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Polymer characterization using on-line coupling of thermal field flow fractionation and hydrodynamic chromatography

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Abstract

The on-line coupling of thermal field-flow fractionation (ThFFF) and hydrodynamic chromatography (HDC) was used for the two-dimensional characterization of polymers and polymer blends. In the coupled system, distinct fractions of the solute band leaving the ThFFF channel were on-line injected into a HDC column. Since ThFFF separates polymers on the basis of the ratio of the thermal diffusion and molecular diffusion, whereas HDC separates only according to molecular mass, i.e., molecular diffusion, a two-dimensional separation of a polymer sample can be obtained with respect to size and thermal diffusion. The thermal diffusion coefficient can act as a measure of the chemical composition. The total analysis time for one polymer sample was about 30 min. The applicability of the coupled system to detect composition drift in copolymers was illustrated.

Keywords: Field-flow fractionation; Hydrodynamic chromatography; Thermal field-flow fractionation; Polymers; Styrene–acrylonitrile

1. Introduction

For the processing and application of polymers, the molecular mass and the chemical composition, together with their respective distributions, are the most important characteristics of copolymers. The molecular mass is usually determined by means of size-exclusion chromatography (SEC), while several techniques such as gradient-elution chromatography [1,2] and thin-layer chromatography [3] are available for determination of the chemical composition. However, these methods have one major drawback, i.e., only the mean composition and not, as desired, the composition as a function of the molecular mass, can be determined. In order to gather this information, it is necessary to couple different techniques, e.g., a size separation technique with a technique that gives information about the chemical composition.

Examples of this are off-line coupling of size-exclusion chromatography (SEC) and pyrolysis gas chromatography (PGC) and of SEC and liquid adsorption chromatography, which have been used to determine the chemical composition of styrene–acrylonitrile copolymers (SAN) [4] and of styrene–methylmethacrylate copolymers [5], respectively.

A different technique, which also provides chemical information, is thermal field-flow fractionation (ThFFF) [6–8].

In ThFFF, separation is governed by the ratio of the normal diffusion coefficient, D, and the thermal

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diffusion coefficient, D_T. Thermal diffusion is still an ill-understood phenomenon. However, from results obtained so far, it has become clear that the D_T is strongly dependent on the polymer–solvent system. Therefore, it can provide information about the chemical structure of a polymer. Thus, it is interesting to use values of D_T as a characteristic for the chemical nature of a polymer, as a substitute for less easily controlled techniques such as temperature rising elution fractionation (TREF) [9] and gradient precipitation elution chromatography (GPEC) [1,2].

ThFFF retention is also a function of molecular size, as it is determined by D_T/D. Therefore, useful information can only be obtained when the ThFFF method is used in combination with a sizing technique, such as light scattering (LS), SEC or hydrodynamic chromatography (HDC).

In the past, an off-line SEC–ThFFF technique has been used to first fractionate a polymer according to size and then to inject these fractions in ThFFF [10]. This system produced good results. However, due to experimental limitations, the total amount of separate polymer fractions could not exceed eight. Furthermore, the total analysis time of one sample could last up to 3 h because both coupled fractionation techniques are relatively slow.

Another separation technique capable of determining the size of a polymer is HDC [11,12]. An important advantage of HDC over SEC is its high separation speed, making it attractive as a second stage in a coupling with the slow ThFFF.

In this paper, a rapid method is described to characterize polymer and polymer blends two-dimensionally, with respect to chemical nature via the D_T value by ThFFF and with respect to size with HDC.

The applicability of the combination is demonstrated with standards and real polymer samples.

2. Theory

When coupling two separation techniques on-line, not only has an interface to be constructed but attention has to be given to the effects of the injection volume and flow-rates on the performance of the coupled system.

Fortunately, with ThFFF and HDC, the migration behaviour of polymers and band dispersion can be accurately described by theory. In the following section, a brief description of the retention and dispersion behaviour in these separation techniques will be given, followed by a more elaborate evaluation of the coupling requirements. More extensive descriptions of both separation techniques can be found in [11–16].

2.1. Retention in ThFFF

In ThFFF, use is made of an external temperature gradient that is perpendicular to the solvent flow through an open flat-walled channel [15]. This temperature gradient can be created by heating one wall of the channel and cooling the other wall. In this temperature gradient, macromolecules tend to concentrate preferentially at the cold wall. This phenomenon is called thermal diffusion [15–17]. This concentration effect at one channel wall is counteracted by the molecular diffusion of the polymers. As a result, each polymer species, on average, will reside at a specific distance from the cold wall, the so-called cloud thickness, L. Due to the parabolic flow profile in the channel, macromolecules with a small cloud thickness migrate more slowly through the system and hence fractionation can be obtained.

