Molar Mass Distributions and Hydrodynamic Interactions in Random Copolyesters Investigated by Size Exclusion Chromatography/Matrix-Assisted Laser Desorption Ionization

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Received January 6, 1998; Revised Manuscript Received March 30, 1998

ABSTRACT: Matrix-assisted laser desorption ionization−time-of-flight mass spectrometry (MALDI−TOF MS) was used in combination with size exclusion chromatography (SEC) to characterize a series of copolyesters with butylene adipate (BA), butylene succinate (BSu), and butylene sebacate (BSe) units. These copolyesters, synthesized by condensation polymerization from 1,4-butanediol and dimethyl esters, have flexible chains, are random, and do possess a homogeneous composition. The SEC fractionation of these polymers allowed to collect numerous fractions that were then analyzed by MALDI−TOF. The mass spectra of these nearly monodisperse fractions allowed the computation of the corresponding molar masses (MM). The calibrated SEC traces could then be used to compute average MM and molar mass distribution of the unfractionated samples. Furthermore, the SEC/MALDI data allowed an estimate of the effect of the hydrodynamic interactions of comonomers A and B along the copolymer chain and a comparison with the theoretical predictions. Sensible deviations from the simple additivity have been found for the four copolymers studied.

Introduction

Polymer characterization is playing an increasing role in the current research work, doubtless due to the development of new powerful techniques of polymer analysis allowing to disclose structural and molecular details hitherto unaccessible.

Matrix-assisted laser desorption ionization−Time-of-Flight Mass Spectrometry (MALDI−TOF MS), a high sensitivity technique, allows desorption and ionization of very large molecules, even in complex mixtures.[1] However, molar mass (MM) estimates provided by MALDI for synthetic polymers agree with the values obtained by conventional techniques only in the case of samples with narrow molar mass distribution (MMD).[2]

To overcome this problem, polydisperse polymers such as dextrans,[3] polyesters,[4] and polysiloxanes[5,6] have been fractionated by analytical size exclusion chromatography (SEC), yielding fractions with very narrow distributions which, analyzed by MALDI, were found to give mass spectra with MM values in excellent agreement with those obtained by conventional techniques.[4−6]

These findings open the way to a new development, where the MALDI−TOF is used as the detector in the SEC fractionation of polydisperse polymer samples.

We have now furthered our studies on this hyphenated SEC/MALDI method, applying it to characterize the molecular properties of copolymers.

The analysis of copolymers by SEC is a difficult problem, and much effort has been paid to the task of converting the SEC traces to molar masses of copolymers.[7−13]

Multiple detectors and SEC/light scattering techniques may provide a solution to the problem, but difficulties remain.[8,9,11] The multiple detector approach needs calibration of the detectors and of the column set for each homopolymer. The use of a light scattering detector for copolymers encounters difficulties connected with its low sensitivity for low molar mass molecules, and with the determination of the copolymer concentration in nonhomogeneous materials, where the chain dimensions of copolymers may not depend on the molar mass in a linear way.[8,9]

Being able to discriminate among different masses and possessing a remarkably high sensitivity, the MALDI detector does not suffer these limitations.[4−6]

The aliphatic copolyesters investigated here are listed in Table 1. These copolyesters have flexible chains, are random, and do possess a homogeneous composition, since they were synthesized by condensation polymerization. Some of these materials have recently appeared into the market as biodegradable materials.[14]

Theory

As seen above, the problem of converting the SEC traces to molar masses of copolymers involves complex methodologies and careful work.

To bypass this problem, there have been in the literature attempts to deduce the calibration curve (i.e., molar mass against eluted volume) of an AB copolymer, from the calibration curves corresponding to the homopolymers A and B, respectively.

In an interesting article,[12] the assumption has been made that the size of an AB copolymer molecule is the sum of the sizes of the two portions of the molecule as though each were a homopolymer.

