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Molecular structure characterization of linear and branched polystyrene blends by size exclusion chromatography coupled with viscometry

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Abstract

Owing to their low polydispersity and their well controlled molecular architecture, 3-arms stars polystyrenes made by anionic synthesis are suitable models to study the solution properties of long chain branched polymers. A fine characterization of such polymers by size exclusion chromatography–viscometry has shown that they often contain unwanted linear chains, leading to chromatograms presenting overlapping peaks. A mathematical procedure has been developed in order to deconvolute these chromatograms and has been validated, thanks to blends of polystyrene standards. It allows one to calculate the purity of the sample as well as the intrinsic viscosity and molar mass distribution of each component. For stars with three arms of the same length, branching parameters have also been calculated and a viscosity law has been established.

Keywords: Star polystyrene; Size exclusion chromatography–viscometry; Peak deconvolution

1. Introduction

One of the current trends in polymer chemistry is to improve the properties of common polymers in order to replace more expensive specific materials. For instance, the presence of a small number (about one or less per polymer chain) of long chain branching in polyolefins or polyesters can increase their processability without reduction of the mechanical resistance of the final product. An extensive knowledge of the molecular structure of branched polymers is thus very important, namely molar mass distribution (MMD), number and length of the branches, evolution of the branching content with molar mass, etc.

To characterise deeply the molecular structure of polymers with low long chain branching content, model compounds with a well defined structure are needed, for instance 3-arms stars.

Anionic synthesis has long been used to produce model compounds, mainly from styrene and butadiene as monomers [1]. These polymers have the advantage of having low polydispersity. Moreover, the molar mass and the architecture can be a priori chosen by adjusting the amounts of initiator, monomer and coupling agent. The first non-linear polymers obtained by this way were 4-arms stars [2,3]. Surprisingly, 3-arms stars were not extensively synthesised [4,5], maybe because of the difficulties to separate the star of the precursor arms. Single arms are always present at the end of the synthesis, because the quantity of coupling agent added is below the stochiometry to ensure total coupling. These single arms can, sometimes only partially, be removed by a careful succession of solvent–non-solvent purifications. Anionic synthesis was mainly developed to produce combs, dendrimers [6], and more exotic architectures like the so-called pom-poms [7] or asymmetric stars, with arms of different length or chemical nature [8]. As the aim of this work is to characterise the low branching contents, we choose to work with 3-arms stars, despite the potential problem of purity. Polystyrene was used as reference material since anionic linear polystyrene have been widely characterised.

In order to determine the branching content of polymers, several techniques have been used [9]. The most direct ones are spectroscopic techniques such as nuclear magnetic resonance (NMR). The current problem of these techniques is the difficulty to distinguish short and long branches. Rheology is very sensitive to low long chain branching

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content, but the large amount of material needed for one experiment is not easily compatible with anionic synthesis and quantification is still problematic. Solution properties provide useful information about the molecular structure of branched polymers, as it is well known that branching reduces the hydrodynamic volume of the macromolecule. In order to determine the purity and the composition of a sample, a separation technique is first needed. Size exclusion chromatography (SEC) is very suitable because the separation is based on the hydrodynamic volume [10]. The molecular characteristics of each fraction (molar mass, branching content) can be obtained using different detectors. As a rule, a concentration detector is used. It allows one to calculate the MMD of a polymer, owing to specific calibration made with standards of the same chemical nature as the analysed polymer. Usually, as these standards do not exist, universal calibration can be used if the viscosity law (Mark–Houwink coefficients) of the analysed polymer is known. When none of these possibilities exists for branched polymers, a detector sensitive to the actual molar mass has to be used. Two kinds of detectors can be coupled with an SEC chromatograph: a viscometer or a light scattering detector.

A light scattering detector coupled with SEC allows one to determine the real MMD of any polymer without calibration [11]. If the detector is multi-angular, the radius of gyration can also be measured and the branching content can be calculated [12]. For polymers with low molar mass, light scattering may suffer from a lack of sensitivity; hence, a viscometer coupled with SEC constitutes an interesting alternative. Thanks to the measurement of the intrinsic viscosity of each fraction and to the universal calibration, the molar mass and the intrinsic viscosity distributions can be obtained [13,14]. To determine the branching content, the branching factor $g' = [\eta]_{br}/[\eta]_{lin}$, where $[\eta]_{br}$ is the measured intrinsic viscosity of the branched sample and $[\eta]_{lin}$ is the intrinsic viscosity of the linear polymer with the same chemical nature and molar mass, must be calculated. For the stars, the relation between g' and the number of arms (f) can be obtained by the formula of Douglas and Freed [15]

$$g' = \left(\frac{3f-2}{f^2}\right)^{0.58} \frac{1-0.276-0.015(f-1)}{1-0.276}.$$

This formula is based on empirical results, but less theory has been developed about branching based on the intrinsic viscosity than that based on radius of gyration.

Monte Carlo simulations have also been performed in order to predict g' [16]. For a 3-arms star polymer, g' has been found to be 0.86.

Experimental values of g' for 3-arms polystyrene stars were measured by viscometry without SEC by Herz et al. [5] and later on by Khasat et al. [4]. They found g' to be between 0.75 and 0.90.

As the difference of molar mass between stars and linear impurities is not important, the choice of the columns to use is essential, as well as the choice of the mathematical procedure used to determine the contribution of each compound to the measured signal.