When the dependence of solvent viscosity and thermal conductivity on temperature is neglected [18], the migration of polymers in ThFFF can be described by:

$$R = \frac{t_0}{t_r} = 6\lambda_{FFF}\left[\coth\left(\frac{1}{2\lambda_{FFF}}\right) - 2\lambda_{FFF}\right] \quad (1)$$

where R is the retention ratio, t_r is the retention time of the polymer, t_0 is the retention time of the solvent or an unretained solute and λ_{FFF} represents the dimensionless cloud thickness, defined as:

$$\lambda_{FFF} = \frac{L}{w} = \frac{D}{D_T \Delta T} = \frac{1}{\frac{\alpha}{T}\Delta T} \quad (2)$$

where w is the thickness of the channel, D is the molecular diffusion coefficient, D_T is the thermal diffusion coefficient, ΔT is the applied temperature difference and α is the so-called Soret coefficient.

Although thermal diffusion has been observed for over a century, it is still a relatively uncomprehended

phenomenon. Several theories have been put forward to describe this behaviour [17,20–22]. Unfortunately, the data we have available from our own work and from literature do not substantiate any of the proposed relationships. Thus, in conclusion, D_T values cannot be obtained a priori from basic data and we can rely only on experimental values.

Measurements to date indicate that the thermal diffusion coefficient of a polymer depends strongly on its chemical nature as well as on that of the solvent in which it is dissolved [19,20]. Also, it has been found that, for a given polymer–solvent system, thermal diffusion is independent of the molecular mass, making it possible to use D_T as an empirical parameter to characterize the chemical nature of a polymer.

2.2. Plate height in ThFFF

The efficiency in ThFFF can be described by the plate height according to Ref. [17]:

$$H_{FFF} = \frac{2D}{R < v >} + \frac{\chi w^2 < v >}{D} \tag{3}$$

in which χ is a known function of λ_{FFF} and $<v>$ represents the average linear velocity. The first term of Eq. (3) describes the effect of longitudinal molecular diffusion, whereas the second term is governed by non-equilibrium. Since the diffusion coefficients of polymers are very small, the contribution of the first term to the overall plate height is often negligibly small. The remaining non-equilibrium term yields plate heights in the order of millimetres, which implies that ThFFF is a rather inefficient technique. In order to restrict the peak broadening, small linear velocities have to be used and, as a consequence, long analysis times have to be accepted. It is therefore preferable to use this slow technique as the initial separation method in a coupled system, particularly because HDC is a fast method.

2.3. Retention in packed-column HDC

In packed-column HDC (PC–HDC) separation is achieved by making use of the non-uniform flow profile that occurs in the interstitial space between the particles packed in a column [11–14].

The separation occurs, due to the fact that solutes, depending on their size are excluded differently from the low velocity regions near the surface of the particles of the packing. A large polymer molecule will be more excluded from these regions than a smaller molecule. Hence, the larger polymer will migrate at a higher velocity through the column than a smaller one. The elution order in HDC is therefore the same as in SEC [11,14,23].

The migration of polymers in packed-column HDC can be conveniently described by:

$$\tau = \frac{t_r}{t_0} = \frac{1}{1 + 2\lambda_{HDC} - C\lambda_{HDC}^2} \tag{4}$$

in which λ_{HDC} is the aspect ratio and C is a constant that has a value of 2.8 [12].

The aspect ratio, λ_{HDC}, is the ratio of the effective radius, r_{eff}, of the dissolved polymer molecules and the effective radius, r_c, of the interstitial channels of the packed bed [24]. It then appears, from Eq. (4), that all polymers will elute between $0.73 \cdot t_0$ and t_0, a rather narrow elution window. However, this narrow window implies that in HDC, four injected samples may be present in the column without zone overlapping. Therefore, HDC is attractive as a second stage in a two-dimensional separation.

2.4. Plate height in PC–HDC

For PC–HDC, the plate height, H, can be described by [12]:

$$H = \frac{1.3D}{< v >} + \frac{d_p}{\frac{D}{< v > d_p} + \frac{1}{1.4}} \tag{5}$$

in which d_p depicts the particle diameter of the packing.

