ELSEVIER

PII: S0032-3861(97)00207-3

Polymer Vol. 38 No. 26, pp. 6273–6280, 1997

0032-3861/97/$17.00+0.00

Determination and comparison of molar mass distributions of substituted polystyrenes and block copolymers by using thermal field-flow fractionation, size exclusion chromatography and light scattering

R. Dammert[a],*, M. Jussila[b], P. Vastamäki[b], M.-L. Riekkola[b] and F. Sundholm[a]
[a]Laboratory of Polymer Chemistry, Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 Helsinki, Finland
[b]Laboratory of Analytical Chemistry, Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 Helsinki, Finland
(Received 4 December 1995; revised 11 June 1996)

Anionic polymerisations of *p*-methoxystyrene, *p*-methylstyrene, *p*-chlorostyrene and *p*-cyanostyrene were carried out in tetrahydrofuran (THF) and methylcyclohexane. The block copolymers poly(styrene-*b*-*p*-methoxystyrene-*b*-styrene), poly(styrene-*b*-*p*-methylstyrene-*b*-styrene) and poly(styrene-*b*-*p*-cyanostyrene) were also polymerised by using THF as solvent. The initiators included *n*-butyllithium (*n*-BuLi) and sodium naphthalenide. The use of both *n*-BuLi and sodium naphthalenide usually produced higher values of $\bar{M}_n$ than were calculated. In the former case this could be explained by the lower reactivity of the initiator, which has been found to aggregate in THF. The molar masses were determined by thermal field-flow fractionation (ThFFF), size exclusion chromatography (s.e.c.) and light scattering (LS). ThFFF and the s.e.c. were used for determining the molar mass distributions. The agreement between the three methods was satisfactory. © 1997 Elsevier Science Ltd.

(Keywords: synthesis; block copolymers; control of molar masses)

INTRODUCTION

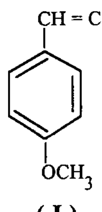
The anionic polymerisation of styrene-based monomers has been studied very extensively. Polymerisation conditions, such as the solvent, initiator and temperature, have an influence on the properties of the polymers. The interesting properties are, for example, tacticity, molar mass and molar mass distribution. These properties have an effect on the crystallinity and rheology of the polymer. Anionic polymerisation is an excellent method to control the molar mass of the synthesised polymer. When a suitable initiator is chosen and the polymerisation conditions (absence of moisture, oxygen and other impurities) meet the requirements of anionic polymerisation, the resulting polymer has a predictable molar mass and a narrow molar mass distribution. These two properties are affected differently by various kinds of anionic initiator; in some cases the molar mass distribution is a little broader than in an ideal case of anionic polymerisation.

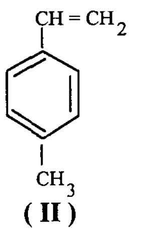
There are several methods available for the determination of molar mass distributions. Common methods are size exclusion chromatography (s.e.c.) and light scattering (LS), but also new methods such as thermal field-flow fractionation (ThFFF) have also been developed[1]. Because the separation in ThFFF and s.e.c. is based on different physical phenomena, it is interesting to compare these methods especially in the study of block copolymers. ThFFF is a versatile method for polymer analysis has many advantages like high selectivity, adjustable retention, programmability, low shear, etc.[2]. However, the heterogeneous chemical composition of copolymers may decrease the accuracy of ThFFF, if calibration is made by using homopolymer standards only[3]. On the other hand, the accuracy of s.e.c. is affected by the dissimilarity of the samples and standards as well. Light scattering, in turn, does not require calibration, but accurate refractive index increments and careful sample preparation are required in order to obtain reliable results. All the three methods mentioned above have their own specific advantages and shortcomings.

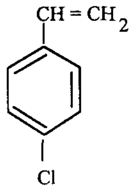
The purpose of this study was to control the molar mass of substituted polystyrenes and block copolymers in anionic polymerisation, and to determine and compare the molar mass distributions obtained by use of three different methods. The control of molar masses was performed by varying the solvents and the initiators in the synthesis. *p*-Methoxystyrene (**I**), *p*-methylstyrene (**II**), *p*-chlorostyrene (**III**) and *p*-cyanostyrene (**IV**) were polymerised in tetrahydrofuran or methylcyclohexane with *n*-butyllithium and sodium naphthalenide as initiators. The block copolymers poly(styrene-*b*-*p*-methoxystyrene-*b*-styrene), poly(styrene-*b*-*p*-methylstyrene-*b*-styrene) and poly(styrene-*b*-*p*-cyanostyrene) were also prepared by using tetrahydrofuran (THF) as solvent. The molar mass distributions were determined by means of s.e.c. and ThFFF, and the absolute molar masses were determined by LS.

