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Use of thermal field flow fractionation for the fractionation of polybutadiene in various organic solvents

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ABSTRACT

It is shown that thermal field flow fractionation (ThFFF) can be a valuable tool for the fractionation of polybutadiene (PB). The thermal diffusivity of four PB standards of different molecular mass was determined in six organic solvents. The results indicate that for this polymer species, the thermal diffusion coefficient varies significantly with the choice of the solvent but seems to be independent of the molecular mass. The highest retention for a given molecular mass was found with toluene and ethylbenzene as solvents. With respect to the speed of separation of polybutadiene, the best results were obtained with toluene. The influence of the temperature drop across the channel and the polymer concentration on retention was also studied. The use of an evaporative light-scattering detector made it possible to work with polymer sample concentrations as low as 0.1 mg/ml. The unique separation possibilities offered by ThFFF are demonstrated with the separation of polybutadiene, polyisoprene and polystyrene standards of the same molecular mass using tetrahydrofuran as solvent.

INTRODUCTION

After its introduction by Giddings [1] in 1966, field flow fractionation (FFF) has steadily developed and it now covers a fairly broad ensemble of separation methods. Retention and separation are accomplished by the use of an external field perpendicular to the direction of the laminar flow of a carrier liquid through an open channel [2]. FFF techniques are especially suited to the separation and characterization of macromolecules, colloids and particles.

Thermal field flow fractionation (ThFFF) is a variety of FFF in which a temperature gradient is used as the field. Over the years it has been shown that ThFFF is a valuable tool for the analysis of synthetic polymers in various organic

solvents [3–8]. Only very recently has it been demonstrated that ThFFF is also useful for the separation of particles in aqueous and non-aqueous solutions [9,10]. In ThFFF, retention is determined by the ratio of the ordinary and thermal diffusion coefficients. This ratio is also expressed as α/T , where α is the Soret coefficient and T is the temperature.

Although studied for over a century [11], thermal diffusion in liquids is still a poorly understood process. Various theories have been developed that vary widely in conceptual basis [12–16]. However, Schimpf and Giddings [3] demonstrated that none of the existing theories is able to describe accurately the phenomenon of thermal diffusion of polymers in solution. In order to gain more knowledge of and insight into the effect of thermal diffusion, it is necessary to measure thermal diffusion coefficients for various polymer–solvent systems. In combination with another technique for the measurement of

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diffusion coefficients, ThFFF will yield highly accurate data on thermal diffusion coefficients.

Schimpf and Giddings [3] found for polystyrene (PS), poly- α -metastyrene (PaMS), poly(methyl methacrylate) (PMMA) and polyisoprene (PI) in different organic solvents that the thermal diffusion coefficient is independent of the molecular mass of the polymer. However, thermal diffusion was found to be related to the chemical composition of both the polymer and the solvent. An empirical relationship linked the thermal diffusion coefficient to the thermal conductivity of the polymer and the solvent and the activation energy of viscous flow. In other studies by the same group it was found that the thermal diffusion of polystyrene in ethylbenzene is independent of the branching configuration of the polymer [17]. ThFFF studies of random and block copolymers [4] demonstrated that for random copolymers a linear relationship exists between the thermal diffusion coefficient and the mole fraction of one of the monomers. However, for block copolymers it was found that the monomer species in the outer regions of the solvated polymer predominantly determines the extent of thermal diffusion. Further complications arise from the fact that the thermal diffusion coefficient is strongly temperature dependent. Brimhall *et al.* [18] found for polystyrene in ethylbenzene a linear relationship between the thermal diffusion coefficient and the temperature in the centre of the solute zone.

The use of ThFFF for the analysis of water-soluble macromolecules has been very limited because only for very few polymer species [poly(ethylene oxide), polyvinylpyrrolidone and poly(styrene sulphonate)] has thermal diffusion in aqueous environments been observed [19].

In comparison with other polymer fractionation methods, ThFFF offers unique separation possibilities. Polymer species are separated not only according to size but also according to thermal diffusion. Because thermal diffusion depends on the chemical nature of the polymer, ThFFF can be used for the separation of macromolecules which are equal in size but differ in chemical composition [20].

In this paper, the use of ThFFF for the fractionation of polybutadiene (PB) is demon-

strated. Values for α/T , which we believe are accurate, for four PB standards of different molecular mass were determined in six organic solvents. The effects of the polymer concentration and the temperature drop across the channel were investigated. Further, the unique separation capabilities of ThFFF are demonstrated with the separation of three different polymer species of the same molecular mass.

THEORY

Conversion of retention ratios into α/T values

The retention ratio in FFF, which is equal to the ratio of the void volume and the retention volume, can be expressed as [21]

$$R = \frac{\langle C(x)v(x) \rangle}{\langle C \rangle \langle v \rangle} \quad (1)$$

where x is the coordinate in the direction of the channel thickness, $\langle \rangle$ denotes values averaged over the cross-section of the channel and $C(x)$ and $v(x)$ are the concentration of the solute and the linear carrier fluid velocity, respectively, as functions of the position across the channel thickness.

The retention ratio can easily be obtained from the fractogram. When no temperature and concentration effects are considered, eqn. 1 leads to the following well known expression:

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

where the dimensionless parameter λ represents the mean layer thickness of the compressed solute zone. For ThFFF the λ value can be approximated by

$$\lambda \approx \frac{D}{D_T \Delta T} = \frac{1}{\frac{\alpha}{T} \Delta T} \quad (3)$$

where D and D_T are the ordinary and the thermal diffusion coefficient of the polymer species in the given solvent, respectively, ΔT is the temperature drop across the channel thickness and α is the Soret coefficient. With the use of eqns. 2 and 3 it is possible to convert retention data into α/T values. When diffusion data for the polymer-solvent system are available these α/T

values can be used to determine thermal diffusion coefficients.