At higher solvent velocities, this equation reduces to $H = 1.4 \cdot d_p$. Therefore, applying these velocities in PC–HDC has the advantage that the plate height, i.e., the efficiency, is very small and independent of the solvent's velocity. This means that the analysis speed can be increased significantly without influencing the resolution.

2.5. Coupling of ThFFF and PC–HDC

When the two techniques are coupled, several aspects such as solvent choice, injection concentration, injection volume and sample rate have to be taken into consideration. One should consider that the technique with the primary fractionation action should be slower. Because the analysis speed of ThFFF is slow compared to that of HDC, ThFFF has to be selected as the primary technique.

2.6. Sampling rate

In the sampling of the elution profile of the first (ThFFF) method, the loss in resolution is determined by the number of samples, n_s, taken per standard deviation, σ_v. A value of n_s of between one and two is reasonable. The sampling rate, t_{sam}, can then be given by:

$$t_{sam} = \frac{\sigma_t}{n_s} = \frac{\sigma_v}{F_c n_s} \quad (6)$$

in which σ_t is the standard deviation in time units of the peak in the ThFFF channel and can be derived from Eq. (3), n_s is the number of fractions taken and F_c is the flow-rate.

Obviously, the sampling rate must be larger with a high flow-rate, high efficiency and large n_s. Fig. 1 shows the estimated time between fractions as a function of molecular mass in order to obtain n_s values of between one and two for monodisperse Polystyrene (PS) in tetrahydrofuran (THF) in our ThFFF system. The figure indicates that for the early eluting fractions, below a molecular mass of 100 kDa, a sampling rate of 10 to 40 s would be required. Later fractions, with a mass of 500 kDa, can be sampled with a sampling rate that is twice as high.

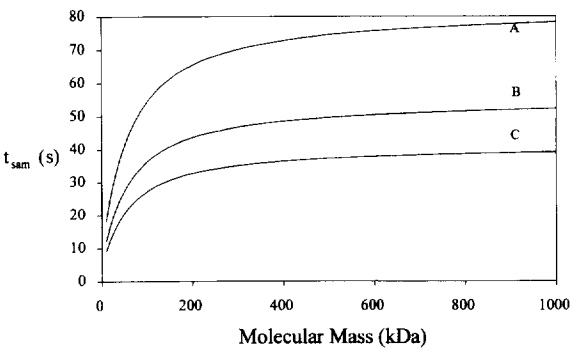

Fig. 1. Theoretical minimum sample rate as a function of PS molecular mass in ThFFF, $w = 127$ μm, $L = 46$ cm, $V_0 = 0.45$ ml, $F_c = 0.1$ ml/min, $\Delta T = 60$ K. (A) $n_s = 1$; (B) $n_s = 1.5$ and (C) $n_s = 2$.

When working in real time, the second fractionation technique should be capable of analysing at a sufficient rate. With the HDC column used, we could get sufficient resolution with a total analysis time of 120 s. Because the chromatogram occupies one fourth of the total retention time, we could inject samples at repetition times of around 40 s. That is, we injected a new sample before the sample previously injected was eluted.

2.7. Polymer concentration in ThFFF

The concentration of the polymers eluting from the ThFFF must be high enough to allow their detection after separation in the HDC system. In general, the polymer concentration at the maximum of the eluting Gaussian peak can be described by:

$$C_{top} = \frac{V_{inj}}{\sqrt{2\pi}\sigma_v} \cdot C_{inj}$$

where V_{inj} is the injection volume and C_{inj} is the injection concentration.

In the coupled system, C_{inj} is given by the polymer concentration leaving the ThFFF channel. The concentration of the eluting peak after the HDC separation can be estimated by:

$$C^{HDC} = \frac{1}{2\pi}\left(\frac{V_{inj}^{HDC}}{\sigma_v^{HDC}}\right)\left(\frac{V_{inj}^{FFF}}{\sigma_v^{FFF}}\right) \cdot C_{inj} \quad (8)$$

where σ_v for both techniques can be calculated from Eqs. (3,5), respectively.

Eq. (8) clearly shows that, for a given system, three options are available for increasing the polymer concentration detected. First, the injection concentration into the ThFFF channel can be increased. Unfortunately, it has been found that concentration can influence the migration behaviour [7,25], probably due to viscosity effects. The second and third ways are to increase the injected volume of polymer sample on both the ThFFF and the HDC system. In those cases, an injection volume that is too large must be avoided, as it will cause decreased res-

olution. In particular, the highly efficient HDC column is very vulnerable to peak broadening caused by an injection volume that is too large and the commonly used injection volume of 0.5 μl is already close to the limit. Therefore, during the following experiments, only the injection volume into the ThFFF system was optimized to improve the signal-to-noise ratio.