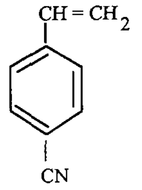
---

* To whom correspondence should be addressed


(I)


(II)


(III)


(IV)

THEORY OF FIELD-FLOW FRACTIONATION (FFF)

Since s.e.c. and LS are familiar methods to the polymer chemist, only the principle of ThFFF is presented briefly here. Field-flow fractionation (FFF) is a family of analysis techniques covering a wide range of molecular size from a few thousand Daltons of molar mass to a particle size of *ca.* 100 μm. Many types of external field can be utilised in FFF including gravitational, centrifugal, electrical and magnetic fields. Also, a thermal gradient and another perpendicular flow can affect the retention in an FFF channel. For soluble polymers thermal and flow field-flow fractionation are the most useful techniques. Thermal FFF (ThFFF) is most suitable for polymers that are soluble in organic solvents, while flow FFF (FlFFF) is suitable for polymers that are soluble in both water and organic solvents.

Separation in FFF takes place in a laminar flow of fluid through a thin, ribbon-like channel (*Figure 1*). The flow velocity is at highest in the middle of the channel and slows down by frictional drag closer to the wall, obeying a parabolic function. An external force field, applied perpendicular to the flow, conveys the sample molecules towards the wall of the channel. As a consequence, an exponential concentration distribution of sample molecules is built up against the wall. The average distance between a sample molecule (i.e. the mean layer thickness, l) and the wall depends on the force exerted by the field and the diffusion coefficient of the sample molecule. Owing to the opposing effects of the field and diffusion of the analytes, large molecules with slower diffusion rate have smaller mean layer thickness (l) than the faster diffusing, smaller molecules. The velocity by which the analytes are swept down the channel is determined by the layer thickness according to the parabolic velocity profile. Hence smaller molecules with higher layer thickness elute out from the channel before larger ones. If the radius of the sample particles is of the same magnitude as their layer thickness, a steric mechanism takes over the control of retention. Soluble polymers usually elute obeying the theory of normal mode of FFF, although with ultrahigh-molar-mass polymers steric effects have been observed[4].

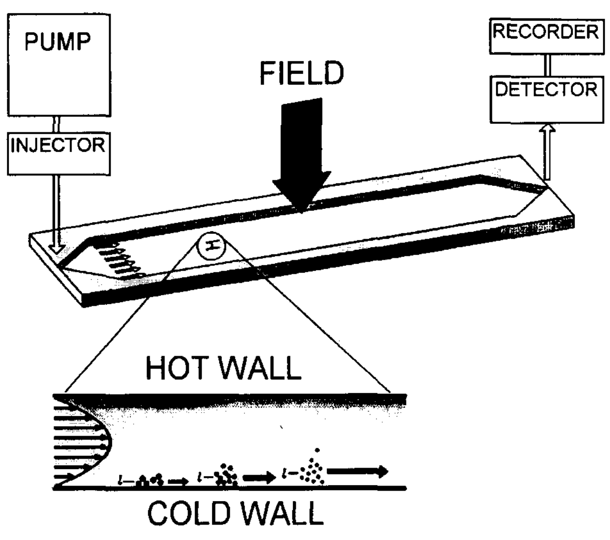


Figure 1 Principle of thermal field-flow fractionation

Retention in FFF is a function of the mean layer thickness l of the solute layer compressed against the accumulation wall of the channel. If the retention factor λ is defined as $\lambda = l/w$, where w is the thickness of the channel, the retention ratio can be expressed by[5]

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

If $\lambda < 0.1$, equation (1) can be approximated by

$$R \approx 6\lambda \tag{2}$$

The retention factor, λ, in ThFFF depends on the thermal diffusion factor, α_T, of the solute, the thermal gradient inside the channel, dT/dx, and absolute temperature, T, according to the following equation[6]

$$\lambda = \left(\frac{w\alpha_T}{T}\frac{dT}{dx}\right)^{-1} \tag{3}$$

The thermal diffusion factor, in turn, is proportional to the ratio of the thermal diffusion coefficient, D_T, the ordinary diffusion coefficient, D, and the absolute temperature according to

$$\alpha_T = \frac{D_T T}{D} \tag{4}$$

Since the diffusion coefficient of a polymer can be approximated by

$$D \approx AM^{-b} \tag{5}$$

where A and b are polymer-specific coefficients, equations (2), (3), () and (5) and the definition of retention ratio ($R = t_0/t_R$) can be combined to obtain an expression for retention times *versus* molar mass:

$$t_R \approx \frac{t_0 D_T}{6A}\Delta T M^b \tag{6}$$

where $\Delta T = w \times dT/dx$ is the temperature difference between the channel walls. equation (6) expressed in logarithmic form as

$$\ln t_R \approx \ln\left(\frac{t_0 D_T \Delta T}{6A}\right) + b \ln M \tag{7}$$

Considering equation (7), it can be seen that the calibration plot ($\ln t_R$ *versus* $\ln M$) is a linear function if the run parameters (ΔT and t_0) are kept constant. The high slope of the calibration plot (b~0.6) reflects the good selectivity of ThFFF, which is approximately five times higher than that of s.e.c.[7]. The performance of s.e.c. and ThFFF has been compared in several publications[8,9].

