig. 1 the maximum \( \Delta D \) value is given as function of \( D \) for various \( \lambda \) values. The results displayed in Fig. 1 have been calculated for a ThFFF channel with a thickness of 127 \( \mu \)m and a channel flow-rate of 0.2 ml/min, which corresponds to a void time of 153 s. These values have been chosen because the cross-fractionation experiments described in the Results and discussion section were performed under these conditions. Eq. 9 demonstrates that the maximum \( \Delta D \) value decreases with decreasing channel thickness and \( \lambda \) value and increasing void time. This illustrates that a more detailed cross-fractionation is possible when the ThFFF system dispersion is minimized. However, for our set-up the use of channel thicknesses below 127 \( \mu \)m led to asymmetrical zone shapes due to imperfections in the smoothness of the channel walls. These imperfections made it also necessary to adjust the \( \Delta T \) value in such a way that for the fractions of higher molecular mass the \( \lambda \) value was never below 0.05. It should be noted that eventually for the fractions containing polymer material of very low molecular mass, even the use of the maximum \( \Delta T \) value (in our set-up this maximum value was 80°C) will not lead to sufficient retention. For the SEC fractions ana-

\[ \text{Fig. 1. The maximum } \Delta D \text{ value as determined by ThFFF as function of } D \text{ for various } \lambda \text{ values, with } w = 127 \mu \text{m, } t_v = 153 \text{ s and } f = 0.46. \]  

a: \( \lambda = 0.2 \); b: \( \lambda = 0.15 \); c: \( \lambda = 0.1 \); d: \( \lambda = 0.05 \).
lyzed with ThFFF in this study, the λ value gradually increased from 0.06 to 0.16 with the average molecular diffusion coefficient in the fractions. The maximum ΔD value can also be lowered by a decrease of the flow-rate. However, this increases the analysis time and the dilution of the polymer zones in the channel.

For a specific SEC column, the migration behaviour of a polymer is directly related to its size. So the migration behaviour, generally expressed by the τ value which is defined as the ratio of the migration volume of the polymer and the total column volume (inter- and intra-particle volume), is for a given solvent a specific function of molecular diffusion. Therefore, the range in τ values in a SEC fraction (Δτ) is related to the corresponding ΔD value by

\[ Δτ = \left| \frac{dτ}{dD} \right| \cdot ΔD \]  

(10)

If with the use of a calibration procedure (see Results and discussion section) τ is known as function of D, the maximum Δτ value can be evaluated as function of D for specified ThFFF conditions. This enables one to plot Δτ against τ and to calculate maximum sample times at any moment during the SEC fractionation. The sample volume and sample time are easily obtained by multiplying the corresponding Δτ value with the total column volume and the migration time of a totally included molecule, respectively.

With the adopted approach sample times will usually be larger than the SEC standard deviation caused by system dispersion. However, in the case that the zone broadening in the SEC column leads to standard deviations which are higher than the calculated maximum sample times, SEC must be considered as the limiting factor.

2.2.2. Polymer concentration in the SEC fractions

Another issue that should be addressed is the polymer concentration in the various fractions. If the polymer concentration in the fractions drops below the detection limit of the ThFFF set-up no accurate cross-fractionation is possible. For Gaussian peak shapes the dilution in the SEC column can be described by

\[ C_{\text{max}} = \frac{V_{\text{inj}} \cdot C_{\text{inj}}}{\sqrt{2π} \cdot σ_v} \]  

(11)

where \( C_{\text{max}} \) is the concentration in the center of the eluting zone, \( σ_v \) is the standard deviation in volumetric units, and \( V_{\text{inj}} \) and \( C_{\text{inj}} \) are the injection volume and sample concentration, respectively.

For the fractionation of a polydisperse sample, peak broadening caused by system dispersion can usually be neglected. The dilution in the SEC column will mainly be caused by the actual fractionation of the polymer. Provided that the MMD is Gaussian, which is not necessarily true for polydisperse samples, \( σ_v \) can be expressed as

\[ σ_v = V_p \cdot S \cdot \sqrt{P(μ)} \]  

(12)

where \( V_p \) is the mean migration volume, \( S \) is the mean mass selectivity, which is defined as \( |d(\ln V_p)/d(\ln M)| \) \cite{43}, and \( P \) is a specific function of the polydispersity, which increases with \( μ \) and converges to \( μ - 1 \) for \( μ \) values below 1.05.

The polydispersity is defined as the ratio of the weight- and number-average of the molecular mass distribution \( (μ = M_w/M_n) \). With the use of Eqs. 11 and 12 and the definition of τ the following result is obtained

\[ \frac{C_{\text{max}}}{C_{\text{inj}}} = \frac{V_{\text{inj}}}{V_o} \cdot \frac{1}{Sτ} \cdot \left[2πP(μ)\right]^{-1/2} \]  

(13)

where \( V_o \) is the total volume of the SEC column.