3. Experimental

3.1. Instrumentation

In Fig. 2, a schematic representation of the ThFFF–HDC set-up is given. The ThFFF system consisted of a HPLC pump (Spectroflow 400, Applied BioSystems, Ramsey, NJ, USA), delivering a flow-rate of 0.1 ml/min THF. The ThFFF system was a T100 Thermal Fractionator (FFFractionation, Salt Lake City, UT, USA). The dimensions of the channel were 46 cm×1 cm×127 μm, resulting in a void volume of 0.45 ml. Several injection volumes ranging from 20 to 200 μl were used. It was found that for an unretained solute an injection volume of 50 μl could be used without excessive peak broadening; there was less than a 10% increase in peak width with respect to 20-μl injections.

The outlet of the ThFFF channel was connected to the sample loop of an air pressure driven (Vici, Schenkon, Switzerland) injection valve (7010, Rheodyne, Berkely, CA, USA), with an injection loop of 0.5 μl. The valve was controlled by a laboratory-made timer that allows the injection of a sample into the HDC column at 1-min intervals.

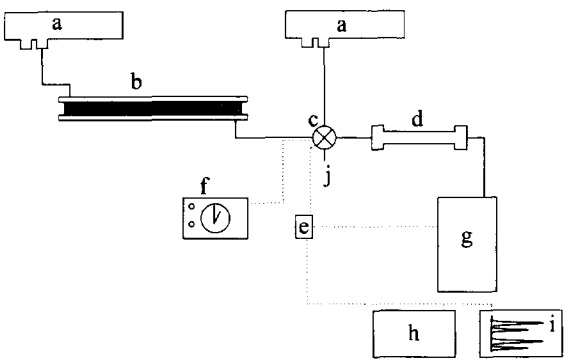

Fig. 2. Schematic representation of the ThFFF–HDC set-up, (a) HPLC pump; (b) ThFFF channel; (c) pneumatic injection valve; (d) HDC column; (e) relays; (f) timer; (g) ELSD; (h) integrator and (i) recorder.

The laboratory-made HDC column [13] was a stainless steel column with dimensions 150×4.6 mm, packed with 1.5 μm non-porous spherical silica particles. The mobile phase (THF) was propelled by a HPLC pump (Spectroflow 400, Applied BioSystems) at a flow-rate of 0.6 ml/min and a pressure of 270 bar. Detection of polymers was carried out using an evaporative light scattering detector (ELSDIIA, Varex, Burtonsville, MD, USA).

Signals were registered on a flat-bed recorder (BD 40, Kipp en Zonen, Delft, Netherlands) and integrator (3394, Hewlett-Packard, Avondale, PA, USA).

Calibration of the HDC column was carried out with PSs and a UV detector (Spectroflow 757, Applied BioSystems), equipped with a capillary slit cell [12].

3.2. Chemicals

Analytical grade THF was purchased from Acros (Geel, Belgium). Prior to use, all solvents were filtered through a 0.02-μm inorganic filter (Anodisc 47, Anotec, Banbury, UK). PS standards were obtained from Machery-Nagel (Düren, Germany), Merck (Darmstadt, Germany), Pressure Chemicals (Pittsburgh, PA, USA) and Toyo Soda (Tokyo, Japan). Polyisoprene (PIP) standards were purchased from Polymer Laboratories (Church Stretton, UK).

Styrene–acrylonitrile copolymers were kindly provided by General Electric Plastics (Bergen op Zoom, Netherlands). All sample solutions were prepared by dissolving the polymer in THF, without stirring, at a total polymer concentration of 0.5 mg/ml unless stated otherwise.

3.3. Procedures

After injection of the sample into the ThFFF channel, the solvent flow was interrupted for 5 min in order to achieve equilibrium. After this relaxation period, the flow was restored and the integrator and the timer were activated. The mobile phase of the ThFFF consisted of pure THF containing a small marker solute, PS 580 Da, while the mobile phase

for the HDC system consisted solely of pure THF. The marker solute was used to determine, during the run, the dead time of the HDC column, thereby reducing errors caused by flow-rate fluctuations.