The theoretical basis of thermal diffusion in the liquid phase is not very well known. It has been shown that D_T

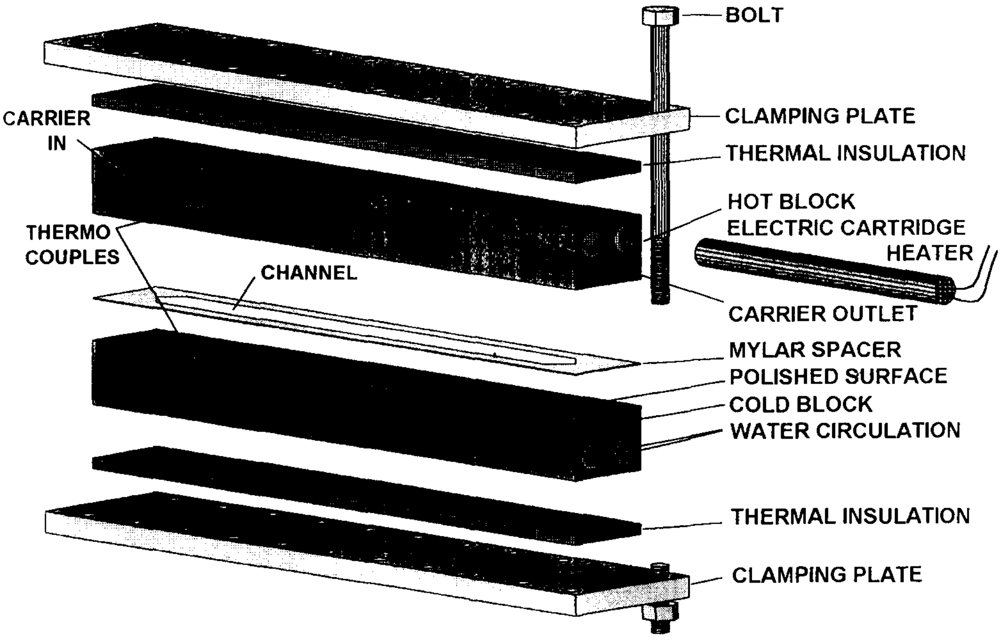


Figure 2 Construction of a thermal FFF channel

is almost independent of molar mass but strongly dependent on the chemical composition of the polymer and solvent. Thermal diffusion in aqueous solution is usually weak, which limits the use of ThFFF for the analysis of water-soluble polymers.

Only limited data on thermal diffusion coefficients are available and hence calibration is often necessary in ThFFF work. Usually, narrow molar mass standards are used for calibration. Universal calibration is possible only if the thermal diffusion coefficients of samples and standards are known, otherwise the standards should be of the same polymer as the samples. This is, unfortunately, often impossible, because of the limited availability of standards.

Copolymer analysis by means of ThFFF is often complicated by heterogeneous chemical composition of the copolymers. The thermal diffusion coefficient of a random copolymer is dependent on the weight fraction of D_T values of its constituent units. The usefulness of homopolymer calibration in copolymer studies relies on the similarity of the D values of the sample and standard polymers. On the other hand, a block copolymer is usually able to form a micelle-like structure in solution by turning the more soluble block A outwards. If block A interacts predominantly with the solvent, block B being closed inside the micelle[10], this may either increase or decrease the error caused by differences in the thermal diffusion coefficients. If block A interacting mostly with solvent has a similar D_T value as the standard polymer used in calibration, inaccuracy in the results could be diminished.

EXPERIMENTAL

Materials

Styrene (Merck-Schuchardt; > 99%), *p*-methoxystyrene (Aldrich; > 97%), *p*-methylstyrene (Aldrich; > 97%) and *p*-chlorostyrene (Aldrich; > 97%) were dried over CaH_2 and purified by fractional distillation *in vacuo*. The monomers were stored in ampoules sealed with Young's Teflon stopcocks at − 25°C. *p*-Cyanostyrene was prepared by one-pot reaction of 4-vinylbenzaldehyde with the hydroxylammonium chloride/pyridine/toluene system followed by azeotropic separation of water in 74% yield[11–13].

THF (Prolabo, France) was dried and purified by refluxing and distilling from sodium wire onto CaH_2. It was repeatedly refluxed with CaH_2 and distilled into a flash where sodium and bifenylene were added. THF was distilled into the dry ampoules sealed with Young's Teflon stopcocks[14]. Methylcyclohexane (Merck-Schuchardt; > 98%) was purified by passing it through activated basic Al_2O_3. The solvent was refluxed and distilled over sodium wire into dry ampoules[15]. *n*-Butyllithium (1.6 M in hexane; Aldrich, Steinheim, Germany) was used as received. Sodium naphthalenide was prepared as described previously[16].

Methods

The ThFFF instrument used in this study consisted of a syringe pump (model SFC 500; Instrument Specialties Inc., Lincoln, NE, USA), an injection valve (C6W; Valco Instrument Co., Inc., Houston, TX, USA), a ThFFF channel made in-house and an ultraviolet (u.v.) detector (SP8450; Spectra Physics Inc., USA) (*Figure 2*). The shape of the channel was cut into a 100 μm thick Mylar sheet, which was then clamped between two copper bars, the upper one heated by four electrical cartridge heaters (4 × 1600 W) and the lower one cooled by water circulation. The surfaces of the bars were nickel plated and highly polished. The dimensions of the channel were 45 cm (length) by 2 cm (breadth) by 100 μm (thickness) and the volume was 0.7 ml. An electrically actuated six-port valve (C6W; Valco Instrument Co., Inc.) was used for switching the flow to bypass the channel during relaxation. To avoid boiling of the carrier, the channel was pressurised by connecting the outlet of the detector to a vessel which was pressurised by gas up to 690 kPa (100 psi).