The dilution of the polymer sample in the SEC column as calculated with Eq. 13 can only serve as a rough estimate since for broad MMDs \( S \) and τ cannot be considered as constants. Both Schimpf and Giddings \cite{41} and Knox and McLennan \cite{45} have derived expressions for \( P(μ) \) in the case of Gaussian mass distributions. However, both expressions generate somewhat peculiar \( P(μ) \) values for large polydispersities. The expression given in Ref. \cite{41} predicts a decreasing \( P(μ) \) for \( μ \) values larger than 1.33 whereas with the expression derived in Ref. \cite{44} a staggering increase in \( P(μ) \) is found when \( μ \) is
larger than 2. This once more indicates that Eq. 13 serves qualitative purposes only.

Nevertheless, it is not surprising that Eq. 13 clearly illustrates that polymer concentration in the sample slices can be increased by increasing both the sample concentration and injection volume. However, the contribution to peak broadening caused by injection should always be small compared to system dispersion. Furthermore, deviating migration behaviour and asymmetrical zone broadening at high polymer concentrations, caused by the increased viscosity of the sample and mutual interaction of the polymer chains, should be avoided [46]. Therefore, the polymer concentration in the SEC fractions can only be increased to a certain extent. In other words, the SEC-ThFFF cross-fractionation of samples with a very high polydispersity could be cumbersome and calls for a sensitive detection device. In the present set-up polymer zones eluting from the ThFFF channel are detected by means of evaporative light-scattering detection (ELSD). This universal polymer detection system exhibits an extremely high sensitivity. Moreover, if the volume of the fractions is large enough, polymer concentrations in the sample slices could be enhanced by evaporation prior to the ThFFF analysis.

3. Experimental

3.1. Instrumentation

In Figs. 2 and 3 the schematic diagrams are given of the SEC and ThFFF set-up, respectively. For the SEC system the HPLC pump (Model 300C; Gynkotek, Germering, Germany) delivered a flow-rate of 0.5 ml THF/min during the sampling process. The total volume of the SEC column (PL Gel, 5 μm, 10^5 Å, 300 x 7.5 mm; Polymer Labs., Church Stretton, UK) was equal to 10 ml. A Rheodyne injection valve (Berkeley, CA, USA) was used with a 20- or a 50-μl sample loop. For fraction collection usually 50 μl of the sample was injected. A thermostat (Haake,
Fig. 3. Schematic representation of the ThFFF set-up. a = Helium supply for degassing of the solvent; b = solvent reservoir; c = pulse damper; d = HPLC pump; e = flow restrictor; f = injection valve; g = ThFFF channel; h = personal computer; i = recorder; j = switching valve; k = fused-silica capillary; l = evaporative light-scattering detector.

Berlin, Germany) was used to keep the temperature in the main part of the ventilation box at 30 ± 1°C. UV detection (Model 757; ABI, Ramsey, NJ, USA) was performed at a wavelength of 254 nm and the signal was monitored on a recorder (Model BD40; Kipp and Zonen, Delft, Netherlands). A fused-silica capillary (40 cm × 100 μm I.D. × 360 μm O.D.; Polymicro Technologies, Phoenix, AZ, USA) was used to transport the eluate from the detector to the fraction collector. The Technicon autosampler (Tarrytown, NY, USA) was equipped with a laboratory-made time switch to serve as a fraction collector. The sample slices of 500 μl each (see Results and discussion section) were collected in 2-ml glass vials. For the fractionation of polydisperse material a sample concentration of 5 mg/ml was used (see Results and discussion section), whereas concentrations never exceeded 1 mg/ml for the measurements involving polymer standards with a narrow MMD. For the calibration procedure and plate height measurements also the 20-μl sample loop was used instead of the loop with a volume of 50 μl.

The T100 ThFFF system used in this study was obtained from FFFractionation (Salt Lake City, UT, USA). The channel had a thickness of 127 μm, a length of 46 cm, a breadth of 1 cm, and a void volume of 0.5 ml. Temperature drops ranging from 20 to 80°C were used for the ThFFF analysis of the various fractions. Cold wall temperatures of 20 up to 32°C were measured, depending on the ΔT value used. The flow-rate of the HPLC pump (Model 400, ABI) was set at 0.2 ml THF/min. A flow restrictor (a small column packed with silica particles) and a pulse damper (Model 812; Tegimenta, Rotkreuz, Switzerland) were used to eliminate pulsation of the solvent flow. Of each sample 20 μl were injected in the ThFFF channel. The switching valve (Model EQ60; VICI, Houston, TX, USA) was used to perform stop flow procedures. This set-up ensured that during the relaxation of the sample (in this work a stop flow time of 1 min was used) in the ThFFF channel there was still a solvent flow through the evaporative light scattering detector (Model 2A; Varex, Bedford, MA, USA). The detector signal was monitored on a recorder (Model BD111, Kipp and Zonen). The outlet of the ThFFF channel was connected to the detector by means of a fused-silica capillary (100 cm × 100 μm I.D. × 360 μm O.D., Polymicro Technologies). In this way sufficient back pressure was generated to avoid boiling of the
Table 1
Polymer standards used for this study