However, theoretical complications arise from the fact that a number of important parameters are temperature dependent. Because of the temperature gradient used in ThFFF, these parameters will vary across the channel thickness. Gunderson *et al.* [22] showed that the temperature dependence of the viscosity and the thermal conductivity of the solvent can be accounted for by using empirical relationships. For the solvent viscosity η , the temperature dependence is expressed as

$$\frac{1}{\eta} = a_0 + a_1 T + a_2 T^2 + a_3 T^3 \quad (4)$$

where T is the temperature and a_i are empirical constants.

For the solvent thermal conductivity κ , the following equation is used to describe the temperature dependence:

$$\kappa = b_0 + b_1(T - T_c) \quad (5)$$

where b_0 and T_c are the thermal conductivity and the temperature at the cold wall, respectively. The term b_1 , often expressed as $d\kappa/dT$, is considered to be constant in the temperature range of interest. In previous work [23] we have shown that the temperature dependence of the solvent viscosity has a significant effect on the shape of the velocity profile of the carrier liquid. The effect of the temperature dependence of the thermal conductivity on the velocity profile is negligible. However, it is important to consider the temperature dependence of this latter parameter because it has a significant effect on the concentration profile of the solute. As was shown by Brimhall *et al.* [18], α/T itself is also strongly temperature dependent. The temperature dependence of α/T can be expressed empirically with a second-degree polynomial function. To account for the influence of the temperature gradient across the solute zone on α/T , retention data should therefore be available for at least three different cold wall temperatures [23]. In this work this latter effect was neglected because the corresponding systematic error is only small. Using a numerical integration routine

the temperature dependence of the solvent viscosity and thermal conductivity has been accounted for. The α/T values have been directly assigned to the temperature in the centre of gravity of the corresponding solute zones [18].

Effect of solvent and polymer type on time optimization in ThFFF

As was demonstrated by Giddings *et al.* [24], theoretical considerations of time optimization in FFF are largely equivalent to those in chromatography. The number of plates N needed to achieve a separation with a resolution R_s of two discrete polymer fractions is given by

$$N = 16R_s^2 \left(\frac{M}{\Delta M} \right)^2 \left(\frac{d \ln M}{d \ln V_r} \right)^2 \quad (6)$$

where ΔM is the difference in molecular mass of two polymer fractions having a mean molecular mass M and V_r is the retention volume.

The time required to generate one plate can be expressed as

$$t_p = \frac{H}{R\langle v \rangle} \quad (7)$$

where H is the plate height and $\langle v \rangle$ is the mean velocity of the carrier liquid. Combining eqns. 6 and 7 yields the following expression for the analysis time t_a necessary to obtain a separation with resolution R_s :

$$t_a = 16R_s^2 \cdot \left(\frac{M}{\Delta M} \right)^2 \cdot \frac{H}{R\langle v \rangle} \cdot \left(\frac{d \ln M}{d \ln V_r} \right)^2 \quad (8)$$

The first two factors on the right-hand side of eqn. 8 do not need any further consideration because they only reflect the demands put on the separation. The third factor reflects the efficiency and the last factor corresponds to the molecular mass selectivity of the separation mechanism.

Using this last equation, Giddings *et al.* [24] concluded that substantial improvements in separation speed and analysis time could be obtained with decreasing channel thickness and increasing temperature drop. However, when eqn. 8 is studied it can be expected that also the choice of the polymer and the solvent will have a signifi-

cant effect on the analysis time. In order to examine the influence of the solvent and polymer type on the separation speed in ThFFF, the analysis time has to be evaluated for a fixed channel thickness and temperature drop.

In the following discussion it has been neglected that the use of a temperature gradient in ThFFF disturbs both the velocity profile of the carrier liquid and the concentration profile of the solute. Although it is known that these temperatures effects have a significant effect on retention and plate height [22], we shall assume that the conclusions regarding time optimization will retain their validity.

The plate height in FFF is dominated by non-equilibrium effects [25]. The polydispersity of the polymer sample is also an important factor to consider in practice. However, polydispersity is not taken into account here, because only the separation power of the fractionation method is discussed. If only the non-equilibrium contribution is considered, the plate height in FFF is given by [26]

$$H = \chi \cdot \frac{w^2 \langle v \rangle}{D} \quad (9)$$

where w is the channel thickness and χ is a complicated function of the parameter λ . The influence of the diffusion coefficient on the plate height in ThFFF is not straightforward. The diffusion coefficient will influence λ (see eqn. 3) and thereby χ . In the limit of $\lambda \rightarrow 0$, χ can be approximated by $24\lambda^3$ [26]. As λ is proportional to D , the plate height will in this case be proportional to D^2 , indicating that the efficiency will increase dramatically with increasing molecular mass of the polymer.

The parameter S , describing the molecular mass selectivity of a polymer fractionation method, is generally defined as [5]

$$S = \left| \frac{d \ln V_r}{d \ln M} \right| \quad (10)$$

This can be rearranged to

$$S = \left| \frac{d \ln R}{d \ln \lambda} \frac{d \ln \lambda}{d \ln M} \right| \quad (11)$$

Using eqn. 2 the term $d \ln R/d \ln \lambda$ can be

evaluated. For all polymer–solvent systems studied so far it has been found that the thermal diffusion coefficient is independent of the molecular mass. Therefore, M will influence λ only through its effect on the diffusion coefficient. The correlation between the diffusion coefficient and the molecular mass of a polymer is often expressed using the following empirical relationship:

$$D = A/M^b \quad (12)$$

where A and b are constants which are determined by both the solvent and the polymer.