The temperature difference across the channel was measured by thermocouples mounted in the wells drilled very close to the channel surface. A micro computer (M24; Ing. C. Olivetti & C. S.p.A., Italy) controlled the bypass valve actuator and the heating power by means of a solid-state relay. The same computer was also used to acquire data from the detector and for simple data handling.

Table 1 Reliability of ThFFF. $\bar{M}_n$, $\bar{M}_w$ and polydispersities of PMeOS2 and KPM10 and their standard deviations (**1**). Backcalculated $\bar{M}_n$ and $\bar{M}_w$ of one standard in the calibration series compared with corresponding nominal values (**2**). Long-term stability represented as molar mass averages and RS values of two samples (PS6 = home-made polystyrene sample). Calculations are based on 10 different calibrations carried out within 21 days (**3**)

Sample	Number of runs	$\bar{M}_n$ (g/mol)	RSD (%)	$\bar{M}_w$ (g/mol)	RSD (%)	PDI	RSD (%)
PMeOS1	4	225 000	5.6	277 000	47	1.23	0.9
KPM10	6	116 000	10.5	147 000	10.4	1.27	13.4

Table 2

	Measured value	RSD (%)	Nominal value	Difference (%)
$\bar{M}_n$ g/mol	19 400	3.70	19 750	1.77
$\bar{M}_w$ g/mol	20 900	4.20	19 850	5.29
PDI	1.07	0.70	1.01	6.34

Table 3

Sample		Measured value	RSD (%)	Nominal value	Difference (%)
PS19800	$\bar{M}_n$ g/mol	20 000	8.00	19 750	1.27
	$\bar{M}_w$ g/mol	21 700	8.10	19 850	9.32
	PDI	1.07	0.30	1.01	6.04
PS6	$\bar{M}_n$ g/mol	44 000	8.10	—	—
	$\bar{M}_w$ g/mol	20 900	4.20	—	—
	PDI	1.07	0.70	—	—

The solvent used as carrier was HPLC-grade tetrahydrofuran (Merck, Darmstadt, Germany). Polystyrene standards were delivered by Waters Associates Inc., MA, USA. The injection volume was 10 μl and the concentration of the sample solution was in the range 0.05–0.1% (w/w). The detection was performed at 258 nm.

A ThFFF run consisted of three steps: injection, relaxation and run. After the sample had been injected in the FFF channel the carrier flow was kept on until the sample zone was carried to the beginning of the channel. Because the analyte molecules at this stage are uniformly distributed over the thickness of the channel, a special relaxation period was used to give sample molecules time to reach their equilibrium locations. During this relaxation the carrier flow was stopped (stop-flow relaxation) and the field was kept on. The relaxation time of 1 min was usually adequate. Finally, the carrier flow was turned on again and the sample was eluted out from the channel in a chromatographic manner. To avoid errors caused by inaccuracy of the temperature control and possible changes occurring inside the channel, calibration was carried out every day and every time the temperature gradient was changed.

S.e.c. was performed at 40°C with toluene (HPLC-grade; Merck, Darmstadt, Germany) (homopolymers and KPM10) and at 25°C with THF (HPLC-grade; Merck) (KPM1-9, KM6, KM10-11) as solvents with Shodex GPCA-80M (Showa Denko, K.K., Japan) and three GMH$_{XL}$-HT (TosoHaas, PA, USA) columns, respectively. When toluene was used as solvent the flow rate was 1.0 ml min^{-1} and the detector was a refractive index (RI) detector (ERC-7515B; ERMA CR. Inc). For THF the flow rate was 0.7 ml min^{-1} with a u.v. detector (UV-2; Pharmacia Ab., Sweden). The solvent was delivered by means of an HPLC pump (Waters 510; Millipore Corp., MA, USA). In both cases the injection volume was 20 μl and the concentration of sample 3.0 mg ml^{-1}. The data were analysed with a Varian DS

Table 4 $\bar{M}_n$, $\bar{M}_w$ and polydispersities of the samples obtained by using ThFFF, s.e.c. and LS. KPM1-KPM6 = poly(styrene-b-*p*methoxystyrene-b-styrene); KPM7-KPM10, KM6 = poly(styrene-*b*-*p*-methylstyrene-*b*-styrene); KM10, KM11 = poly(styrene-*b*-*p*-cyanostyrene); PMeOS1, PMeOS2 = poly(*p*-methoxystyrene); PMeS1, PMeS2, PMeSB1 = poly(*p*-methylstyrene); PClS1, PClS2 = poly(*p*-chlorostyrene)