Two kinds of techniques are effective to increase the separation of overlapping peaks in a chromatogram. The first one consists in correcting the axial diffusion. Indeed, the diffusion of the macromolecules during the analysis is known to cause broadening of the signals, affecting mainly the results in the case of polymers with low polydispersity [17]. The extent of this phenomenon strongly depends on the quality of the columns and on the total dead volume of the system. Axial dispersion correction needs to solve the Tungs' integral [18], for which several mathematical treatments have been proposed [18–21]. In all cases, rather arbitrary assumptions have to be made on the shape and the elution volume dependence of the dispersion. With modern columns, axial dispersion is reduced. These treatments improve the resolution but do not completely eliminate peak overlapping.

The second possibility is to deconvolute the chromatogram in several peaks of a chosen shape by fitting the shape parameters of each peak. Each component then keeps its axial diffusion. One of the simplest model proposed for the chromatographic peak is the exponentially modified gaussian model (EMG) [22]. The peaks are described by a gaussian function convoluted with an exponential to take into account an asymmetry at high retention time. This model is adapted when the asymmetry is not too large and needs only four parameters (position, area, width, distortion) for each peak [23]. If the asymmetry is more pronounced, models with more parameters can be used, such as generalised exponential function [24], polynomial modified function [22,23,25,26].

In this study, our objective is to characterise deeply the molecular structure of polymers with low degree of long chain branching. Therefore, we tried to obtain 3-arms polystyrene stars by anionic synthesis as model compounds and to determine their solution properties. As it turns out to be rather difficult to obtain very pure stars of high molar mass, a fractionation technique was necessary. Hence, we used SEC and viscometry for their characterisation. As the different peaks of the chromatograms strongly overlapped, a mathematical deconvolution based on an EMG model was also applied.

This paper presents the development and the validation of a procedure to characterise blends of polystyrene with low polydispersity. Applied to blends of stars and linear polymers, it allows to obtain the composition of the sample, the real MMD of each component and the branching parameters for the stars.

2. Experimental section

2.1. Materials

2.1.1. Solvent

Solvent was tetrahydrofuran for HPLC from Fluka.

2.1.2. Linear polystyrene

Standards of monodisperse polystyrene of molar mass (MM) of 706,000, 355,000, 190,000, 96,400, 37,900, 18,100, 9100 and 5570 g/mol were supplied by Tosoh, Japan.

Standards of MM of 186,000, 156,000, 76,600, 66,000, 35,000, 28,500, 11,600, 11,300 and 7000 g/mol were supplied by Polymer Laboratories, The Netherlands.

Standards of MM of 200,000 and 30,000 g/mol were supplied by Pressure Chemicals, USA.

All these standards have been used for the determination of the specific and the universal calibrations.

2.1.3. Star polystyrene

SB2 and SB3 were kindly provided by Professor N. Hadjichristidis (University of Athens, Greece). These samples are pure 3-arms stars synthesised following the procedure described in Ref. [4], coupling agent is CH_3SiCl_3.

SA1 was synthesised in the 'Centre d'Etudes et de Recherche sur les Macromolécules' at the Université de Liège (Belgium), using a technique similar to SB2–3. It contains 3-arms star and linear precursor.

SC4–6 were synthesised in the 'Laboratoire de Chimie des Polymères Organiques', Bordeaux (France), using $CH_3C(CH_2O(CH_2)_2O(CH_2)_2Cl)_3$ as coupling agent. Even after extensive purification, these samples remained blends of the precursor, of the desired 3-arms star and of a third species of intermediate molar mass. This could arise either from coupling of only two precursor arms on the core molecule, one functionality remaining free or from a linear coupling of two arms, possibly due to oxygen. The synthesis route is the same as in Ref. [27], with a trifunctional coupling agent to obtain a star instead of a comb.

In the following sections, linear precursor will be called '1-arm', linear coupled precursor and incompletely reacted star will be called '2-arms' and the stars will be called '3-arms'.

SD7 is a 3-arms star supplied by Polymer Source, Canada. After fine SEC analysis, it appears that it still contains 1-arm and 2-arms.

The range of molar masses covered by these samples goes from 40,000 to 300,000 g/mol.

2.2. Characterization

2.2.1. SEC–viscometer chromatography

SEC–viscometer experiments were performed on a GPCV-2000 apparatus from Waters, where solvent was tetrahydrofuran, flow rate 1.023 ml/min, temperature 40 °C, and volume of the injection loop 215.5 μl. The inter-detector volume (0.045 μl) has been measured as the difference between the retention times at the top of the peak of PS 190,000 g/mol (standard). It has been validated using the same calculations with other standards.

Data were acquired with Alliance GPCV 2000 from Waters.

Two sets of columns have been used: first four Shodex AT80M/S (mixed bed columns) and then four Waters Styragel: HR5, 4, 3 and 2.

The problem observed with the first columns set was the lack of resolution between the 2-arms and the stars. This can be seen on Fig. 1, which presents the DRI chromatograms of the sample SC6 analysed with the two columns sets in the same experimental conditions. The main peak due to the star and the small peak to the remaining 1-arm can be observed with both sets. However, with the second set (Styragel columns), a shoulder can be seen on the star peak due to the 2-arms, while with the Shodex columns set, the peak seems more symmetrical and the 2-arms peak remains undetectable.