According to Fig. 1, a sample time of about 1 min, or less, is required. At the maximum attainable flow-rate of 0.6 ml/min, the HDC analysis of a single fraction took about 2 min. Fortunately, in HDC, the polymers were eluted in the above-mentioned restricted window ($0.73 \cdot t_0 - t_0$) and this allowed the injection of a sample every 60 s, while avoiding overlap with the peaks from a previous injection. The obtained retention data were evaluated using a program written in Turbo Pascal 6.0 (Borland International, Scotts Valley, CA, USA). This program corrects the data for temperature effects in the ThFFF channel, such as changing viscosity and thermal conductivity, and, after correction, calculates D_T, D and α/T values.

4. Results and discussion

4.1. Calibration of the HDC column

In order to obtain reliable diffusion coefficients of the selected polymers, the HDC column has to be calibrated with a set of standard polymers. This was done by injecting PS standards dissolved in THF into the HDC column and determining the relative residence times, τ, for all standards.

For PS, both the effective radius as well as the diffusion coefficient are known as a function of the molecular mass.

The effective radius is derived from the radius of gyration [26]:

$$r_{eff} = \frac{\sqrt{\pi}}{2} r_g = \frac{\sqrt{\pi}}{2} 1.39 \cdot 10^{-5} M^{0.588} \quad (9)$$

in which r_{eff} is the effective radius (in μm).

The diffusion coefficient, D, in $mm^2\ s^{-1}$ can be described by [27]:

$$D = \frac{3.861 \cdot 10^{-2}}{M^{0.571}} \quad (10)$$

The τ values of the PS standards in the HDC column were used to construct a calibration curve between τ and D. A regression program was used to find the best fit between τ and the diffusion coefficient, and this appeared to be:

$$D = \frac{a + c\tau + e\tau^2}{1 + b\tau + d\tau^2 + f\tau^3} \cdot 10^{-5} \quad (11)$$

with $a = 0.026$, $b = -3.17$, $c = -0.057$, $d = 3.35$, $e = 0.031$ and $f = -1.18$.

The measured data and the fit are shown in Fig. 3. At the flow-rate used (0.6 ml/min), the column is only suited to fractionating polymers that have a τ value between 0.84 and 1. In practice, this means that the column can be used for polymers with an equivalent PS mass between 70 and 600.

This tedious calibration method can be avoided by a second method, which was used in this case as a check of the former method. In this method, a polydisperse PS sample was directly fractionated using the coupled system. With the obtained Soret coefficient, α/T ($=D_T/D$), τ values and the known thermal diffusion coefficient, D_T, of PS in THF, a calibration curve of the diffusion coefficient, as a function of the τ value, can be constructed. It was found that this method produced the same result as the former method. This calibration technique will be very convenient when a different HDC column has to be used because it circumvents the tiresome calibration using monodisperse standards.

4.2. Polymer blends

In order to test the coupled system, a model

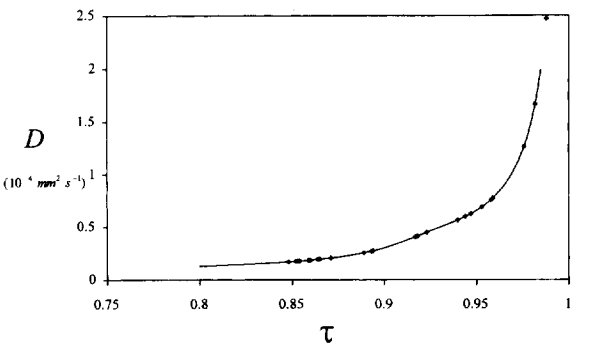

Fig. 3. Diffusion coefficient as a function of τ in the HDC column for PS in THF. (♦) measured data, (solid line) fit.

poly-compositional sample was prepared by mixing PS 336 kDa and PIP 590 kDa, each at a concentration of 0.2 mg/ml. The ratio between molecular diffusion and thermal diffusion of these polymers is almost identical [17], PS 336 kDa, $D=2.7\cdot10^{-5}$ mm^2 s^{-1}, $D_T=1\cdot10^{-5}$ mm^2 s^{-1} K^{-1}, PIP 590 kDa, $D=1.7\cdot10^{-5}$ mm^2 s^{-1}, $D_T=0.57\cdot10^{-5}$ mm^2 s^{-1} K^{-1}. This means that hardly any separation of these polymers occurs with ThFFF. However, due to the differences in size, both polymers can be easily separated with HDC.