With the use of eqn. 12 it can easily be found that the term $d \ln \lambda/d \ln M$ equals b . In systems in which retention is high ($\lambda < 0.05$), the retention ratio can be approximated by 6λ [27]. In this case the term $d \ln R/d \ln \lambda$ equals 1 and the mass selectivity is therefore equal to b . However, if the retention is lower the value of S will be significantly lower. This is demonstrated in Fig. 1, where $d \ln R/d \ln \lambda$ is plotted as a function of λ .

In the limit of $\lambda \rightarrow 0$, when R is equal to 6λ , χ can be expressed as $24\lambda^3$ and S is equal to b , the analysis time will be proportional to

$$t_a \sim \frac{1}{b^2} \cdot \left(\frac{w}{\Delta T} \right)^2 \cdot \frac{D}{D_1^2} \quad (13)$$

The constant b is in the range 0.5–0.6 for most polymer–solvent systems. The second factor on the right-hand side of eqn. 13 corresponds to the experimental parameters of the ThFFF set-up. As Giddings *et al.* [24] concluded, a gain in

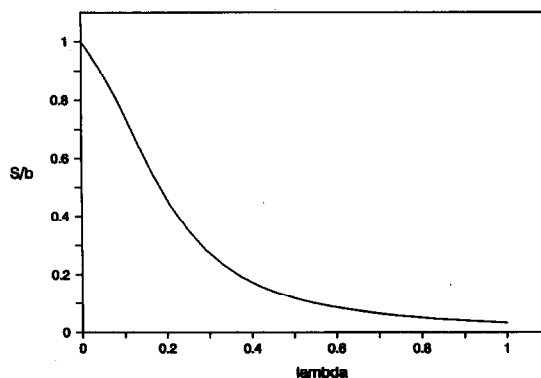


Fig. 1. S/b ($d \ln R/d \ln \lambda$) as a function of λ .

separation speed can be obtained when the temperature drop and channel thickness are increased and decreased, respectively. The last factor is determined by the mean molecular mass of the two polymer fractions and the polymer–solvent system that is considered. Decreasing diffusion and increasing thermal diffusion will improve the separation speed of ThFFF. To demonstrate the effect of the polymer–solvent system and the molecular mass of the polymer fractions on the analysis time in ThFFF under normal working conditions, eqn. 8 was fully evaluated for a fixed ThFFF set-up. Nowadays a channel thickness of $76 \mu\text{m}$ with a temperature drop across the channel of 80 K can be used routinely, and these values were therefore used in the calculations.

By combining eqns. 8 and 9, it can be seen that the analysis time is independent of the flow-rate of the carrier liquid. Therefore, with w and ΔT regarded as constants, the analysis time is only a function of M , A , b and D_T . The last three parameters are all dependent on the chemical nature of both the solvent and the polymer. If these three parameters are known it is possible to plot the analysis time as a function of the molecular mass for a given polymer–solvent system. This is illustrated in Fig. 2, from which it can be concluded that the separation

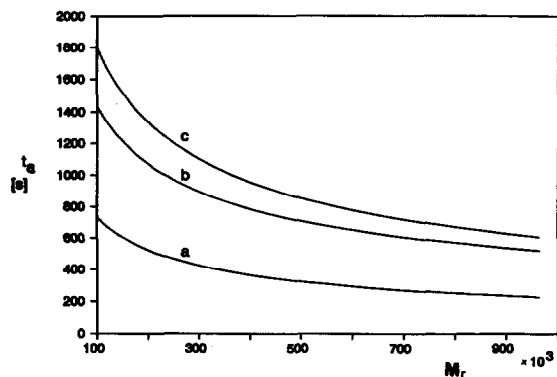


Fig. 2. Analysis time as a function of the molecular mass (M_r) for polystyrene in (a) THF and (b) cyclohexane and for (c) polyisoprene in THF. $w = 76 \mu\text{m}$; $\Delta T = 80^\circ\text{C}$; $R_s = 1$; $M/\Delta M = 3$. Polystyrene in THF: $A = 3.861 \cdot 10^{-4}$, $b = 0.571$, $D_T = 1.0 \cdot 10^{-7} \text{ cm}^2/\text{s} \cdot \text{K}$. Polyisoprene in THF: $A = 3.371 \cdot 10^{-4}$, $b = 0.570$, $D_T = 0.57 \cdot 10^{-7} \text{ cm}^2/\text{s} \cdot \text{K}$. Polystyrene in cyclohexane: $A = 1.061 \cdot 10^{-4}$, $b = 0.497$, $D_T = 0.66 \cdot 10^{-7} \text{ cm}^2/\text{s} \cdot \text{K}$.

speed in ThFFF varies significantly with the choice of the polymer and the solvent. Further, it can be seen that the use of ThFFF becomes more advantageous when samples of high molecular mass have to be analysed. However, these conclusions must be adjusted for ultra-high molecular masses for which lift forces will play a dominant role at high flow-rates [28].