The specific resolution (R_{sp}) of the column sets can be calculated by [28]

$$R_{sp} = \frac{0.58}{\sigma D_2}$$

where σ is the peak standard deviation, which has been calculated for PS 96,400 g/mol and D_2 is the slope of a linear specific calibration curve. Calculated R_{sp} is 2.67 for the first columns set (Shodex) and 2.86 for the second one (Styragel) and confirms the higher resolution of the Styragel columns.

2.2.2. Calibration of the refractometer

In order to calculate the intrinsic viscosity of each chromatogram slice, the concentration of polymer corresponding to the slice has to be known. Therefore, the refractometer was calibrated in order to link the area of a chromatogram slice and the concentration. This method leads generally to better results than the use of the total injected mass determined by weighting the samples [29]. The calibration constant depends on the response of the detector and on the refractive index increment (dn/dc) of

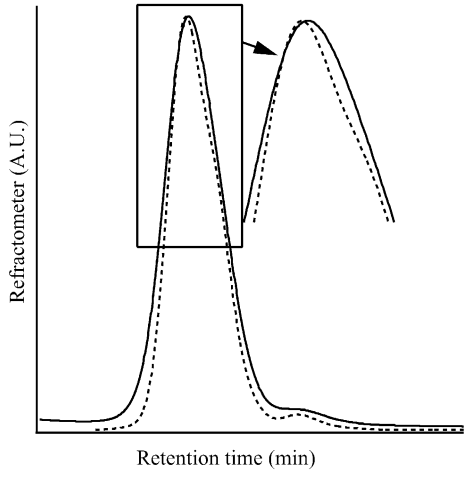

Fig. 1. Comparison of the refractometers chromatograms of a blend of 3-arms star and linear 1-arm and 2-arms (SC6) with the two different columns sets: —, 4 Shodex columns; ---, 4 Styragel columns.

the analysed polymer. For the only analyses of polystyrene, both contributions were not separated (despite this could easily be done). The constant was determined by a linear regression between the concentrations and the areas of the chromatograms for PS 18,100 g/mol and PS 355,000 g/mol, each at six different concentrations from 0.5 to 2 mg/ml.

2.2.3. Data processing

Mathematical deconvolution of the chromatograms and determination of the molecular structure parameters were performed with a procedure developed in our laboratory using IGOR software from WaveMetrics as detailed in Section 3.

3. Results and discussion

3.1. Calibrations curves

In order to determine molar masses and branching parameters by SEC–viscometry, the specific and the universal calibration curves have first to be established. The procedure described below was applied to 20 standards of PS, chosen to cover a wide range of molar mass (MM) with many standards of MM close to expected ones of the branched samples. This gives the retention time and the intrinsic viscosity at each peak maximum.

The specific calibration was obtained by a three-order regression on the MM values given by the supplier as a function of the retention time (RT). The specific calibration is presented in Fig. 2. Its equation is

$$\log M = 19.595 - 1.026(\mathrm{RT}) + 0.023719(\mathrm{RT})^2 - 0.00021097(\mathrm{RT})^3.$$

The universal calibration is obtained by a three-order regression on the product of intrinsic viscosity ($[\eta]$) and MM (as given by the supplier) as a function of the retention time. The universal calibration is presented in Fig. 3. Its equation is

$$\log([\eta]M) = 37.504 - 2.5477(\mathrm{RT}) + 0.067231(\mathrm{RT})^2 - 0.00065662(\mathrm{RT})^3.$$

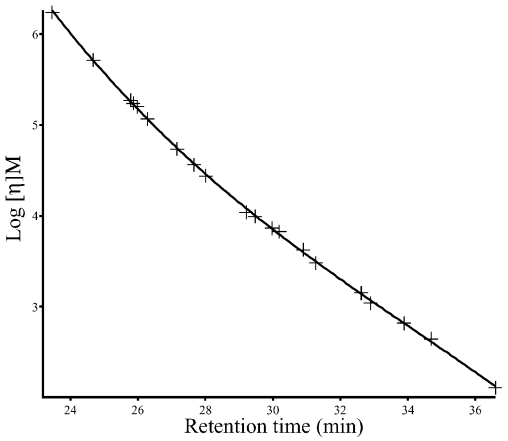

Fig. 3. Universal calibration. +, $[\eta]$ measured at the peak top * MM of the PS standards given by the supplier; —, third-order polynomial fit.

The viscosity law was also determined by relating $[\eta]$ measured at the peak maximum and the molar mass (as given by the supplier). It is presented in Fig. 4. Its equation is

$$[\eta] = 1.7 \times 10^{-4} M^{0.707} (\mathrm{dl/g})$$

in good agreement with the literature [30]. To validate the calibration, some standards used to construct the calibrations were reanalysed. The results are presented in Table 1 (I is the polydispersity (M_w/M_n), M_p and $[\eta]_p$ are the molar mass and the intrinsic viscosity at the top of peak of the refractometer chromatogram.)

The results show that the molar masses calculated with the two calibrations lie close to the one given by the supplier, which has been used to establish the calibration

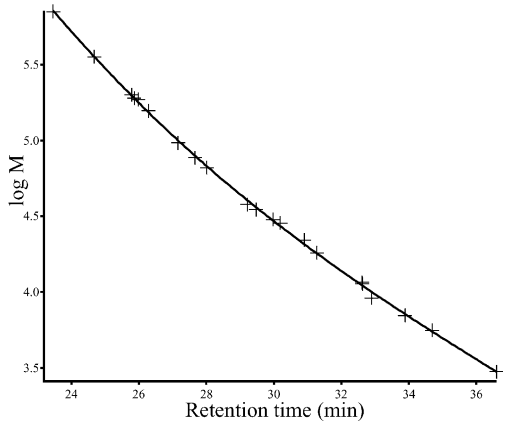

Fig. 2. Specific calibration. +, MM of the PS standards given by the supplier; —, third-order polynomial fit.