Accordingly, the molar mass of a copolymer molecule was assumed as given by[12]

$$\log(M_C) = w_A \log(M_A) + (1 - w_A) \log(M_B) \qquad (1)$$

S0024-9297(98)00019-9 CCC: $15.00

Table 1. Structure and Properties of the Copolyesters Analyzed

sample[a]	solubility	feed[b]	$\eta_{\mathrm{inh}}{}^{c}$	$M_{\mathrm{w(SEC)}}{}^{d}$	$M_{\mathrm{w}}{}^{e}$	$M_{\mathrm{n}}{}^{e}$	$M_{\mathrm{w}}/M_{\mathrm{n}}$
PBA/PBSe	THF, $CHCl_3$	50/50	0.20	13200	12800	8500	1.51
PBSu/PBA	THF, $CHCl_3$	50/50	0.19	14200	11600	6900	1.68
PBSu/PBSe	THF, $CHCl_3$	50/50	0.19	15400	8600	5400	1.59
PBSu/PBA/PBS[e]	THF, $CHCl_3$	33/33/33	0.17	8400	15000	8300	1.81

[a] PBA = Poly(butylene adipate), PBSe = poly(butylene sebacate), PBSu = poly(butylene succinate), and PBT = poly(butylene terephthalate). [b] Molar ratio of monomers in the feed. Polymerization reactions were led to completion. The composition was checked by NMR analysis. [c] Inherent viscosity values were obtained in THF at 30 ± 0.1 °C. [d] Molar mass computed using the universal calibration curve obtained in THF (see Experimental Section). [e] Weight average and number average molar masses computed using the SEC−MALDI method (see Experimental Section; values obtained in $CHCl_3$).

where M_C, M_A, and M_B are, respectively, the molar masses of the copolymer and of the two homopolymers measured at the same elution volume (V_e), and where w_A is the weight fraction of A units in the copolymer.

The above equation was proposed,[12] without theoretical justification, to evaluate the molar masses of fractions of a styrene−butadiene block copolymer obtained from multiple detectors SEC experiments, assuming that the molar mass of a copolymer molecule can be calculated simply by averaging the molar masses of a mixture of the two parent homopolymers, measured at the same elution volume of the copolymer.

Recently,[13] eq 1 was tested in the case of a styrene−methyl methacrylate block copolymer, and was found to hold fairly well.

Block copolymers are likely to simulate the behavior of a simple mixture of homopolymers, since the bond connections between the two comonomers are not numerous. However, random copolymers should represent a different case, and departures from the simple additivity assumed in eq 1 are expected.

In the following, we derive a prediction based on current theories.

The universal calibration concept[15] states that the hydrodynamic volumes $[\eta]M$ of two polymer molecules measured at the same elution volume (V_e) are the same (this applies when k and a of the two homopolymers are similar in the law $[\eta] = kM^a$)

$$\log([\eta]_C M_C) = \log([\eta]_A M_A) \tag{2}$$

$$\log([\eta]_C M_C) = \log([\eta]_B M_B) \tag{3}$$

where $[\eta]_A$, $[\eta]_B$, and $[\eta]_C$ are the viscosities of the two homopolymers and of the copolymer. Rewriting eqs 2 and 3, one obtains

$$\log([\eta]_C M_C) = 1/2[\log([\eta]_A M_A) + \log([\eta]_B M_B)] \tag{4}$$

which states that the hydrodynamic volume of the copolymer molecule is the average of the hydrodynamic volumes of the two homopolymer molecules.

However, this does not mean that the molar mass of a copolymer molecule can be calculated simply averaging the molar masses of a mixture of the two parent homopolymers, measured at the same elution volume of the copolymer. Therefore, eq 1 is not correct.

Multiplying eq 2 by w_A and eq 3 by $(1 - w_A)$, summing, and rearranging, at the same elution volume, one has

$$\log(M_C) = w_A \log(M_A) + (1 - w_A)\log(M_B) + \beta \tag{5}$$

$$\beta = w_A \log([\eta]_A) + (1 - w_A)\log([\eta]_B) - \log([\eta]_C) \tag{6}$$

It is apparent that eq 5 (theoretically justified) is more complex with respect to eq 1, but when $\beta = 0$, the two equations are coincident (see Appendix for the complete form of eq 5).

β is a hydrodynamic interaction parameter; i.e., it is a measure of the deviation of the AB copolymer molar mass from the simple additivity rule assumed in eq 1. A finite value of β means that the presence (and sequence) of the two comonomer units along the copolymer chain induces changes in the overall chain dimensions that cannot be accounted for by averaging the molar masses of the two homopolymers A and B.

In the framework of the universal calibration concept, eq 1 is an approximation of eq 5, which is valid when the interaction term β is negligibly small. In this case, one has

$$\log([\eta]_C) = w_A \log([\eta]_A) + (1 - w_A)\log([\eta]_B) \tag{7}$$

There is no a priori reason to believe that eq 7 is likely to hold. For instance, in the case of a block styrene−methyl methacrylate copolymer,[9] large deviations from the behavior suggested by eq 7 were observed.