A computer program was developed based on eqns. 2 and 9 to simulate fractograms for specific polystyrene samples with THF and cyclohexane as solvents. Fig. 3 shows the results obtained using data for ordinary and thermal diffusion coefficients given by Schimpf and Giddings [3]. For the three simulations shown, a constant temperature drop and channel thickness were chosen. The flow-rate was adjusted in such a way that for all three fractograms the analysis time was the same. In this way, differences in separation speed are illustrated by means of differences in resolution.

When the fractograms in Fig. 3a and b are compared, the effect of the molecular mass of the polymer fractions can be clearly seen. Higher molecular masses will result in lower λ values and therefore will allow a higher separation speed to be obtained by adjusting the flow-rate of the carrier liquid. Note that the standards in both fractograms have the same relative difference in molecular mass. For the fractograms in Fig. 3b and c the molecular mass of the three standards is the same. The difference in resolution, which is fairly large, is the result of the use of different solvents. For the fractogram in Fig. 3b THF was selected as the solvent, whereas for that in Fig. 3c cyclohexane was chosen. Although the thermal diffusion of polystyrene is much lower in cyclohexane than in THF, the λ values are comparable, because the diffusion coefficients for polystyrene standards are also much lower in cyclohexane than in THF. From the literature a general trend can be observed that high thermal diffusion is accompanied by relatively high ordinary diffusion. Because of the relatively higher diffusion without the loss of retention, the use of THF leads to much better resolution of the PS standards in the same analysis time.

One of the aims of this work was to find the

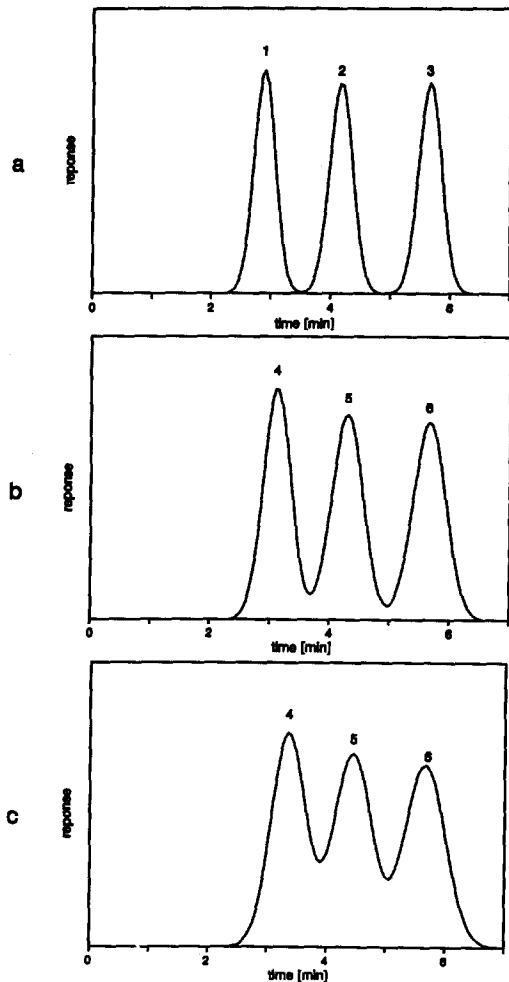


Fig. 3. Simulated ThFFF fractograms for polystyrene in (a, b) THF and (c) cyclohexane. Molecular mass: 1 = 250 000, 2 = 500 000, 3 = 875 000, 4 = 50 000, 5 = 100 000, 6 = 175 000. $w = 76 \mu\text{m}$; $\Delta T = 80^\circ\text{C}$; flow-rate, (a) 0.942 ml/min, (b) 0.4 ml/min and (c) 0.394 ml/min; no polydispersity effects were considered. Values for A , b and D_T as in Fig. 2.

best solvent for the ThFFF analysis of polybutadiene. From eqn. 8 it can be seen that the solvent for which lowest λ values are obtained for a given molecular mass will yield the highest separation speed. However, if for two or more solvents comparable λ values are found, additional measurements have to be made to determine which solvent can best be used. In this case the solvent in which the polymer species has

the highest diffusion coefficient (and highest thermal diffusion coefficient) will give the shortest analysis time.

EXPERIMENTAL

Instrumentation

A T100 thermal polymer fractionator was obtained from FFFractionation (Salt Lake City, UT, USA). A Mylar spacer (thickness $127 \mu\text{m}$) was cut out and clamped between the two chrome-plated copper bars to form the channel. The tip-to-tip length of the channel was 46 cm and the channel breadth was 2 cm. The channel ends were tapered to allow a smooth fluid flow at the channel inlet and outlet. The void volume was 0.98 ml. For the determination of the α/T values a temperature drop of 60°C was used. The cold wall temperature ranged from 30 to 35°C . For some of the fractograms a higher ΔT value of 80°C was used; the accompanying cold wall temperature in this instance was 36°C . In all experiments the solvent flow was stopped for 5 min after injection to allow relaxation. A constant-flow pump (Spectroflow 400; ABI, Ramsey, NJ, USA) was used to deliver the solvents. Prior to use all solvents were filtered by vacuum suction over a $0.5\text{-}\mu\text{m}$ filter (Model FH; Millipore, Bedford, MA, USA). During the experiments the organic solvents were continuously degassed with helium. A small, laboratory-made column packed with silica particles and a pulse damper (Model 812; Tegimenta, Rotkreuz, Switzerland) were used to obtain a reliable solvent flow with minimum pulsation. The injection valve had a loop volume of $20 \mu\text{l}$. Detection was performed with an evaporative light-scattering detector (Model 2A; Varex, Burtonsville, MD, USA). The outlet of the channel was connected to the detector by means of a fused-silica capillary of I.D. $100 \mu\text{m}$ and O.D. $360 \mu\text{m}$ (Polymicro Technologies, Phoenix, AZ, USA). A capillary length of 1 m was chosen to combine a small dead volume (0.008 ml) with a sufficiently large back-pressure (ca. 7 bar at a flow-rate of 0.2 ml/min) to elevate the boiling points of the organic solvents in the ThFFF channel.