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (g/mol)</th>
<th>$\mu$ (= $M_n$/M_a)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>1 260 000</td>
<td>&lt;1.06</td>
<td>Merck</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>775 000</td>
<td>1.01</td>
<td>Toya Soda</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>700 000</td>
<td>&lt;1.08</td>
<td>Merck</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>675 000</td>
<td>1.07</td>
<td>Machery-Nagel</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>475 000</td>
<td>1.03</td>
<td>Machery-Nagel</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>310 000</td>
<td>&lt;1.05</td>
<td>Merck</td>
</tr>
<tr>
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<td>160 000</td>
<td>&lt;1.06</td>
<td>Pressure Chemical Co.</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>97 200</td>
<td>&lt;1.06</td>
<td>Pressure Chemical Co.</td>
</tr>
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<td>Polystyrene</td>
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<tr>
<td>Polystyrene</td>
<td>43 900</td>
<td>1.01</td>
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</tr>
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<td>Pressure Chemical Co.</td>
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<tr>
<td>Polytetrahydrofuran</td>
<td>99 000</td>
<td>1.08</td>
<td>Polymer Labs.</td>
</tr>
</tbody>
</table>

THF in the ThFFF channel. Components f, g and i in Fig. 3 together with the computer board for data acquisition and system control were provided by FFFractionation.

3.2. Materials

Stabilizer-free, HPLC-grade THF obtained from Janssen Chimica (Geel, Belgium) was used as the solvent in both the SEC and ThFFF system. The polymer standards used in this study are listed in Table 1. BDH (Poole, UK) was the supplier of the PS sample having a broad MMD. The PMMA sample and the B-MMA and dimethylbutadiene (DMB)-MMA copolymers were prepared at Akzo Research Labs. (Arnhem, Netherlands). The S-MMA copolymers were provided by the Laboratory of Polymer Chemistry and Technology, Eindhoven University of Technology (Eindhoven, Netherlands).

4. Results and discussion

4.1. SEC calibration

In order to obtain $\tau$ as function of $D$ (see Theory section) the SEC column was first calibrated using PS standards with narrow MMDs of different molecular mass. The results are displayed in Fig. 4. Each point in this figure corresponds to the mean value of three measurements. The molecular diffusion coefficient for a given molecular mass was determined using the empirical relationship $D = 3.45 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} M^{-0.564}$, which was found for PS in THF ($T=24$°C) with the use of dynamic light scattering [47]. According to the well known Stokes-Einstein equation ($D = T/\eta$, where $T$ is the temperature and $\eta$ is the solvent viscosity), $D$ values for a temperature of 30°C (the working temperature in the SEC system) were calculated from the

![Fig. 4. $\tau$ as function of $D$ for PS standards of different molecular mass dissolved in THF, with $T=30$°C, flow-rate = 0.5 ml/min, $V_{in} = 20$ μl, $C_{in} = 0.5$ mg/ml, $V_o = 10$ ml, and UV detection at 254 nm.](image-url)
above given relationship. The molecular masses of the PS standards ranged from 12,500 to 1,260,000. The solid line in Fig. 4 corresponds to a fifth degree polynomial fit of the calibration data:

\[
\tau = e_0 + e_1 D + e_2 D^2 + e_3 D^3 + e_4 D^4 + e_5 D^5
\]  

(14)

with \( e_0 = 0.3482 \), \( e_1 = 0.1218 \), \( e_2 = -1.6029 \times 10^{-2} \), \( e_3 = 1.2488 \times 10^{-3} \), \( e_4 = -5.0625 \times 10^{-5} \) and \( e_5 = 8.0852 \times 10^{-7} \) when \( D \) is expressed in units of \( 10^{-7} \text{ cm}^2 \text{ s}^{-1} \).

### 4.2. Choice of the sample size

Since with the use of Eq. 14 \( d\tau/dD \) can easily be found, Eqs. 9 and 10 illustrate that \( A\tau \) can be evaluated as function of \( D \) within the range of diffusion coefficients covered by the polymer standards used for calibration. Due to the complex nature of Eq. 14 \( \Delta \tau \) cannot analytically be expressed as function of \( \tau \). However, with the use of a spread sheet program it is possible to plot \( \Delta \tau \) against \( \tau \) because both parameters are a function of \( D \). This is illustrated in Fig. 5. For the higher \( \tau \) values the decrease in \( \Delta \tau \) is caused by the flatness of the \( \tau-D \) calibration curve given in Fig. 4. The decrease in \( \Delta \tau \) at lower \( \tau \) is caused by the decrease in \( \Delta D \) with \( D \), as is shown in Fig. 1. Keeping in mind that the \( \lambda \) values for the ThFFF analysis gradually increased from 0.06 to 0.16 with the average molecular diffusion coefficient of the SEC fractions, a constant \( \Delta \tau \) value of 0.05 over the entire \( \tau \) range seems an appropriate choice. As the total column volume was equal to 10 ml and a migration time of 20 min was measured for the non-excluded compound toluene, this \( \Delta \tau \) value corresponds to a sample time and volume of 1 min and 0.5 ml, respectively.