Sample	M_{Theory}	$\bar{M}_n$ (g/mol)		$\bar{M}_w$ (g/mol)			*PDI*	
		SEC	ThFFF	SEC	ThFFF	LS	SEC	ThFFF
KPM1	5 800	102 000	102 600	137 300	133 200	180 000	1.35	1.3
KPM2	4 000	266 964	238 400	388 084	369 000	502 000	1.45	1.55
KPM3	2 000	87 333	98 600	123 906	115 699	18 650	1.42	1.17
KPM4	3000	47 619	40 800	73 217	61 100	75 100	1.54	1.5
KPM5	5 000	16 073	17 000	24 819	21 000	27 100	1.54	1.23
KPM6	20 000	155 572	110 000	246 011	275 000	26 100	1.58	2.5
KPM7	40 000	51 671	48 400	102 563	80 500	80 350	1.98	1.66
KPM8	10 000	24 373	20 800	36 418	29 200	35 550	1.5	1.4
KPM9	30 000	95 507	86 800	122 655	105 000	111 500	1.28	1.21
KPM10	22 000	85 889	93 300	117 675	117 500	179 000	1.37	1.26
KM6	11 100	46 664	55 300	77 285	67 500	218 000	1.66	1.22
KM10	15 800	14 471	19 900	36 124	28 500	28 500	2.49	1.43
KM11	15 300	59 826	70 900	118 284	114 900		1.97	1.62
PMeOS1	5 600	20 237	23 600	29 251	28 800	47 100	1.46	1.22
PMeOS2	7 000	51 731	72 200	98 620	101 000		1.91	1.93
PMeS1	10 000	291 813	193 500	481 364	332 500	460 000	1.65	1.72
PMeS2	41 400	44 517	41 600	66 505	50 100	70 200	1.49	1.2
PMeSB1	12 700	4 084	2 400	4 982	3 500	10 800	1.22	1.43
PClS1	6 100	33 722	71 800	62 755	104 500	125 000	1.86	1.46
PClS2	7 000	104 398	88 600	145 000	472 400	470 000	1.74	1.65

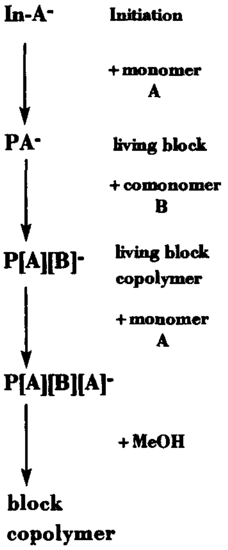
Table 5 The refractive index increments of homo- and block copolymers measured in toluene if no other solvent mentioned. KPM1-KPM6 = poly(-styrene-*b*-*p*-methoxystyrene-*b*-styrene), KPM7-KPM10, KM6 = poly(styrene-*b*-*p*-methylstyrene-*b*-styrene), KM10-KM11 = poly(styrene-*b*-*p*-cyanostyrene), PMeOS = poly(*p*-methoxystyrene), PMeS = poly(*p*-methylstyrene), PClS = poly(*p*-chlorostyrene)

Sample	d*n*/d*c*
KPM1	0.1028
KPM2	0.1028
KPM3	0.1071
KPM4	0.1028
KPM5	0.1003
KPM6	0.0934
KPM7	0.1025
KPM8	0.0955
KPM9	0.0959
KPM10	0.0878
KM6	0.1847
KM10	0.1847
KM11	0.1847
PS2	0.0985
PS6	0.1028
PSA1	0.1006
PSB1	0.0835
PMeOS1	0.0967
PMeS1	0.0967[a] 0.1326[b]
PMeS2	0.0980[a] 0.1570[b]
PMeSB1	0.0980[a] 0.1538[b]
PClS1	0.0889
PClS2	0.0844
PCNS	0.2233[c]

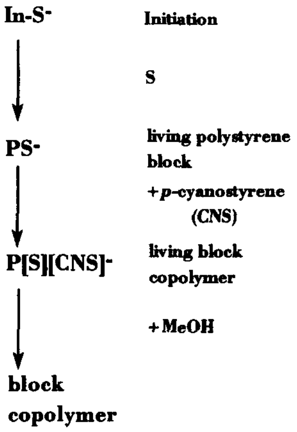
[a] In toluene
[b] In THF
[c] In DMF

Table 6 The refractive indices of the homopolymers[20]

Polymer	*n*
Polystyrene	1.591
Poly(2-methylstyrene)	1.5874
Poly(*p*-methoxystyrene)	1.5967
Poly(2-chlorostyrene)	1.6098



Scheme 1



Scheme 2

651 data station. The calibration was performed by using narrowly distributed polystyrene standards.

Light scattering measurements were performed at 25°C with a Brookhaven instrument (Brookhaven Instruments Corp., NY, USA) equipped with a 2030AT correlator and He–Ne (60 mW) laser. The wavelength was 632.8 nm. The refractive index increments were measured with an Optilab 903 (Wyatt Technology Corp., CA, USA) refractometer. The solvents used were toluene, chloroform [for poly(*p*-methylstyrene)s], *N*,*N*-dimethylformamide (DMF) [for poly(*p*-cyanostyrene)s] and THF [for poly(styrene-*b*-*p*-cyanostyrene)s].