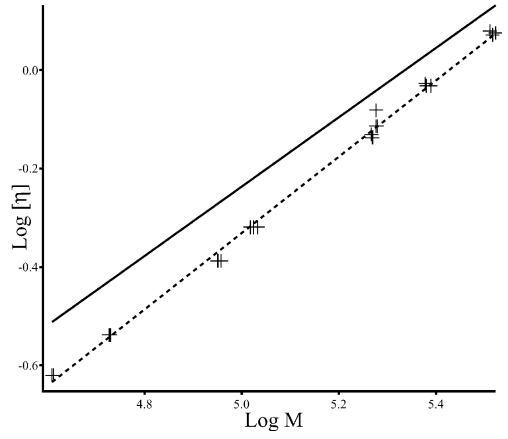

Fig. 4. Viscosity laws measured in THF at 40 °C. —, linear PS; +, $[\eta]_p$ and M_p measured for the 3-arms PS stars; ---, 3-arms PS stars: linear fit.

Table 1
SEC results for polystyrene standards: specific and universal calibrations (I is the polydisperity (M_w/M_n), M_p and $[\eta]_p$ are the values at the top of the peak)

M supplier	Specific calibration				Universal calibration					
	M_n (g/mol)	M_w (g/mol)	I	M_p (g/mol)	$[\eta]$ (dl/g)	$[\eta]_p$ (dl/g)	M_n (g/mol)	M_w (g/mol)	I	M_p (g/mol)
35,000	36,200	37,100	1.03	36,700	0.27	0.28	37,000	38,900	1.05	37,400
66,000	65,600	67,400	1.03	68,600	0.42	0.43	64,400	68,200	1.06	69,000
76,600	76,100	78,100	1.03	78,800	0.46	0.47	76,300	80,400	1.05	79,700
96,400	97,800	100,000	1.02	100,200	0.57	0.57	94,200	99,000	1.05	98,400
156,000	151,300	155,000	1.02	155,000	0.78	0.79	145,200	153,800	1.06	149,600
200,000	194,200	199,400	1.03	196,400	0.94	0.94	182,900	196,900	1.08	189,600

curves. Although the molar masses obtained with the universal calibration are slightly higher than those obtained with the specific calibration, both methods give quite similar results.

These calibrations will allow to determine the MMD of any unknown sample.

3.2. Blend analysis: deconvolution procedure

A SEC analysis of the star polystyrene has revealed that for the samples containing linear species, the different peaks strongly overlap, as it can be seen in Fig. 5. Therefore, a mathematical deconvolution of the chromatograms has to be applied in order to obtain the MMD and the molecular structure parameters of each species.

The chromatograms from the refractometer and from the viscometer are independently deconvoluted, then the peaks of each species are put in correspondence and the molecular structure parameters are calculated. The procedure has been verified using six blends of linear standards polystyrenes having molar masses in approximate ratio 1:2:3 to approach the blends of 1-arm, 2-arms and 3-arms.

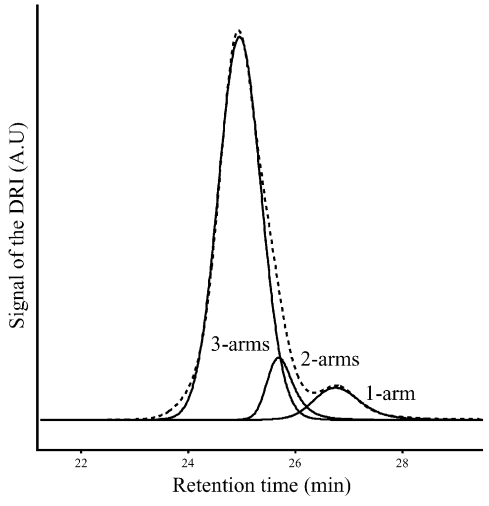

Fig. 5. Refractometer chromatogram of a blend of 3-arms star and linear 1-arm and 2-arms (SD7). ---, untreated chromatogram; —, deconvolution into three peaks corresponding to the different species.

3.2.1. Composition and apparent MMD: deconvolution of the refractometer chromatogram

First, a linear baseline is subtracted from the chromatogram. The latter is then deconvoluted into three peaks assuming an EMG shape. The area, position, width and distortion of each peak are adapted in order to fit the chromatogram. An example of such a deconvolution applied to a blend of three linear standards PS is shown in Fig. 6 (test 2: PS 76,600 g/mol, PS 156,000 g/mol and PS 200,000 g/mol). The chromatogram is well fitted, except the peak tail at low retention time. This can be due to some impurities present in the standards. We have tried to improve the fit using a second peak at higher mass for each standard in order to simulate some coupling often present in anionic synthesis, but this needlessly multiply the number of adjustable parameters. The results of the main peak are unaffected by the second peak, and the amount of this component is too low to characterize it properly. Moreover, the problem does not appear on the chromatogram of the blends of stars and linear PS. Therefore, this peak tail was not further investigated.

For each peak, the concentration of each fraction is calculated using the calibration constant of the refractometer.