Besides the migration behaviour also the zone broadening of the PS standards in the SEC column was measured. Surprisingly, for a flow-rate of 0.5 ml THF/min a \( \sigma_{sd,SEC} \) of approximately 9 s was found for most polymer standards, irrespective of their molecular mass. Studies on system dispersion in packed column hydrodynamic chromatography have indicated that the actual \( \mu \) values of the PS standards of Toya Soda (\( M = 43,900 \) and 700,000) are as low as 1.0005 [48]. Indeed, the polydispersity given by the manufacturers of the polymer standards is usually a very conservative estimate [41]. Therefore, it can be concluded that the standard deviation is not influenced by the MMDs of the PS standards. For the given SEC column the decrease in efficiency with molecular mass is exactly counteracted by the corresponding decrease in residence time, resulting in a constant value for \( \sigma_{sd,SEC} \). Experimental parameters such as column length, particle diameter and mobile phase velocity usually strongly affect SEC efficiency. However, for PS 43,900, PS 68,000 and PS 160,000 no significant change in plate height was observed when the flow-rate was decreased from 0.5 down to 0.2 ml/min. This indicates that for this type of SEC column the number of plates can only be increased by increasing the column length.

As was expected, the \( \sigma_{sd,SEC} \) is much lower than the estimated sample time on basis of the ThFFF efficiency. Consequently, a constant sample time and volume of, respectively, 1 min and 0.5 ml were chosen for the cross-fractionation experiments, since the fraction collector used in this study was capable of handling this sample frequency and volume without any problems.
4.3. Test of the SEC sampling process

To test the sampling process a PS sample with a broad MMD ($M_w = 247,000$ and $\mu = 3.15$) was fractionated. The SEC chromatogram of this sample and that of a mixture of PS standards are shown in Fig. 6. Due to the high polydispersity of the sample, polymer material elutes over the entire working range of the SEC column. As was stated in the Theory section, polymer concentration in the individual slices can be increased by either increasing the injection volume or the sample concentration. However, a significant increase in peak broadening or a shift in migration volume should be avoided [46]. For this set-up an injection volume of 50 $\mu$l in combination with a sample concentration of 5 mg/ml could be used without any problems. For the further fractionation of polymer samples with a broad MMD these conditions have been used because this sample load enabled a direct ThFFF analysis of each individual SEC fraction.

Next, the sample slices of the broad PS sample were reinjected on the SEC column in order to determine the polydispersity and the mean molecular diffusion coefficient of the individual fractions. The results are shown in Fig. 7. Some overlap of the detector signals of adjacent fractions can be seen. However, it should be noted that the SEC analysis of each sample slice causes an additional contribution to peak broadening due to the system dispersion in the SEC column. With the use of the PS standards the efficiency as function of the molecular mass was already determined and, therefore, this additional contribution can be corrected for. If the mass selectivity for every mass range would be known, Eq. 12 [with $P(\mu) = \mu - 1$] could be employed to obtain the $\mu$ values of the fractions. The mass selectivity can be rearranged to [43]:

$$S = \left| \frac{d \ln \tau}{d \ln D} \right| \left| \frac{d \ln \tau}{d \ln M} \right|$$

(15)

If the empirical relationship $D = AM^{-b}$, where $A$ and $b$ are constants, is used to relate molecular diffusion to polymer mass, it is easily shown that the last factor on the right hand side of Eq. 15 is equal to $b$. The value of $b$ ranges from 0.5 to 0.6 depending on the quality of the solvent. With the use of the $\tau-D$ calibration curve, $d \ln \tau/d \ln D$ can be evaluated. Table 2
Table 2
Fraction parameters of the SEC sample slices of a polydisperse PS sample

<table>
<thead>
<tr>
<th>Fraction</th>
<th>$D^{ab}$ $(10^{-7} \text{cm}^2/\text{s})$</th>
<th>$M_p^{c}$ (g/mol)</th>
<th>$S^{ab}$</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.34</td>
<td>1118 500</td>
<td>0.14</td>
<td>1.02</td>
</tr>
<tr>
<td>2</td>
<td>1.73</td>
<td>710 800</td>
<td>0.15</td>
<td>1.05</td>
</tr>
<tr>
<td>3</td>
<td>2.28</td>
<td>433 200</td>
<td>0.15</td>
<td>1.06</td>
</tr>
<tr>
<td>4</td>
<td>3.02</td>
<td>263 600</td>
<td>0.15</td>
<td>1.06</td>
</tr>
<tr>
<td>5</td>
<td>4.16</td>
<td>149 600</td>
<td>0.14</td>
<td>1.06</td>
</tr>
<tr>
<td>6</td>
<td>5.77</td>
<td>83 900</td>
<td>0.12</td>
<td>1.07</td>
</tr>
<tr>
<td>7</td>
<td>8.17</td>
<td>45 300</td>
<td>0.10</td>
<td>1.08</td>
</tr>
<tr>
<td>8</td>
<td>11.90</td>
<td>23 200</td>
<td>0.08</td>
<td>1.09</td>
</tr>
<tr>
<td>9</td>
<td>19.93</td>
<td>9 300</td>
<td>0.04</td>
<td>1.3</td>
</tr>
</tbody>
</table>