Polymerisation

Polymerisations were carried out under high vacuum at −78°C in THF and at room temperature in methylcyclohexane in the usual way. *n*-BuLi and sodium naphthalenide were used as initiators and methanol was the terminator. The living nature of the polymerisations was observed as a typical orange/red colour in the reaction mixture.

For the synthesis of the ABA-type block copolymers, the first blocks were prepared from comonomers A and the initiator with good stirring in THF. After 10–30 min the second comonomer, B, was added; then, again after 10–30 min, the rest of the first comonomer, A, was added. The polymerisations were terminated by methanol (*Scheme 1*).

Poly(styrene-*b*-*p*-cyanostyrene)s are AB-type block copolymers because of the low nucleophilicity of the living poly(*p*-cyanostyrene) (*Scheme 2*)[17].

The polymers were precipitated into cold methanol, filtered off and dissolved in THF or DMF [poly(*p*-cyanostyrene)s]. This process was repeated two or three times and the resulting white polymers were dried *in vacuo*.

RESULTS AND DISCUSSION

The repeatabilities of two different FFF runs are listed in *Table 1*. The calibration accuracy was estimated by calculating the molar mass averages of one individual standard in the standard series used for calibration. The standard deviations, calculated and nominal molar mass averages are in *Table 2*. The long-term stability of the system was estimated by calculating molar mass averages of one single run using 10 different calibrations carried out during 21 days (*Table 3*). Since the relative standard deviations (RSDs) were usually less than 10%, the repeatability and stability of ThFFF can be considered to

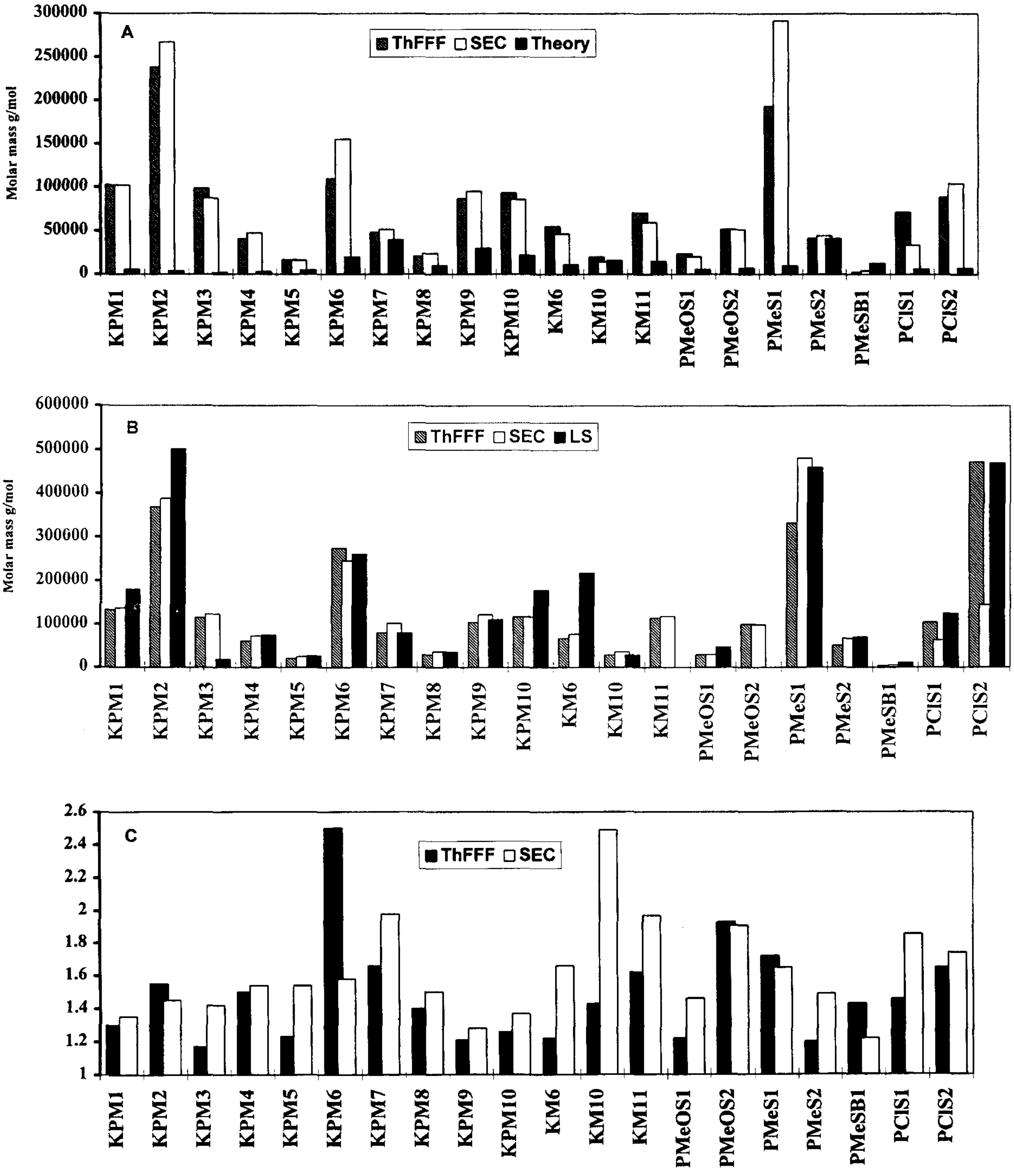


Figure 3 $\bar{M}_n$ (A) and $\bar{M}_w$ (B) and polydispersities (C) obtained by using ThFFF and s.e.c. Also, the calculated values for the synthesis (A) and the light scattering results (B) are included

be satisfactory. Also, the backcalculated molar mass averages correlated quite well with the nominal values given for the standard. In s.e.c. the RSD of the retention times was less than 5%. The difference between the calculated and nominal molar mass average values of the standards was usually less than 5% as well.