The deconvolution of the refractometer chromatogram allows one to determine the composition of the sample and the molar mass of each component expressed in linear PS equivalent thanks to the specific calibration. This procedure has been applied on our six test blends (tests 1–3: PS 76,600 g/mol, PS 156,000 g/mol and PS 200,000 g/mol, tests 4–6: PS 35,000 g/mol, PS 66,000 g/mol and PS 96,400 g/mol). As the test samples are made from linear PS, these molar masses are in fact the true ones. Table 2 compares the injected and the calculated compositions and Table 3 presents the molar masses obtained for each component with the specific calibration. The M_p values are compared to the one obtained when the standard was analysed alone (M_p^*).

The correlation between injected and calculated composition is good, except for the two lowest concentrations (PS 200,000 in test 3 and PS 96,400 in test 6). The MM obtained with the specific calibration are reproducible (differences between the three tests are $\leq$3% for each standard) and agree with those obtained when the standards are not blended (differences between M_p and M_p^* are $\leq$3%). These results clearly validate the procedure.

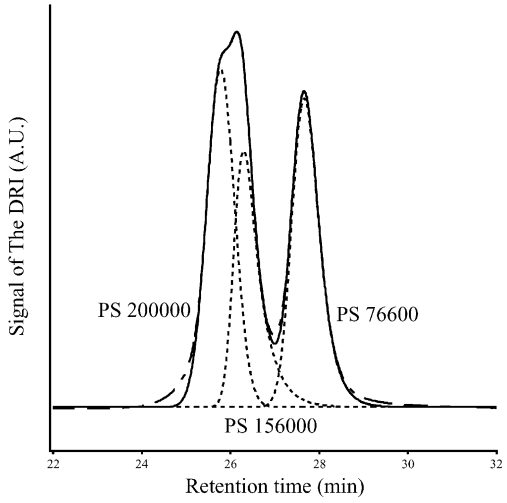

Fig. 6. Deconvolution of the refractometer chromatogram of a blend of three standards PS (test 2). -·- ·-, untreated chromatogram; —, fitted chromatogram; ---, deconvolution into three peaks corresponding to the different species.

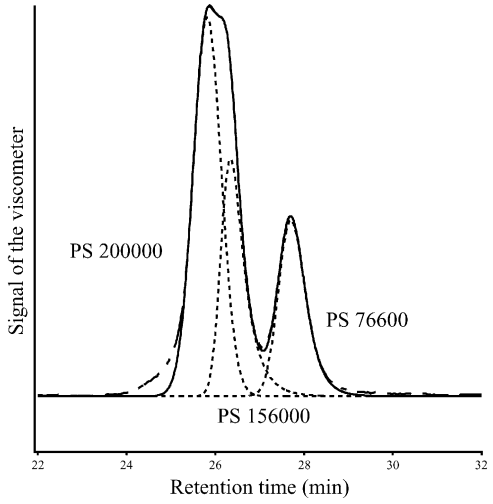

Fig. 7. Deconvolution of the viscometer chromatogram of a blend of PS 76,600 g/mol, PS 156,000 g/mol and PS 200,000 g/mol (test 2). -·-·-, untreated chromatogram; —, fitted chromatogram; ---, deconvolution into three peaks corresponding to the different species.

3.2.2. Intrinsic viscosity and real molar mass: deconvolution of the viscometer chromatogram

The viscometer signal is proportional to the relative viscosity (η_{rel})

$$\frac{p}{p_0} = \frac{\eta}{\eta_0} = \eta_{rel}$$

where p and p_0 are the pressure drops due to the solution and the pure solvent. By subtracting 1 from the chromatogram, the specific viscosity (η_{spec}) is obtained:

$$\eta_{spec} = \frac{\eta - \eta_0}{\eta_0} = \eta_{rel} - 1.$$

The specific viscosity chromatogram is then deconvoluted in the same way as the refractometer chromatogram. An example of this deconvolution on the same blend as in Fig. 6 is presented in Fig. 7.

For each peak, the concentration and the specific viscosity are put in correspondence taking the interdetector volume into account. The reduced viscosity of each slice is then calculated dividing the specific viscosity by the concentration. As concentration is low, the reduced viscosity is taken as an approximation of the intrinsic viscosity. Thanks to both chromatograms, the intrinsic viscosity of each polymer fraction eluting from the SEC columns has thus been calculated. The evolution of the intrinsic viscosity with the retention time is presented in Fig. 8. This intrinsic viscosity can be either used directly for the calculation of the molar mass or can be first fitted with a predefined mathematical function. This fit can be done on all the slices of the chromatograms or only on the ones showing a high signal to noise ratio (concentrations below 30% of the concentration at the peak maximum are neglected). The results obtained on a linear PS standard using in each case a linear fit or a third-order polynomial fit are presented in Table 4.

The various approximations do not bring noticeable changes in the results.