Fig. 4 shows the result obtained using the two-dimensional fractionation of this polymer sample. The small peaks visible every minute are the marker solutes. The large peak after approximately 7 min is caused by solutes that are unretained in ThFFF. The drawn/dashed lines through the peak tops represent the ThFFF fractograms of the individual polymers. Summation yields the total ThFFF fractogram of the mixture. As can be seen, the on-line coupling of ThFFF and HDC is effective in separating poly-compositional samples.

In the previous experiment, the PS and PIP polymers were well resolved on the HDC column because these solutes have a very low polydispersity ($\mu<1.01$). For more disperse polymer samples, the interpretation of the fractogram becomes more complicated. To check whether the ThFFF–HDC combination would perform well using more polydisperse samples, a mixture containing PS 274 kDa with a $\mu\approx3$ and PIP 590 kDa with a $\mu<1.01$ was separated using the same conditions as in Fig. 4. Fig. 5

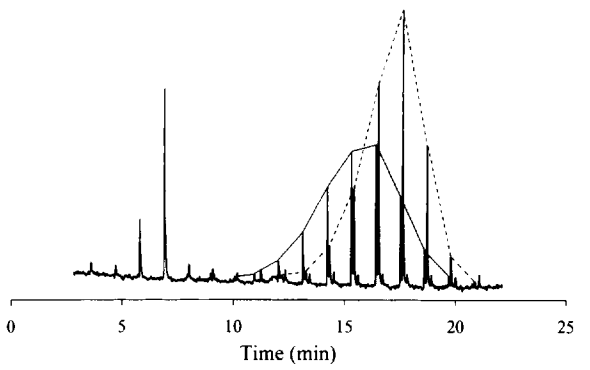

Fig. 4. ThFFF–HDC fractogram of a mixture containing PS 336 kDa (dashed line) and PIP 590 kDa (solid line) in THF, $\Delta T=40$ K; flow-rate (ThFFF), 0.1 ml/min; flow-rate (HDC), 0.6 ml/min.

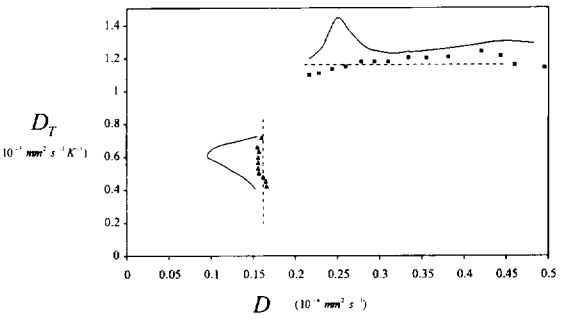

Fig. 5. Thermal diffusion as a function of diffusion for a mixture containing (■) PS 274 kDa and (▲) PIP 590 kDa. $w=127$ μm, $L=46$ cm, $V_0=0.45$ ml, $F_c=0.1$ ml/min and $\Delta T=60$ K.

shows the two-dimensional plot of the calculated thermal diffusion versus measured molecular diffusion coefficient, together with their separate fractograms composed from the HDC peak heights. As was expected, the observed diffusion coefficient of the polydisperse PS sample has a wide range whereas the calculated D_T is constant, which is expected, due to the fact that a homopolymer was used. The PIP shows a constant D, based on the PS calibration in Fig. 3, which is good agreement with expectations, as a narrow standard was used. However, it seems that the measured D_T is not constant. This apparent change in D_T can be attributed to dispersion in the ThFFF channel. This can be more easily explained by looking at Fig. 4. In this figure, although narrow standards were injected, broad peaks emerge from the ThFFF channel. This is caused by the low efficiency of ThFFF. As the retention time in the ThFFF in the coupled system is used to calculate the ratio between D_T and D, fractions of a polymer with the same molecular mass and diffusion but eluting, due to this dispersion, at different times suggests that the D_T value changes. However, the proper D_T value can be obtained from the data at the peak maximum, which is supposed to be the same position as in the case of no dispersion.

The calculated D_T value of PS is $1.15\cdot10^{-5}$ mm^2 s^{-1} K^{-1}, which is in reasonable agreement with previous measurements [17] (where a value of $1\cdot10^{-5}$ mm^2 s^{-1} K^{-1} was found). For PIP, a D_T value of $0.6\cdot10^{-5}$ mm^2 s^{-1} K^{-1} was found, which was in excellent agreement with previous measurements ($D_T=0.57\cdot10^{-5}$ mm^2 s^{-1} K^{-1}) [17]. The fluctua-

tions in the PS curve is caused by small fluctuations in the flow-rate, which caused errors in the measured D_T values of 5%. This implies that when analyzing a heterogeneous sample, the measured change in D_T should exceed 10% before any conclusion can be drawn concerning the chemical composition distribution.