*a* Mean value.
*b* Dissolved in THF at 30°C.
*c* Calculated with $b = 0.564$ [47].

shows the mean molecular diffusion coefficient, the mean molecular mass, and the polydispersity of each fraction. The parameter $S$ is about 0.15 in the higher molecular mass range, but its value readily drops off for fractions 6 up to 9. This is caused by the flatness of the $\tau-D$ calibration curve for the lower molecular masses. The average polydispersity is approximately 1.06. Somewhat lower values were found for the first two fractions, whereas a slight increase in $\mu$ was observed for the sample slices containing polymer material of lower molecular mass. For the last fraction an unacceptably high $\mu$ value of 1.3 was found. However, the $\tau$ value of this fraction lies outside the calibration range. Furthermore, the corresponding mean molecular mass ($M \approx 9000$) is so low that the ThFFF analysis will be cumbersome anyway.

4.4. SEC-ThFFF cross-fractionation of PS sample

After the collection of the sample slices each fraction was analyzed with ThFFF. The polymer concentration in the fractions was sufficiently high for a direct injection of 20 $\mu$l of the collected solutions. As the mean molecular mass varies strongly for the different fractions, the $\Delta T$ value had to be adjusted in order to assure reasonable retention in each analysis. As was expected, the polymer material in the last fraction could not be properly retained even at the highest temperature drop. For the other fractions only one peak was observed in the fractograms. The measured retention ratios were converted into $D_\tau/D$ values. The Stokes–Einstein relationship was used to determine the molecular diffusion coefficient at the temperature in the center of gravity of the compressed solute zone [49]. The product of the two above given parameters yielded the $D_\tau$ value for every fraction. The results are shown in Fig. 8. In agreement with the data, the $D_\tau$ values show a decrease with increasing $M_p$.
with the measurements of Schimpf and Giddings [33], a mass independence of the thermal diffusion coefficient was found. The mean \( D_T \) value of \( 0.92 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1} \text{ K}^{-1} \) (the dashed line in Fig. 8) is in reasonable agreement with the value of \( 1.00 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1} \text{ K}^{-1} \) that has been reported in literature [33]. The constant \( D_T \) value indicates that no significant systematic errors occurred during the SEC–ThFFF cross-fractionation. Moreover, the mass independence of \( D_T \) and the fact that only one peak was observed in the fractograms, confirm the initial assumption that the BDH sample consists of pure polystyrene over the entire molecular mass range.

Fig. 8 demonstrates that the SEC–ThFFF coupling can also very effectively be used for the study of thermal diffusion of polymers in solution. Instead of an expensive kit of polymer standards, which is necessary when ThFFF is used separately from the method with which molecular diffusion coefficients are determined, this cross-fractionation method requires only a polymer sample with a broad MMD to obtain \( D_T \) as function of the molecular mass.

4.5. SEC–ThFFF cross-fractionation of PS–PB–PTHF blend

To illustrate the potentials of the SEC–ThFFF coupling, a cross-fractionation of the BDH PS sample, blended with a PB (\( M = 330 \, 000 \), \( \mu = 1.04 \)) and a PTHF (\( M = 99 \, 000 \), \( \mu = 1.08 \)) standard, was performed next. Although the SEC chromatogram in Fig. 9A does not look as smooth as the one displayed in Fig. 7, this fact alone is not sufficient to conclude that a polymer mixture has been fractionated. As for each fraction the molecular diffusion coefficient is approximately constant, the distributions in the fractograms shown in Fig. 9B directly contain information on the chemical composition of the corresponding sample slices. For fractions 3–6 the presence of two polymer species is clearly observed. For fractions 3 and 4 the ThFFF analysis was also performed at a \( \Delta T \) of 80°C in order to obtain reliable retention ratios for compound b. From this data a \( D_T \) value of \( 0.22 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1} \text{ K}^{-1} \) was extracted, whereas for compound c a thermal diffusion coefficient of \( 0.47 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1} \text{ K}^{-1} \) was found. These values correspond very well to the thermal diffusion coefficients of PB (\( 0.23 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1} \text{ K}^{-1} \)) and PTHF (\( 0.50 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1} \text{ K}^{-1} \)) in THF determined by ThFFF in combination with dynamic light scattering [50]. Because both PB and PTHF have relatively low thermal diffusion coefficients in THF, the more retained com-
pound a must be PS. Indeed, a mean $D_T$ value of $0.97 \cdot 10^{-7}$ cm$^2$ s$^{-1}$ K$^{-1}$ was found for compound a. It should be noted that the average molecular mass given in Table 2 for fraction 3 (433 000) and fraction 5 (150 000) does not correspond to the $M_p$ values given by the manufacturer of the PB and PTHF standard. However, calibration of the SEC column was done with the use of PS standards. The SEC fractionation is performed according to molecular diffusion and the constants in the empirical relationship $D = AM^{-b}$ depend on the chemical composition of the polymer.