Materials

All solvents were of analytical-reagent grade. THF and toluene were obtained from Janssen Chimica (Geel, Belgium), ethylbenzene, cyclohexane and dioxane from Merck (Darmstadt, Germany), benzene from Baker (Deventer, Netherlands) and polybutadiene, polyisoprene and polystyrene standards from Polymer Laboratories (Church Stretton, Shropshire, UK).

Data handling

Data from the fractograms were collected using the FFFractionation data acquisition board in combination with a personal computer. The data were analysed using the manufacturer's analysis software (version 2.0). Lotus 123 and Lotus Freelance Plus (Lotus Development, Cambridge, MA, USA) were used to create the fractograms from the data files. To correct for the temperature dependence of the solvent viscosity and solvent thermal conductivity, a computer program, which has been described in detail previously [23], was used for the conversion of the measured retention ratios into α/T values. This program, together with the computer program for the fractogram simulations, was written using Turbo Pascal 6.0 (Borland International, Scotts Valley, CA, USA). The empirical constants, needed to account for the temperature dependence of the viscosity and thermal conductivity of the various organic solvents, are given in

Table I. Data concerning the temperature dependence of these two parameters were taken from the literature [18,22,29–31].

RESULTS AND DISCUSSION

To test the ThFFF set-up, retention measurements were made for three different polystyrene standards of different molecular mass (68 000, 310 000 and 700 000) in toluene. A temperature drop of 60°C was used and the polymer concentration of the injected samples was 0.2 mg/ml for each standard. Using diffusion data from Schimpf and Giddings [3], a thermal diffusion coefficient of $0.98 \cdot 10^{-7} \text{ cm}^2/\text{s} \cdot \text{K}$ was found for all three standards. This value is in good agreement with other reported measurements.

Next the retention was determined of four polybutadiene standards (120 000, 330 000, 500 000 and 950 000) in six organic solvents. The results are shown in Fig. 4, where the λ values are plotted as a function of $M^{-1/2}$. The linear dependence indicates that the thermal diffusion coefficient is independent of the molecular mass (this follows from eqns. 3 and 12, bearing in mind that $b \approx 0.5$ for most polymer–solvent systems). This is in agreement with the results obtained for other polymer species. However, diffusion measurements have to be made to verify these preliminary conclusions. The highest retention for a given molecular mass was found in toluene and ethylbenzene. In contrast to other

TABLE I

EMPIRICAL CONSTANTS NEEDED TO DESCRIBE THE TEMPERATURE DEPENDENCE OF THE VISCOSITY AND THERMAL CONDUCTIVITY OF THE FIVE GIVEN SOLVENTS

Solvent	a_0	a_1	a_2	a_3 ($\times 10^5$)	κ (293 K) (W/s · K)	b_1 ($\times 10^5$) (W/s · K ²)
Benzene	6445.30	−80.057	0.2936	−26.477	0.1477	−35.00
Cyclohexane	4081.22	−40.278	0.1094	−25.481	0.1209	−25.19
Ethylbenzene	2892.92	−35.176	0.1284	−8.395	0.1321	−24.37
THF	7622.73	−88.933	0.3344	−32.587	0.1398	−19.89
Toluene	3109.76	−45.318	0.1818	−15.078	0.1320	−27.24

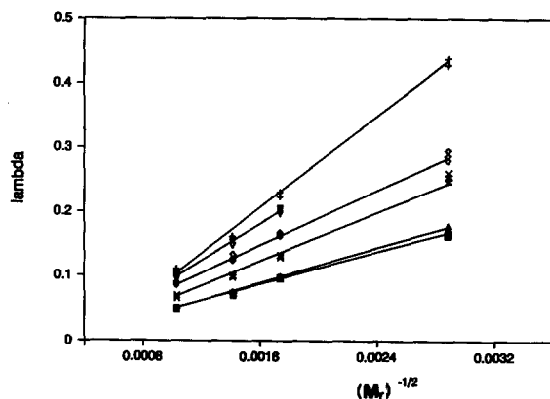


Fig. 4. λ Values for the four PB standards in six organic solvents. $w = 127 \mu\text{m}$; $\Delta T = 60^\circ\text{C}$; $T_c = 32^\circ\text{C}$; flow-rate, 0.2 ml/min; polymer concentration, 0.2 mg/ml. ■ = Toluene; + = THF; ◇ = cyclohexane; △ = ethylbenzene; × = dioxane; ▽ = benzene.