When using the coupled system, concentration effects that which will result in fluctuating D_T values must be avoided. When these effects do occur, it was found that the apparent D_T increased due to prolonged retention in the ThFFF channel. This effect has been found before [7,25] and is probably caused by a viscosity effect due to the high polymer concentration near the cold wall. This viscous plug near the wall will be transported through the system at a lower velocity than the pure solvent, thereby increasing the migration time.

The maximum total polymer concentration at which no excessive retention effects occur was found to be 0.5 mg/ml.

4.3. SAN copolymers

The coupled system can be used not only for homopolymers but also for copolymers. Because thermal diffusion is closely related to the chemical structure of a copolymer, it should be possible to detect potential compositional drift. When this occurs, it will be expected that the measured thermal diffusion is not constant over the mass range.

Subsequently, three styrene acrylonitrile samples (SAN) were analysed. Two of the standards appear to have a homogeneous chemical composition, while the third contained a chemical distribution that was determined by means of gradient elution chromatography, performed by the supplier [28]. The standards contained 27 and 35% acrylonitrile and had a molecular mass of about 130 kDa. The compositionally heterogeneous sample had a mean acrylonitrile content of 34% and a molecular mass of 140.

Fig. 6 shows the obtained D_T as a function of D of the two SAN standards, a polydisperse PS (274 kDa) standard and the heterologous sample.

As can be seen, the 27 and 35% copolymers and the PS exhibit a constant thermal diffusion coefficient, which indicates that the composition is constant. The observed D_T seems to increase with increasing acrylonitrile content. For SAN 27%, a mean D_T of $1.3 \cdot 10^{-5}$ mm^2 s^{-1} K^{-1} was found and for SAN 35%, a mean D_T of $1.46 \cdot 10^{-5}$ mm^2 s^{-1} K^{-1} was obtained. The suspected sample clearly shows a decrease of the observed D_T with increasing D. This may indicate that more acrylonitrile is incorporated in higher molecular masses. Assuming that the D_T is proportional to the percentage of acrylonitrile, it is possible (using the values of the PS and SAN standards) to construct a calibration curve between the observed D_T and the acrylonitrile content of the polymer.

Fig. 7 shows the chemical distribution for the SAN 34% sample using such a calibration curve. It

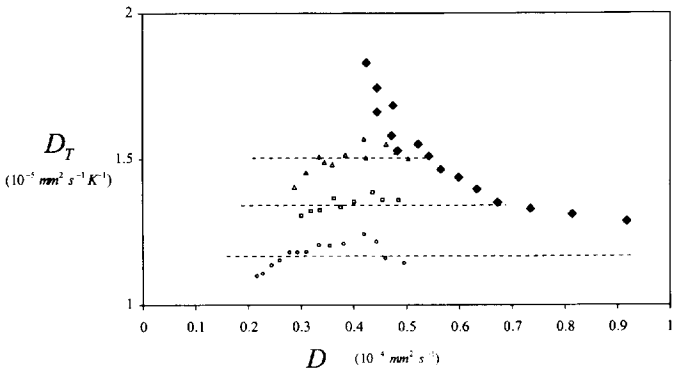

Fig. 6. Thermal diffusion as a function of diffusion for (○) PS 274 kDa, (□) SAN 27%, (△) SAN 35% and (♦) SAN 34%. $w = 127$ μm, $L = 46$ cm, $V_0 = 0.45$ ml, $F_c = 0.1$ ml/min and $\Delta T = 60$ K.

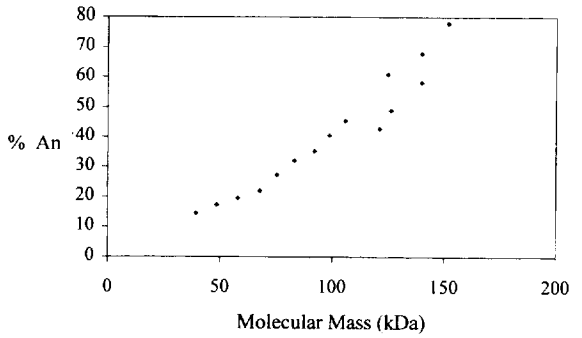

Fig. 7. Percentage acrylonitrile versus molecular mass for SAN 34%.

is clear from this figure that the percentage of acrylonitrile increases from 20% in the lower molecular masses to 80% in the higher molecular masses.