Fig. 9 nicely illustrates the possibilities of the SEC-ThFFF cross-fractionation technique. This method clearly has potentials for the monitoring of product quality in polymer synthesis as long as the molecular mass of the product is high enough to ensure sufficient ThFFF retention. However, the use of SEC-ThFFF for the direct determination of the chemical composition of an unknown polymer sample as function of its molecular mass is not straightforward. Although it is known that the magnitude of $D_T$ depends strongly on the chemical composition of the polymer, the $D_T$ value can not be calculated theoretically for a given polymer-solvent system, due to the lack of understanding of the thermal diffusion phenomenon. This indicates that thermal diffusion coefficients have to be known for a large set of polymer-solvent combinations in order to link the $D_T$ value to the chemical composition of an unknown compound.

Moreover, this data set would enable the optimization of the cross-fractionation of a given polymer sample. The ThFFF analysis of a sample slice will be most effective when the difference in the $D_T$ values of the compounds present in the fraction is substantial. As the $D_T$ value is also strongly influenced by the chemical composition of the solvent, solvent choice can be very important in this respect. In conclusion we can state that some prior knowledge of the polymer sample and a further understanding of thermal diffusion of polymers in solution will increase the applicability of this cross-fractionation technique. For instance, the SEC-ThFFF coupling seems ideally suited to monitor copolymerization reactions of known monomers since Schimpf and Giddings [37] demonstrated that the $D_T$ value is a function of both the chemical composition and the configuration (random or block) of the copolymer material.

4.6. SEC-ThFFF cross-fractionation of B-MMA and DMB-MMA copolymers

Consequently, a PMMA homopolymer ($M_w = 481 000, \mu = 2.62$), two B-MMA copolymers, one consisting of 97% MMA ($M_w = 230 000, \mu = 1.71$) and one of 94% MMA ($M_w = 407 000, \mu = 1.71$), and a DMB-MMA copolymer ($M_w = 254 000, \mu = 1.69$) were analyzed next. The $D_T$ values measured with the SEC-ThFFF cross-fractionation technique are given in Fig. 10. No SEC chromatograms were recorded because these samples do not show UV absorption at 254 nm. However, with the use of the previous measurements with the PS sample, the mean molecular diffusion coefficient of each fraction is known. For all the samples only one peak in the ThFFF fractogram of the various fractions was observed. This suggests that only one polymer compound was present. For the PMMA homopolymer an approximately constant $D_T$ value of $1.39 \cdot 10^{-7}$ cm$^2$ s$^{-1}$ K$^{-1}$ was found. This value is in good agreement with the thermal diffusion coefficient of $1.33 \cdot 10^{-7}$ cm$^2$ s$^{-1}$ K$^{-1}$, that has been reported for the PMMA-THF system [33]. It should be noted that for this analysis a slight increase in $D_T$ was found going from fraction 2 to fraction 8. This is probably caused by the increase of the temperature in the center of gravity ($T_{cg}$) of the polymer zones from 27°C for fraction 2 up to 40°C for fraction 8. Brimhall et al. [49] found for PS in ethylbenzene a linear increase in $D_T$ with $T_{cg}$. To completely omit any temperature effects, the cold wall temperature ($T_c$) should be adjusted in such a way that for each fraction the temperature in the center of gravity is exactly the same. However, this experimental task is difficult to accomplish.

For fractions 4–8 the thermal diffusion coefficients of the three copolymers are similar to those determined for the PMMA sample. This
Fig. 10. Thermal diffusion coefficients for the various fractions of the PMMA (a), B-MMA (b: 97% MMA, c: 94% MMA) and DMB-MMA (d: 94% MMA) samples. For experimental conditions of the SEC fractionation see Fig. 7. ThFFF analysis: \( \Delta T = 20^\circ C \) (\( T_c = 25^\circ C \)) for fractions 2-4, \( \Delta T = 40^\circ C \) (\( T_c = 27^\circ C \)) for fractions 5-7, and \( \Delta T = 80^\circ C \) (\( T_c = 29^\circ C \)) for fraction 8. The flow-rate was set at 0.2 ml/min and the stop flow time was equal to 1 min.