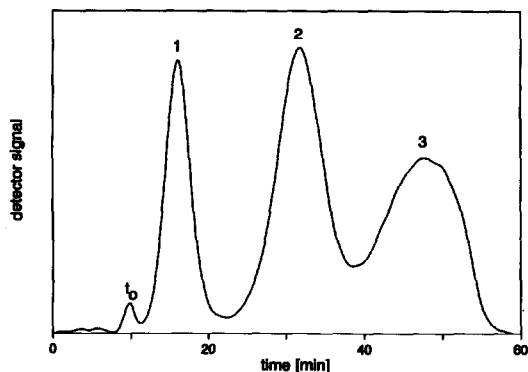


Fig. 5. ThFFF separation of three PB standards in toluene. Molecular mass: 1 = 120 000 ($\mu < 1.03$); 2 = 500 000 ($\mu < 1.03$); 3 = 950 000 ($\mu < 1.03$). $w = 127 \mu\text{m}$; $\Delta T = 60^\circ\text{C}$; $T_c = 32^\circ\text{C}$; flow-rate, 0.1 ml/min; polymer concentration, 0.2 mg/ml. Evaporative light-scattering detection.

polymer species, low retention was found when THF was used as the solvent. The corresponding α/T values are given in Table II. In the determination of the α/T values, the temperature dependence of the solvent viscosity and thermal conductivity was accounted for. The effect of the temperature drop across the solute zone on α/T was neglected and α/T values were directly

assigned to the temperature in the centre of gravity of the solute zones.

The use of ThFFF for the fractionation of polybutadiene is demonstrated in Fig. 5. As was stated earlier, the solvent that gives rise to the highest retention for a certain molecular mass can best be used for the ThFFF analysis. Fig. 6 shows the separation of two PB standards in toluene, ethylbenzene and THF. The flow-rate

TABLE II

α/T VALUES FOR THE PB STANDARDS IN THE DIFFERENT ORGANIC SOLVENTS

For experimental conditions see Fig. 1. Numbers given are mean values of four different measurements; R.S.D. = standard deviation. The temperature in the centre of gravity of the solute zones ranged from 37°C (PB of molecular mass 950 000 in toluene) to 53°C (PB of molecular mass 120 000 in THF). For dioxane no parameters were found describing the temperature dependence of the viscosity and thermal conductivity. The empirical parameters of toluene were taken to calculate the α/T values for this solvent.

Solvent	Molecular mass of PB							
	120 000		330 000		500 000		950 000	
	α/T	R.S.D. (%)	α/T	R.S.D. (%)	α/T	R.S.D. (%)	α/T	R.S.D. (%)
THF	0.0387	0	0.0762	1.5	0.1080	1.3	0.1616	2.2
Benzene	—	—	0.0899	1.9	0.1198	0	0.1730	2.1
Cyclohexane	0.0595	2.7	0.1064	1.5	0.1380	3.4	0.2049	2.4
Dioxane	0.0678	2.1	0.1336	1.3	0.1786	1.5	0.2657	3.1
Toluene	0.1003	1.6	0.1795	1.3	0.2374	0.4	0.3667	0.7
Ethylbenzene	0.1015	1.3	0.1732	1.1	0.2343	1.7	0.3425	1.0

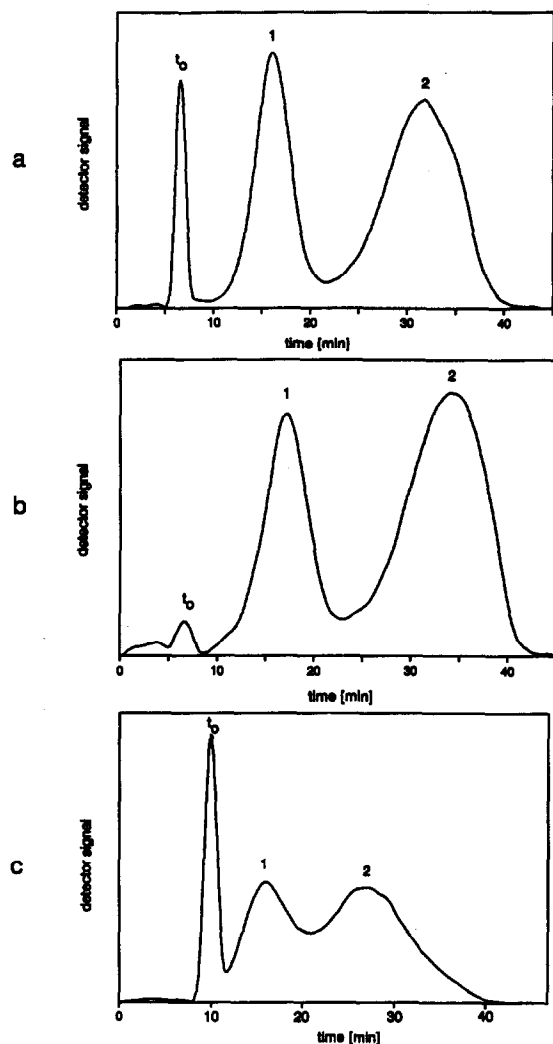


Fig. 6. Separation of two PB standards in (a) toluene, (b) ethylbenzene and (c) THF. Molecular mass: 1 = 330 000 ($\mu < 1.04$); 2 = 950 000 ($\mu < 1.03$). $w = 127 \mu\text{m}$. For THF: $\Delta T = 80^\circ\text{C}$; $T_c = 36^\circ\text{C}$; flow-rate, 0.1 ml/min. For toluene and ethylbenzene: $\Delta T = 60^\circ\text{C}$; $T_c = 31^\circ\text{C}$; flow-rate, 0.15 ml/min. Polymer concentration, 0.3 mg/ml. Evaporative light-scattering detection.