The molar mass average and polydispersities obtained with ThFFF, s.e.c. and LS techniques are collected in *Table 4*. The same data are graphically illustrated in *Figure 3*. Only minor differences can be found in the results obtained by ThFFF and s.e.c., but the LS results of some samples deviate markedly. The refractive index increments used in LS measurements are listed in *Table 5*. It can be seen that there are only minor fluctuations between the d*n*/d*c* values of different homopolymers. Therefore the exceptionally high LS results may be caused by impurities even though the samples were carefully filtered before the measurements. Although the distributions of the samples were usually far from Gaussian, only two samples (KPM3 and KPM6) showed a clear bimodal distribution. This bimodality was found both by ThFFF and s.e.c. and its effect can also be seen in the polydispersity values of these samples. The poor solubility of the chlorinated polystyrene samples PClS1 and PClS2 obviously leads to the disagreement of their results.

Both the *n*-BuLi and the sodium naphthalenide initiated experiments gave in most cases higher $\bar{M}_n$ values than were calculated. It is known that *n*-BuLi forms aggregates,

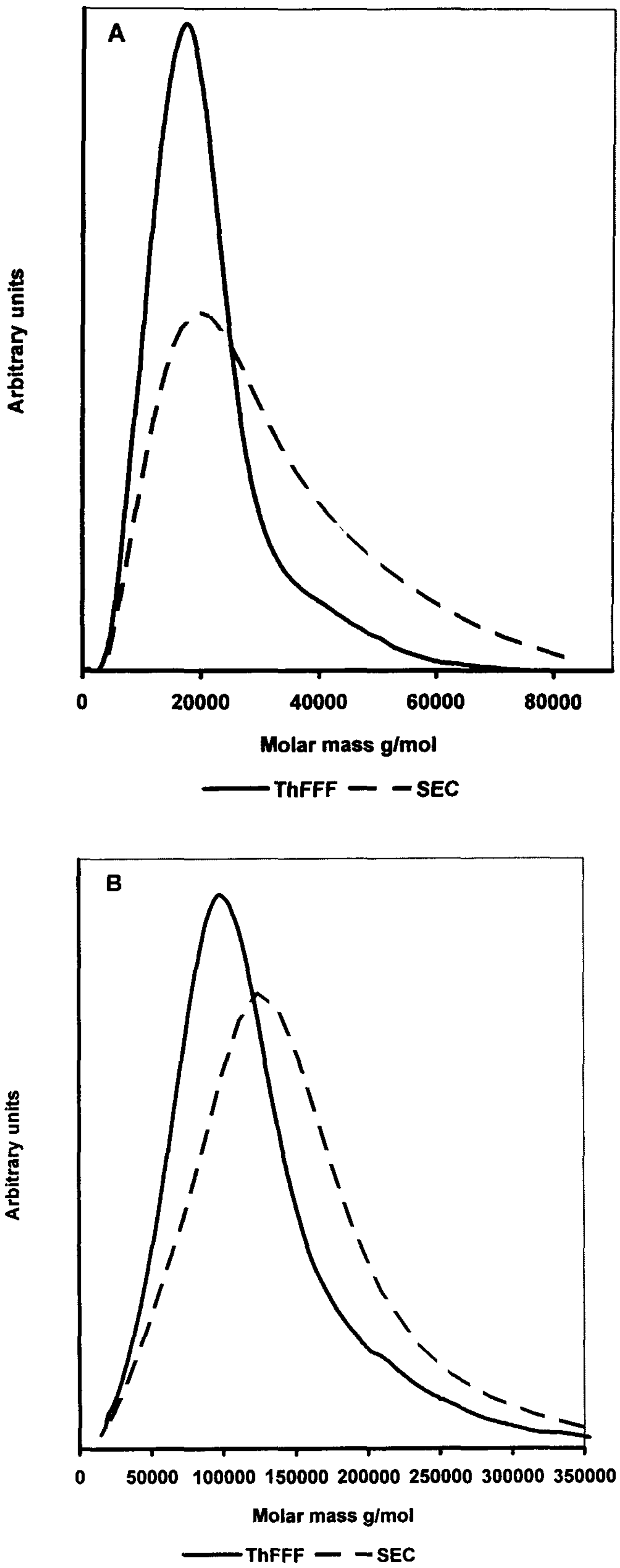


Figure 4 Comparision of the molar mass distributions acquired by using both ThFFF and s.e.c. The samples were KPM5 (A) and KPM10 (B)

usually dimers and tetramers, in THF. This could explain some of the lower reactivity. *n*-BuLi could be replaced with *sec*- or *t*-BuLi as initiators of anionic polymerisation of styrenes. When *sec*- or *t*-BuLi was used the molar masses are closer to the calculated values and the molar mass distributions are narrower. It has been found that those two isomers of BuLi are a monomer/dimer and a monomer, respectively[18,19].