was also expected as the B and DMB content in the copolymers is very low. However, for fractions 2 and 3 somewhat lower \( D_T \) values were found. As the increase in \( T_c \) with fraction number is the same for all four samples, this could indicate that the B and DMB monomers are primarily incorporated into the PMMA macromolecules of higher molecular mass. Because the B and DMB content of the copolymers is so low, causing the observed decrease in \( D_T \) for the lower fractions to be small compared to the natural fluctuations in the measurements, further research is necessary to verify this preliminary conclusion. Nonetheless, it should be noted that the SEC-ThFFF coupling is actually ideally suited for the cross-fractionation of B-MMA copolymers, because the difference in \( D_T \) values for both homopolymers is very large in THF (\( \Delta D_T = 1.33 - 0.22 = 1.11 \cdot 10^{-7} \) cm\(^2\) s\(^{-1}\) K\(^{-1}\)).

Besides the chemical composition also the MMD of a polymer sample is of importance. Usually, the signal in the SEC chromatogram can be converted into a MMD. However, with the use of the detector signal of the ThFFF runs of the sample slices, it is possible to determine the relative amount of polymer material as function of the fraction number. As is illustrated in Fig. 11 this also provides information on the mass distribution of the sample. With the data analysis software of FFFractionation the peak area of the signal was determined for all fractions. The relative amount for a given sample slice was defined as the ratio of the peak area to the total area of all fractions. Although no corrections were made for the non-linearity of the response curves of the ELSD, the diagrams displayed in Fig. 11 correspond well to the data on molecular mass and MMD provided by the supplier of the samples.

4.7. SEC-ThFFF cross-fractionation of S-MMA copolymers

Next, two S-MMA copolymer samples were cross-fractionated by the SEC-ThFFF method. According to the supplier the styrene contents of the samples were 31% (a) and 27% (b). Fortunately, due to presence of the styrene monomer, SEC chromatograms could be recorded. The results are shown in Fig. 12. With the use of the calibration measurements with the PS standards
(this is not entirely correct as the constants in the empirical relationship \( D = AM^{-b} \) depend on the chemical nature of the polymer), a mean molecular mass of 67 000 was estimated for both samples. The polydispersity of the samples is in the range 1.3-1.7.

The \( D_T \) values of the fractions of the S-MMA samples are given in Fig. 13. The dashed lines correspond to the thermal diffusion coefficients of PS and PMMA in THF (1.10 \( \cdot \) 10\(^{-7}\) cm\(^2\) s\(^{-1}\) K\(^{-1}\) and 1.33 \( \cdot \) 10\(^{-7}\) cm\(^2\) s\(^{-1}\) K\(^{-1}\), respectively). For sample b the \( D_T \) values for the various fractions do not differ too much. This indicates that the chemical composition of this copolymer does not change significantly with molecular mass. However, for the a sample a deviating trend is observed. The thermal diffusion coefficients of fractions 3 and 4 of copolymer a are almost equal to the \( D_T \) value of PS in THF. For the other fractions an increase in \( D_T \) is found with fraction number. For fraction 9 a thermal diffusion coefficient of 1.33 \( \cdot \) 10\(^{-7}\) cm\(^2\) s\(^{-1}\) K\(^{-1}\) was measured. These results suggest that for sample a the styrene content increases with the molecular mass of the polymer.

It should be noted that additional experiments are necessary to confirm these conclusions. For these samples the observed trends are also obscured by the uncertainty in the determination of the \( D_T \) values. However, in contrast to the B-MMA samples this is not caused by a very small content of one of the monomers. The problem originates from the small difference in thermal diffusion coefficients for PS and PMMA in THF (\( \Delta D_T = 0.33 \cdot 10^{-7} \) cm\(^2\) s\(^{-1}\) K\(^{-1}\)). Therefore, the use of toluene as the solvent appears to be attractive because Schimpf and Giddings [37] reported \( D_T \) values of 1.03 \( \cdot \) 10\(^{-7}\) cm\(^2\) s\(^{-1}\) K\(^{-1}\) for PS and 1.63 \( \cdot \) 10\(^{-7}\) cm\(^2\) s\(^{-1}\) K\(^{-1}\) for PMMA in this solvent.
Fig. 13. Thermal diffusion coefficients for the various fractions of the S-MMA samples (a: 31% S, b: 27% S). The dashed lines indicate the thermal diffusion coefficients of PS and PMMA in THF. For experimental conditions of the SEC fractionation see Fig. 7. ThFFF analysis: \( \Delta T = 20°C \) (\( T_c = 27°C \)) for fractions 2-4, \( \Delta T = 40°C \) (\( T_c = 29°C \)) for fractions 5 and 6, \( \Delta T = 60°C \) (\( T_c = 30°C \)) for fractions 7 and 8, and \( \Delta T = 80°C \) (\( T_c = 32°C \)) for fraction 9. The flow-rate was set at 0.2 ml/min and the stop flow time was equal to 1 min.