Of course, Fig. 7 should be interpreted keeping in mind that a proportional relationship between the percentage of acrylonitrile and the observed D_T is assumed and that sometimes the D_T is not linearly related to the composition of the copolymer [16]. Furthermore, the calibration curve was constructed using only three standards with the highest acrylonitrile content being 35%, whereas the sample seems to contain up to 80%, introducing an uncertainty caused by extrapolation.

5. Conclusions

The on-line coupling of ThFFF and HDC shows promise as a method for characterizing polymers, both in mass and chemical composition. The combined system can be used to analyse homo- and copolymers, independent of polydispersity, and is capable of detecting compositional heterogeneity.

The current system is suited for the analysis of polymers with molecular masses between 70 and 600. This restricted range is due mainly to the limited molecular mass range covered by the HDC column.

When smaller or larger polymers have to be analysed, the size of particles in the HDC columns has to be adapted. However, by using HDC columns packed with different particle sizes in parallel, it should be possible to extend the molecular mass working range. Furthermore, temperature programming of the ThFFF channel could be used to further speed up the analysis, although this would complicate interpretation of the data. The proposed system may become an additional tool for investigating the structure of copolymers, provided that good standards are available.

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References

[1] G. Glöckner, D. Wolf and H. Engelhardt, Chromatographia, 39 (1994) 557.
[2] G. Glöckner, Pure Appl. Chem., 55 (1983) 1553.
[3] H. Inahaki, T. Kotaka and T.-I. Min, Pure Appl. Chem., 46 (1976) 61.
[4] S. Mori, J. Chromatogr., 194 (1980) 163.
[5] S. Mori, J. Chromatogr., 411 (1987) 355.
[6] P.M. Shiundu, E.E. Remsen and J.C. Giddings, J. Appl. Polym. Sci., 60 (1996) 1695.
[7] A.C. van Asten, E. Venema, W.Th. Kok and H. Poppe, J. Chromatogr., 644 (1993) 83.
[8] M. Antonietti, A. Briel and C. Tank, Acta Polymerica, 46 (1995) 254.
[9] L. Wild and T.R. Ryle, Polym. Prep., Am. Chem. Soc., Polym. Chem. Div., 18 (1977) 182.
[10] A.C. van Asten, R.J. van Dam, W.Th. Kok, R. Tijssen and H. Poppe, J. Chromatogr. A, 703 (1995) 245.
[11] R. Tijssen, J. Bos and M.E. van Kreveld, Anal. Chem., 58 (1986) 3036.
[12] G. Stegeman, J.C. Kraak and H. Poppe, J. Chromatogr., 634 (1993) 149.
[13] G. Stegeman, R. Oostervink, J.C. Kraak and H. Poppe, J. Chromatogr., 506 (1990) 547.
[14] E.A. DiMarzio and C.M. Guttman, Macromolecules, 3 (1970) 131.
[15] M.N. Myers, K.D. Caldwell and J.C. Giddings, Sep. Sci., 9 (1974) 47.
[16] M.E. Schimpf and J.C. Giddings, J. Polym. Sci., Part B, 28 (1990) 2673.
[17] M.E. Schimpf and J.C. Giddings, J. Polym. Sci., Part B, 27 (1989) 1317.
[18] A.C. van Asten, H.F.M. Boelens, W.Th. Kok, H. Poppe, P.S. Williams and J.C. Giddings, Sep. Sci. Techn., 29 (1994) 513.

[19] J.C. Giddings, M.N. Myers and J. Janca, J. Chromatogr., 186 (1979) 37.
[20] M.E. Schimpf and J.C. Giddings, Macromolecules, 20 (1987) 1561.
[21] M. Bender, Macromolecules, 28 (1995) 1309.
[22] T.K. Kazanovich, J. Polym. Sci., Part C, 16 (1967) 2463.
[23] C.A. Silebi and J.G. Dos Ramos, J. Colloid Interface Sci., 130 (1989) 14.
[24] H.J. Small, J. Colloid Interface Sci., 48 (1984) 147.
[25] M.E. Schimpf, J. Chromatogr., 517 (1990) 405.
[26] M.E. van Kreveld and N. van den Hoed, J. Chromatogr., 83 (1973) 111.
[27] M.E. Schimpf and J.C. Giddings, J. Appl. Polym. Sci., Part B: Polym. Phys., 28 (1990) 2673.
[28] M. Hetem, General Electric Plastics BV (Bergen op Zoom, Netherlands), personal communication.