From the intrinsic viscosity of each slice calculated without applying any approximation, its molar mass can be obtained due to the universal calibration curve. So the MMD of each component is obtained. The results for linear PS blends are presented in Table 5. M_p is compared with M_p^* obtained when the standard was analysed alone. The molar mass of each fraction eluting from the columns can thus be

Table 2
Comparison of the injected composition and the calculated composition for blends of three linear polystyrene standards

Sample	M supplier	Injected composition (%)	Calculated composition (%)
Test 1	200,000	35	41
	156,000	35	30
	76,600	30	29
Test 2	200,000	31	38
	156,000	31	27
	76,600	38	35
Test 3	200,000	13	25
	156,000	28	20
	76,600	59	55
Test 4	96,400	34	36
	66,000	28	30
	35,000	38	34
Test 5	96,400	26	33
	66,000	50	45
	35,000	24	22
Test 6	96,400	8	24
	66,000	49	40
	35,000	43	36

Table 3
Results of the deconvolution of the refractometer chromatograms for blends of three linear polystyrene standards (M_p^* is obtained when the PS standard is analysed alone)

Sample name	M supplier	M_n (g/mol)	M_w (g/mol)	I	M_p (g/mol)	M_p^* (g/mol)
Test 1	200,000	194,600	199,700	1.03	197,200	196,400
	156,000	137,700	142,300	1.03	150,600	155,000
	76,600	74,300	76,400	1.03	78,800	78,800
Test 2	200,000	194,800	200,000	1.03	197,200	196,400
	156,000	137,400	142,200	1.03	151,800	155,000
	76,600	75,100	77,000	1.03	78,800	78,800
Test 3	200,000	188,400	194,900	1.03	191,400	196,400
	156,000	137,000	141,900	1.04	149,900	155,000
	76,600	75,400	77,400	1.03	79,200	78,800
Test 4	96,400	99,800	101,900	1.02	101,000	100,200
	66,000	61,200	63,600	1.04	68,400	68,600
	35,000	35,700	36,500	1.02	36,600	36,700
Test 5	96,400	99,500	101,500	1.02	100,600	100,200
	66,000	63,100	65,100	1.03	67,800	68,600
	35,000	35,400	36,300	1.03	36,700	36,700
Test 6	96,400	99,500	101,600	1.02	100,600	100,200
	66,000	62,400	64,500	1.03	67,800	68,600
	35,000	35,600	36,500	1.02	36,600	36,700

calculated by two different ways: either using its retention time and the specific calibration, either using its retention time, its intrinsic viscosity and the universal calibration. The results of these calculated MM for each retention time are presented in Fig. 9.

Most of the results are in agreement with those obtained for the standards analysed alone.

As all standards are linear PS, there are no significant differences between the molar mass obtained by specific or universal calibration. However, it can be seen that the largest variations are observed for the peak of intermediate molar mass (used to model the 2-arms in our samples of interest), because this peak is the most difficult to localise in the blend, as the peak maximum is sometimes hidden by the peak of higher molar mass.

3.3. Application of the deconvolution procedure to branched samples

The procedure tested with blends of linear PS was applied to the branched samples. An example of deconvolution of the refractometer chromatogram is presented in Fig. 5.

If the polymer is branched or has a different chemical nature than polystyrene, the universal calibration will

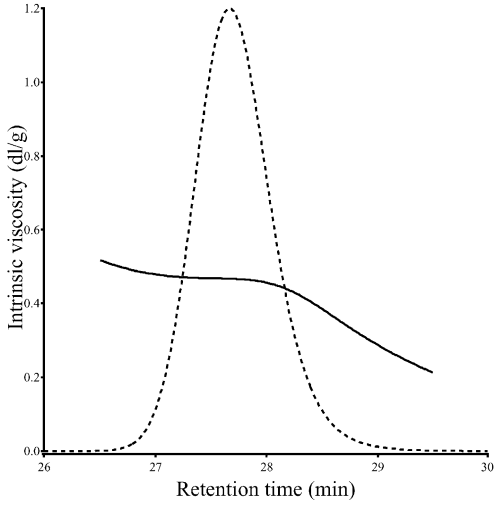

Fig. 8. Evolution of the intrinsic viscosity of a PS standard (76,600 g/mol) with the retention time. ---, refractometer chromatogram; —, intrinsic viscosity.

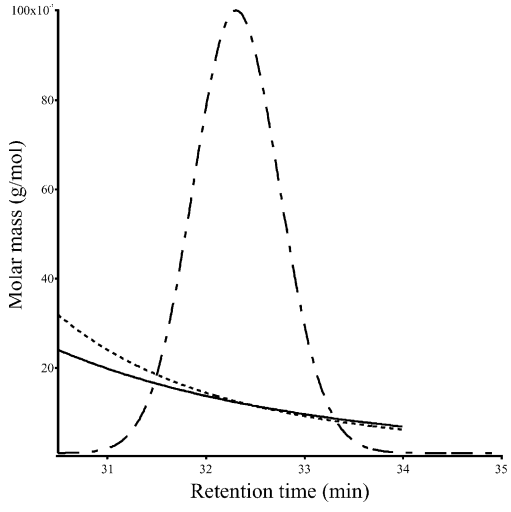

Fig. 9. Evolution of the molar mass of a linear PS (1-arm in SB1) with the retention time. -·-·-, refractometer chromatogram; —, MM calculated with the specific calibration; ---, MM calculated with the universal calibration.

Table 4
Results obtained using different fits for the evolution of the intrinsic viscosity with the retention time

	$[\eta]$ (dl/g)	$[\eta]_p$ (dl/g)	M_n (g/mol)	M_w (g/mol)	M_p (g/mol)
No fit	0.46	0.47	70,200	74,400	69,500
Linear fit on all the peak	0.44	0.44	73,200	78,600	73,200
Linear fit on the peak top	0.46	0.46	69,900	74,300	70,000
Third order fit on all the peak	0.44	0.45	72,700	76,400	72,200
Third order fit on the peak top	0.46	0.47	70,400	75,000	69,600

provide the real molar mass while the specific calibration will provide a molar mass expressed in equivalent linear PS (apparent MM). For a star, this latter is lower than the real molar mass. The evolution of the real molar mass and of the apparent MM with the retention time for a star PS is presented in Fig. 10.