5. Conclusions

The SEC-ThFFF cross-fractionation technique was successfully employed for the study of the chemical composition of polydisperse samples as function of the molecular mass. The lower limit in the mass range that can be analyzed with this method is determined by ThFFF; polymer material of very low molecular mass can hardly be retained by this FFF sub-technique. The upper limit is given by the pore distribution in the SEC column; polymers which are totally excluded from the pore volume are not fractionated with SEC. A high efficiency in both SEC and ThFFF enables a detailed study of the chemical composition as function of molecular mass.

For an accurate cross-fractionation of copolymers with SEC-ThFFF, a sufficient difference in the thermal diffusion coefficients of the corresponding homopolymers is needed. In this respect the choice of the solvent can be very important.

The off-line SEC-ThFFF cross-fractionation seems also promising for the study of thermal diffusion of polymers in solution. With this method only a single polydisperse sample is sufficient to determine \( D_T \) values of the given polymer–solvent system over the entire mass range covered by the sample.

In principle each technique that fractionates according to polymer size can be coupled to ThFFF in order to perform cross-fractionation studies. So both flow FFF and hydrodynamic chromatography (HDC) could be considered as alternatives for SEC. The total analysis time for the cross-fractionation of a polydisperse sample with the off-line SEC-ThFFF system is approximately 4 h. For an on-line coupling this analysis time could be drastically reduced. However, an on-line cross-fractionation can only be successful when the time needed for one run is much smaller for the additional technique than for the initial fractionation method. This could be accomplished for a SEC-ThFFF system for which the SEC flow-rate and the ThFFF channel thickness are both diminished. Also the on-line coupling of ThFFF (as initial method) and packed-column HDC seems promising.

Symbols

- \( A, b \) empirical constants relating \( D \) to \( M \)
- \( C_{inj} \) sample concentration (mol m\(^{-3}\))
- \( C_{max} \) maximum concentration in an eluting Gaussian zone (mol m\(^{-3}\))
- \( D \) molecular diffusion coefficient (m\(^2\) s\(^{-1}\))
- \( D_T \) thermal diffusion coefficient (m\(^2\) s\(^{-1}\) K\(^{-1}\))
\( e_{n-5} \) empirical constants relating \( \tau \) to \( D \)  
\( f \) constant reflecting the accepted decrease in ThFFF efficiency due to the MMD of the sample  
\( M \) molecular mass (g mol\(^{-1}\))  
\( M_n \) number-average molecular mass (g mol\(^{-1}\))  
\( M_p \) average molecular mass as determined with SEC (g mol\(^{-1}\))  
\( M_w \) weight-average molecular mass (g mol\(^{-1}\))  
\( R \) retention ratio  
\( S \) mass selectivity  
\( t_0 \) void time (s)  
\( t_r \) ThFFF retention time(s)  
\( T \) temperature (K)  
\( T_c \) cold wall temperature (K)  
\( T_{cg} \) temperature in the center of gravity of the solute zone (K)  
\( V_o \) total column volume (m\(^3\))  
\( V_{inj} \) injection volume (m\(^3\))  
\( V_p \) migration volume of a polymer (m\(^3\))  
\( w \) channel thickness (m)  
\( \Delta D \) diffusion range covered in a sample slice (m\(^2\) s\(^{-1}\))  
\( \Delta D_T \) difference in thermal diffusion coefficients (m\(^2\) s\(^{-1}\) K\(^{-1}\))  
\( \Delta T \) temperature drop (K)  
\( \Delta \tau \) range of \( \tau \) values in a SEC fraction  
\( \eta \) solvent viscosity (Pa s)  
\( \lambda \) dimensionless zone thickness  
\( \mu \) polydispersity  
\( \sigma_x(y) \) standard deviation in units x caused by y  
\( \tau \) ratio of elution volume of a polymer and the total volume of the SEC column  
\( \chi \) \( \lambda \)-dependent function in the non-equilibrium term of the FFF plate height equation  

Abbreviations  
AN acrylonitrile  
B butadiene  
BMA butylmethacrylate  
CCD chemical composition distribution  
CF cross-fractionation  
DMB dimethylbutadiene  
ELSD evaporative light-scattering detection  
FFF field-flow fractionation  
HDC hydrodynamic chromatography  
HPLC high-performance liquid chromatography  
HPPLC high-performance precipitation liquid chromatography  
IR infrared  
MA methylacrylate  
MMA methyldiacrylate  
MMD molecular mass distribution  
PB polybutadiene  
Py-GC pyrolysis-gas chromatography  
PMMA polymethylmethacrylate  
PS polystyrene  
PTHF polytetrahydrofuran  
RI refractive index  
S styrene  
SEC size-exclusion chromatography  
ThFFF thermal field-flow fractionation  
TLC thin-layer chromatography  
TREF temperature rising elution fractionation  
UV ultraviolet

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