was adjusted in such a way that for all solvents the analysis time was the same. Even though for THF a higher temperature drop was used, it can be seen that the resolution is much smaller than that obtained with the other two solvents. This is caused by the fact that in THF relatively high λ values were found (see Fig. 4). For toluene and ethylbenzene the λ values were about equal for

the different PB standards. As was pointed out in the theoretical section, a large difference in the separation speed of a given polymer species can still exist for solvents for which comparable λ values are found. When for a constant temperature drop and channel thickness the λ values are equal, this only indicates that the ratios of ordinary and thermal diffusion coefficients are the same in both situations. When fractograms a and b in Fig. 6 are compared, it can be seen that the use of toluene leads to slightly better resolution. This indicates that the ordinary and the thermal diffusion coefficient of PB are both higher in toluene than in ethylbenzene. The fact that the difference in resolution is only very small is mainly caused by the large contribution of the polydispersity of the PB standards to the plate height. From the fractograms in Fig. 6 it can be concluded that toluene is the best solvent to use for the ThFFF analysis of polybutadiene. The measurement of the peak width in ThFFF in combination with retention data provides in principle a route to the determination of ordinary diffusion coefficients. Therefore, if truly monodisperse standards (or standards for which the polydispersity is exactly known) could be used, the measurement of the retention ratio and the plate height in ThFFF could yield thermal diffusion coefficients without the need for additional diffusion measurements.

The effect of the temperature drop on retention was studied for PB of molecular mass 330 000 and 950 000 in toluene. The results are given in Fig. 7; the linear relationship between λ and $1/\Delta T$ is in good agreement with eqn. 3. This again indicates that the retention measurements are free from systematic errors caused by the ThFFF set-up.

Schimpf [32] and Caldwell *et al.* [33] stated that for high molecular masses the effect of polymer concentration on retention in ThFFF can be profound. When accurate retention measurements are made for the determination of thermal diffusion coefficients, it is important that the effect of polymer concentration is negligible. With the use of the evaporative light-scattering detector, polymer sample concentrations as low as 0.1 mg/ml can be used. To study the effect of polymer concentration, the retention ratio for

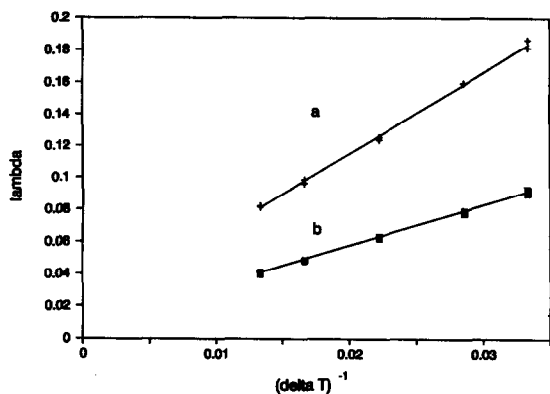


Fig. 7. Effect of ΔT on λ for PB of molecular mass (a) 330 000 and (b) 950 000 in toluene. $w = 127 \mu\text{m}$; $T_c = 26\text{--}32^\circ\text{C}$; flow-rate, 0.2 ml/min; polymer concentration, 0.2 mg/ml.

PB of molecular mass 950 000 in toluene was measured for different sample concentrations; this system was chosen because the lowest λ values were obtained. The polymer concentration at the cold wall was in this instance equal to approximately twenty times the concentration of the injected sample ($\lambda \approx 0.05$). The results, shown in Fig. 8, indicate that significant effects are observed even if the polymer concentration is well below 1 mg/ml. The influence of the polymer concentration can in this instance only be neglected if concentrations of 0.2 mg/ml or lower are used. A systematic error of 10% in the determination of λ was found when the polymer concentration was 1 mg/ml. Because all reten-

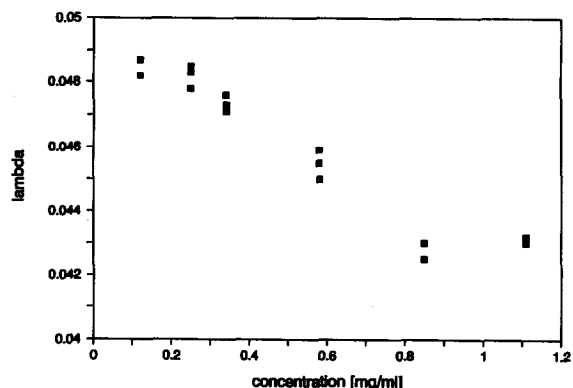


Fig. 8. Effect of polymer concentration on λ for PB of molecular mass 950 000 in toluene. $w = 127 \mu\text{m}$; $\Delta T = 60^\circ\text{C}$; $T_c = 30^\circ\text{C}$; flow-rate, 0.2 ml/min.

tion measurements were made with a polymer concentration of 0.2 mg/ml, it can be concluded that the determined α/T values are virtually free from systematic errors due to concentration effects.

Compared with other polymer fractionation methods such as size-exclusion chromatography [34] and hydrodynamic chromatography (HDC) [35], ThFFF becomes more interesting when polymers of high molecular mass have to be analysed. An additional advantage is that in ThFFF retention is not only determined by the ordinary diffusion coefficient but also by the thermal diffusion coefficient. Because the thermal diffusion coefficient depends on the chemical nature of the polymer, ThFFF can separate polymer species according to both size and chemical characteristics. This unique feature, which was demonstrated for the first time by Gunderson and Giddings [20], makes it possible to perform separations of particle and polymer species that are equal in size but differ in chemical nature.