The deconvolution of the refractometer chromatogram will provide purity and apparent MM of the analysed sample. Then, $[\eta]$ and real MM will be obtained due to the deconvolution of the viscometer chromatogram. The branching parameter g' will then be calculated and a viscosity law for the 3-arms stars will be established.

3.3.1. Purity and molar masses

Some analysed samples are pure stars (3-arms), while others contain different linear PS (1-arm and 2-arms). Their composition is presented in Table 6 and their molar mass in Table 7. These values are averages on three different injections, exhibiting a good reproducibility (variations $<5\%$ on the composition, intrinsic viscosities and molar masses). However, for the linear species present in small quantities, one value of M_w was sometimes discarded.

The results show that there is no difference between the two calibrations for the linear PS while for the stars, the apparent molar mass is smaller than the true one.

3.3.2. Branching parameters

Owing to the measurement of the intrinsic viscosity, the branching parameter g' can be determined. The intrinsic viscosity of a linear PS of the same molar mass has been calculated using the molar mass of the stars at the peak maximum (M_p) and the viscosity law determined with the PS standards in our analysis conditions. For these g' values, the Douglas and Freed equation allows to calculate the number of arms. These results are presented in Table 8.

The g' values calculated for the stars agree with those of Douglas and Freed ($g' = 0.83$) and other values: experimental (Herz et al.: $g' = 0.75$–0.87 [5], Khasat et al. $g' = 0.81$–0.9) or obtained by Monte Carlo simulations [16] ($g' = 0.86$). The recalculated number of arms (f) is

Table 5
Results of the decomposition of the refractometer and viscometer chromatograms for blends of three linear polystyrene standards (M_p^* is obtained when the PS standard is analysed alone)

Sample name	M supplier	$[\eta]$ (dl/g)	$[\eta]_p$ (dl/g)	M_n (g/mol)	M_w (g/mol)	I	M_p (g/mol)	M_p^* (g/mol)
Test 1	200,000	0.99	0.95	176,400	197,300	1.12	188,700	189,600
	156,000	0.69	0.74	139,600	155,700	1.12	152,700	149,600
	76,600	0.46	0.47	72,300	77,500	1.07	79,400	79,700
Test 2	200,000	0.93	0.93	187,000	202,200	1.08	194,700	189,600
	156,000	0.72	0.77	134,800	143,400	1.06	149,900	149,600
	76,600	0.47	0.47	73,100	77,500	1.06	79,200	79,700
Test 3	200,000	0.83	0.79	218,100	220,300	1.01	216,400	189,600
	156,000	0.90	0.88	109,500	114,900	1.05	128,000	149,600
	76,600	0.46	0.47	74,000	80,400	1.09	79,800	79,700
Test 4	96,400	0.57	0.56	96,700	102,900	1.06	102,800	98,400
	66,000	0.40	0.43	59,400	66,600	1.12	68,600	69,000
	35,000	0.28	0.28	35,100	37,800	1.08	37,000	37,400
Test 5	96,400	0.56	0.55	98,300	104,800	1.07	102,200	98,400
	66,000	0.41	0.43	61,800	67,100	1.09	67,900	69,000
	35,000	0.28	0.28	35,100	37,800	1.08	37,000	37,400
Test 6	96,400	0.55	0.55	101,000	106,000	1.05	102,900	98,400
	66,000	0.41	0.43	61,400	65,400	1.06	67,700	69,000
	35,000	0.28	0.28	35,000	37,300	1.06	36,700	37,400

Table 6
Composition of the different branched samples

Sample name	1-Arm (%)	2-Arms (%)	3-Arms (%)
SA1	50	0	50
SB2	0	0	100
SB3	0	0	100
SC4	2	11	87
SC5	11	15	74
SC6	2	15	83
SD7	6	9	85

thus close to the real number we knew a priori from the synthesis ($f = 3$).

However, these results suggest two comments. First, it can be seen that using the Douglas and Freed equation, small variations of g' (about 6%) grow when f is calculated (11%). Secondly, there seems to be a difference between the stars of low molar mass (SA1 to SC4) and the stars with higher molar mass, for which g' increases.

3.3.3. Viscosity law for 3-arms stars PS

As we determined the real molar mass and the intrinsic viscosity of several 3-arms stars PS with arms of equal length, we can determine their viscosity law in THF at 40 °C. It is presented in Fig. 4. Its equation is

$$[\eta] = 0.6 \times 10^{-4} M^{0.775} (\mathrm{dl/g}).$$

This law allows one to determine the real molar mass of a 3-arms star PS with a classical SEC apparatus, as

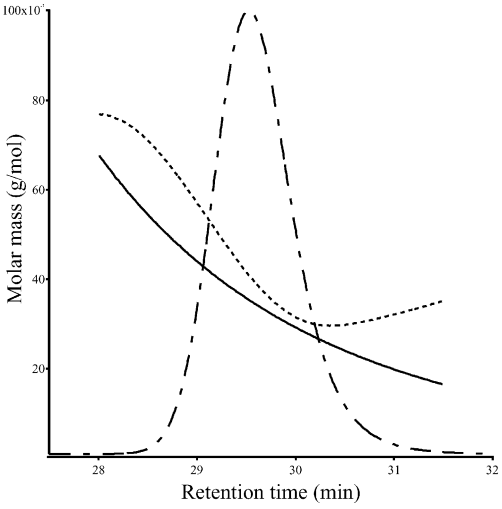

Fig. 10. Evolution of the molar mass of a 3-arms star PS (3-arm in SB1) with the retention time. -·-·-, refractometer chromatogram; —, MM calculated with the specific calibration; ---, MM calculated with the universal calibration.