Although the molar mass averages by ThFFF and s.e.c. seem to agree quite well, the shapes of the distributions were usually different (*Figure 4*). Owing to the high selectivity of ThFFF, the fractograms often had a long tail. A long tail of the peak made baseline definition difficult and could lead to the partial loss of the tail in the baseline. The omitted part of the distribution would, however, have quite a strong effect on the calculated molar mass averages. This may partly explain the somewhat lower molar mass averages (especially $\bar{M}_w$) and polydispersities produced by ThFFF. Also, the moderate efficiency of the columns slightly increased the polydispersities obtained by s.e.c. The accuracy should be unaffected by the differences in the RI detector response for the copolymers since the refractive index values of the corresponding homopolymers are very similar (*Table 6*). The u.v. responses of the homopolymers at 258 nm were quite similar as well. The distributions of the samples were usually far from Gaussian, but only two samples, KPM3 and KPM6, were clearly bimodal.

Because the temperature control system of the FFF instrument could precisely reproduce a specific temperature gradient, but was unable to accurately measure the magnitude of the gradient, isothermal operation was chosen. The use of programmed field FFF might have produced less tailing peaks, but for evaluation of the molar mass distribution from a programmed run, the accurate temperature gradient during the temperature programme would have to be known.

The fairly good agreement of ThFFF and s.e.c. results indicates that possible differences in the thermal diffusion coefficients between samples and standards had no significant effect on the results.

ACKNOWLEDGEMENTS

R. Dammert and M. Jussila thank Neste Ltd. Foundation for financial support. The authors are indebted to E. Aitola for his technical assistance in course of the s.e.c. analysis and to K. Muje for her help in the polymerisations of poly(*p*-cyanostyrene)s.

REFERENCES

1. Thompson, G. H., Myers, M. N. and Giddings, J. C., *Sep. Sci.*, 1996, **2**, 797.
2. Myers, M. N., Chen, P. and Giddings, J.C., Polymer separation and molecular-weight distribution by thermal field-flow fractionation. In *Chromatography of Polymers: Characterization by SEC and FFF*, ed. T. Provder. ACS Symp. Ser. No. 521, American Chemical Society, Washington, DC, 1993.
3. Schimpf, M. E., Wheeler, L. M. and Romeo, P. F., Copolymer retention in thermal field-flow fractionation. In *Chromatography of Polymers: Characterization by SEC and FFF*, ed. T. Provder. ACS Symp. Ser. No. 521, American Chemical Society, Washington, DC, 1993.
4. Giddings, J. C., Li, S., Williams, P. S. and Schimpf, M. E., *Makcromol. Chem., Rapid Commun.*, 1988, **9**, 817.
5. Hovingh, M. E., Thompson, G. H. and Giddings, J. C., *Anal. Chem.*, 1970, **42**, 195.
6. Myers, M. N., Caldwell, K. D. and Giddings, J. C., *Sep. Sci.*, 1974, **9**, 47.
7. Giddings, J. C., *Pure Appl. Chem.*, 1979, **51**, 1459–1471.
8. Giddings, J. C., Yoon, Y. H. and Myers, M. N., *Anal. Chem.*, 1975, **47**, 126.
9. Gundersson, J. J. and Giddings, J. C., *Macromolecules*, 1986, **19**, 2618.

10. Schimpf, M. E. and Giddings, J. C., *J. Polym. Sci., Polym. Phys. Edn*, 1990, **28**, 2673.
11. Ishizone, T., Hirao, A. and Nakahama, S., *Macromolecules*, 1991, **24**, 625.
12. Saednya, A., *Synthesis*, 1982, 190.
13. Hirao, A., Ishino, Y. and Nakahama, S., *Makromol. Chem.*, 1964, **187**, 141.
14. Urwin, J. R. and Stearne, J. M., *Makromol. Chem.*, 1964, **60**, 194.
15. Perrin, D. D. and Amarego, W. L. F., in *Purification of Laboratory Chemicals*, 3rd edn. Pergamon Press, Oxford, 1988, p. 222.
16. Morton, M. and Milkowich, R., *J. Polym. Sci. A-1*, 1963, 443.
17. Ishizone, T., Sugiyama, K., Hirao, A. and Nakahama, S., *Macromolecules*, 1993, **26**, 3009.
18. Bauer, W., Winchester, W. R. and Schleyer, P. v. R., *Organometallics*, 1987, **6**, 2371.
19. Ogle, G. A., Wang, X. L. and Johnson, H. C. III, *Polym. Prepr.*, 1993, **34**, 336.
20. Van Krevelen, D. W., in *Properties of Polymers*, 2nd edn. Elsevier, Amsterdam, 1990, p. 792.