Fig. 9 shows a packed-column HDC separation of polystyrene, polyisoprene and polybutadiene standards of the same molecular mass in THF. Packed-column HDC is a very efficient

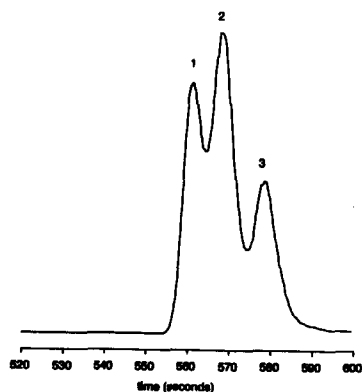


Fig. 9. Packed-column HDC separation of (1) PB of molecular mass 330 000, (2) PI of molecular mass 295 000 and (3) PS of molecular mass 336 000 in THF (courtesy of Mr. G. Stegeman, Laboratory of Analytical Chemistry, University of Amsterdam). (1) $\mu < 1.04$; (2) $\mu < 1.04$; (3) $\mu < 1.05$. Column, $150 \times 4.6 \text{ mm I.D.}$; packing, $1.5\text{-}\mu\text{m}$ non-porous silica; flow-rate, 0.1 ml/min; pressure, 31 bar; polymer concentration, 0.11–0.15 mg/ml. Evaporative light-scattering detection.

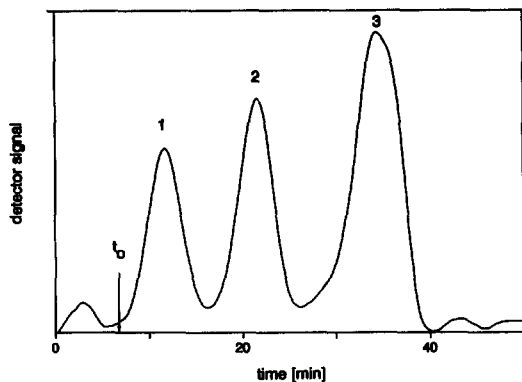


Fig. 10. ThFFF separation of (1) PB of molecular mass 330 000, (2) PI of molecular mass 295 000 and (3) PS of molecular mass 336 000 in THF. $w = 127 \mu\text{m}$; $\Delta T = 80^\circ\text{C}$; $T_c = 28^\circ\text{C}$; flow-rate, 0.15 ml/min; polymer concentration, 0.1–0.3 mg/ml. Evaporative light-scattering detection. For polydispersity of the standards, see Fig. 9.

polymer fractionation method. For sufficiently high molecular masses, the plate height, which is about $2.1 \mu\text{m}$ for a column packed with $1.5\text{-}\mu\text{m}$ particles, is independent of the velocity of the carrier liquid [36]. This indicates that the resolution for a given column length is constant, regardless of the mobile phase velocity. Because the size difference between the three standards is only very small, no baseline separation was obtained using this technique. However, because these three standards possess different thermal diffusion coefficients in THF, a baseline separation was easily obtained using ThFFF, as illustrated in Fig. 10. This ThFFF separation clearly demonstrates how the thermal diffusion effect can be employed to separate polymer species according to chemical characteristics. Note that again the highest thermal diffusion coefficient is accompanied by the highest ordinary diffusion coefficient (in HDC the largest polymers elute first).

CONCLUSIONS

Thermal field flow fractionation can be used effectively for the fractionation of polybutadiene samples. For a given set of experimental param-

eters and molecular mass, the highest α/T values were found when toluene was used as the solvent. For optimum fractionation conditions this solvent should be used for the ThFFF analysis of polybutadiene. Retention measurements of standards of different molecular mass indicate size independence of the thermal diffusion coefficient for polybutadiene in all six organic solvents. However, the effect of thermal diffusion seems to be dependent on the chemical nature of the solvent. Accurate diffusion measurements are currently being made to verify these preliminary conclusions. When samples of high molecular mass are used, special attention should be given to the polymer concentration. For PB of molecular mass 950 000 in toluene ($\lambda \approx 0.05$), a significant increase in retention was found for samples with a polymer concentration of 0.3 mg/ml or higher. The use in this instance of a polymer concentration of 1 mg/ml led to a systematic error of 10% in the determination of the corresponding α/T value.

ThFFF offers unique separation possibilities because retention is determined by both the size and the thermal diffusion coefficient of the polymer in solution. Because the thermal diffusion coefficient depends on the chemical nature of the polymer, ThFFF can be used for the separation of polymers that are identical in size but possess different chemical properties. This feature, which is unique to ThFFF, has been demonstrated with the separation of polybutadiene, polyisoprene and a polystyrene standards of the same molecular mass in THF. This and many other studies demonstrate that high thermal diffusion is often accompanied by high ordinary diffusion. Therefore, it may be possible to use the diffusion coefficient for a given molecular mass as an indicator of the magnitude of the thermal diffusion effect.

SYMBOLS

α	Soret coefficient	
C	Concentration	mol/m^3
C_0	Concentration at the cold wall	mol/m^3
D	Diffusion coefficient	m^2/s

D_T	Thermal diffusion coefficient	$\text{m}^2/\text{s} \cdot \text{K}$
H	Plate height	m
η	Solvent viscosity	Pa s
κ	Thermal conductivity	$\text{J}/\text{m} \cdot \text{s} \cdot \text{K}$
λ	Dimensionless mean layer thickness	
l	Mean layer thickness	m
M	Molecular mass	g/mol
N	Number of plates	
R	Retention ratio	
R_s	Resolution	
S	Selectivity	
T	Temperature	K
T_c	Cold wall temperature	K
ΔT	Temperature drop across channel thickness	K
t_0	Unretained time	s
t_p	Time needed to generate one plate	s
t_a	Analysis time	s
μ	Polydispersity	
v	Linear fluid velocity	m/s
$\langle v \rangle$	Mean linear fluid velocity	m/s
V_r	Retention volume	m^3
w	Channel thickness	m

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