we have

$$M_{\mathrm{star}} = \left(\frac{K_{\mathrm{linear\ PS}} M_{\mathrm{linear\ PS}}^{\alpha_{\mathrm{linear\ PS}}}}{K_{\mathrm{star}}} \right)^{1/\alpha_{\mathrm{star}}} = \left(\frac{1.7 \times 10^{-4} M_{\mathrm{linear\ PS}}^{0.707}}{0.6 \times 10^{-4}} \right)^{1/0.775}.$$

This law is strictly valid for the stars with molar masses between 40,000 and 300,000 g/mol. One remaining unsolved problem is that this law was established with stars made using three different core molecules. The

Table 7
Results of the decomposition of the refractometer and viscometer chromatograms for the different components of the branched samples

Sample name	Arms number	Specific calibration				Universal calibration					
		M_n (g/mol)	M_w (g/mol)	I	M_p (g/mol)	$[\eta]_p$	$[\eta]$	M_n (g/mol)	M_w (g/mol)	I	M_p (g/mol)
SA1	1	12,200	12,500	1.02	12,300	0.15	0.14	12,400	12,700	1.04	12,300
	3	33,700	34,700	1.03	35,400	0.24	0.23	39,000	40,900	1.05	40,900
SB2	3	45,100	46,300	1.03	46,500	0.29	0.28	51,100	54,200	1.06	53,500
SB3	3	75,200	77,200	1.03	78,400	0.41	0.41	84,300	89,500	1.06	89,800
SC4	1	30,700	31,900	1.04	30,000	0.31	0.34	22,600	29,100	1.25	34,100
	2	57,000	59,500	1.04	66,300	0.40	0.40	51,500	62,800	1.22	69,300
	3	93,100	95,600	1.03	94,300	0.48	0.48	103,600	109,800	1.06	106,000
SC5	1	63,600	66,100	1.04	69,400	0.43	0.44	56,700	64,600	1.14	70,100
	2	112,400	116,000	1.03	127,600	0.63	0.58	117,500	126,500	1.08	134,600
	3	173,300	179,200	1.04	176,300	0.79	0.79	179,500	199,600	1.11	189,500
SC6	1	77,700	81,400	1.05	89,200	0.50	0.53	79,900	89,900	1.10	91,700
	2	145,600	151,000	1.04	163,700	0.74	0.69	151,000	178,500	1.18	175,700
	3	219,000	227,200	1.04	223,000	0.93	0.93	228,800	255,700	1.12	241,600
SD7	1	114,600	119,500	1.04	120,500	0.69	0.67	102,900	123,900	1.20	113,300
	2	194,000	199,500	1.03	208,600	0.93	0.91	186,400	199,900	1.07	216,500
	3	298,000	311,900	1.05	305,800	1.19	1.19	305,600	351,700	1.15	328,900

Table 8
Intrinsic viscosities and branching parameters of the 3-arms stars

Sample name	$[\eta]_p$ (dl/g)	$[\eta]_{lin}$ (dl/g)	g'	f
SA1	0.24	0.31	0.78	3.5
SB2	0.29	0.37	0.78	3.5
SB3	0.41	0.54	0.77	3.5
SC4	0.48	0.61	0.79	3.4
SC5	0.79	0.91	0.87	2.8
SC6	0.93	1.08	0.86	2.9
SD7	1.19	1.34	0.89	2.7

influence of the nature of the core was not examined here, since the difference in cores is coupled with a difference in molar mass.

4. Conclusions and perspectives

In order to characterise the molecular structure of polymers with low long chain branching content by solution properties, we have tried to obtain 3-arms polystyrene stars made by anionic synthesis as model compounds. The characterisation of these samples by SEC–viscometry revealed that most of these samples were not totally pure and contain some linear species. Despite suitable columns set, the peaks corresponding to the 3-arms star and the linear 2-arms were overlapping.

We have thus developed a mathematical treatment allowing to analyse these chromatograms. The procedure has been validated on blends of linear PS and then applied on the blends of star and linear PS.

For samples containing up to three polystyrene with low polydispersity, it allows one to determine the composition (purity), the MMD and the intrinsic viscosity of each component with an accuracy of 5%.

For branched compounds, the branching parameter g' was also determined and agrees with other values from the literature. Thanks to samples in a wide molar mass range, a viscosity law for stars PS with three arms of equal length in THF at 40 °C was also determined.

This procedure could be adapted to treat chromatograms obtained with a multi-angle light scattering detector. This should allow one to obtain the radii of gyration of each component as well as their evolution with the molar mass and the branching factor g. The limitation of this technique is that it is less sensitive to low molar mass and in this case, our lower MM samples could be useless.

In order to approach conditions encountered in industrial polymers, namely a broad MMD, it should be interesting to test the sensitivity of the technique and the procedure to lower branching content on blends of linear polystyrene with broad MMD and branched polystyrene with narrow MMD.

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