The previous treatment can be extended to the case of a copolymer with three different repeat units. A relationship can be derived between the calibration lines of the terpolymer and of the three homopolymers, namely

$$\log(M_C) = w_1 \log(M_1) + w_2 \log(M_2) + (1 - w_1 - w_2)\log(M_3) + \gamma \tag{8}$$

$$\gamma = w_1 \log([\eta]_1) + w_2 \log([\eta]_2) + (1 - w_1 - w_2)\log([\eta]_3) - \log([\eta]_C) \tag{9}$$

where M_1, M_2, M_3, and M_C are the molar masses of the three homopolymers and of the terpolymer measured at the same elution volume, and where $[\eta]_1$, $[\eta]_2$, and $[\eta]_3$ are the inherent viscosities of the three homopolymers.

The SEC/MALDI data, reported below, allow the evaluation of the parameters β and γ for some of the copolymers in Table 1 and, therefore, permit one to test the respective validity of eqs 5, 8, and 1 in the case of flexible-chain, random copolymers.

Experimental Section

Materials. Dimethyl succinate, dimethyl adipate, dimethyl sebacate and dimethyl terephthalate were purchased from Sigma-Aldrich (Mi, Italy) whereas 1,4-butanediol was purchased from Jansen Chimica. Dimethyl terephthalate was purified by crystallization from *n*-hexane, whereas the other reagents were purified by vacuum distillation before use.

Polymer Synthesis. Homopolyesters and copolyesters were synthesized by melt polymerization starting from stoichiometric amounts of dimethyl esters and 1,4-butanediol in the presence of a mixture of $Zn(OOCCH_3)_2$ and Sb_2O_3 (80/20, w/w) as trans-esterification catalyst. For homopolyesters, the feed was constituted by a single dimethylester and 1,4-butanediol, whereas for copolymers an equimolar mixture of two or three dimethylesters was reacted with the diol to obtain copolymers with two and three components. The reaction was carried out at 180 °C for 2 h and for 5 h at 230 °C under reduced pressure (1.5 Torr) to eliminate the methanol formed in the reaction. In the following the synthesis of poly(butylenadipate-*co*-butylensebacate) is described as an example. First 1.71 g (0.0088 mol) of dimethyl adipate and 2.024 g (0.0088 mol) of dimethylsebacate were poured in a flask together with 1.58 g. (0.0175 mol) of 1,4-butanediol and with 3.95 mg (0.25% of the diol weight) of catalyst. The temperature of the mixture was gradually risen up to 180 °C and kept at this value for 2 h, under stirring. Thereafter, the pressure was reduced to 1.5 Torr and the temperature was gradually increased up to 230 °C and kept at this value for 5 h. To remove the residual catalyst from reaction mixture, the crude homopolymers and copolymers were dissolved in the minimum amount of $CHCl_3$, filtered, and precipitated into methanol. The solid materials were filtered washed several times with methanol, dried at 50 °C under vacuum and characterized by viscosimetry, SEC, TG, NMR, and MS.

SEC Analysis and Fractionation. The analyses were performed on a Waters 600A apparatus, equipped with five Ultrastyragel columns (7.8 × 300 mm) (in the order 10^5, 10^3, 500, 10^4, and 100 Å pore size) connected in series, and a Waters R401 differential refractometer. Then 60 μL of 15 mg/mL THF or $CHCl_3$ solutions were injected and eluted at a flow rate of 1 mL/min. The fractionation of homopolymers and copolymers were performed by collecting 30 drops for each fraction, corresponding to 0.33 mL for $CHCl_3$ and 0.70 mL for THF. For each sample 50 fractions were collected. SEC traces for the three homopolyesters and four copolyesters investigated are reported in Figures 1S−10S (Supporting Information)

MALDI−TOF Mass Spectra. A Bruker Reflex mass spectrometer was used to obtain the matrix-assisted laser desorption/ionization time-of-flight mass spectra. The spectrometer is equipped with a nitrogen laser (337 nm, 5 ns), with a flash ADC (time base 4 ns), and with two detectors. The first detector works in the linear mode, whereas the second detector is placed at the end of the second flight tube and allows the detection of ions in the reflectron mode. The detection in linear mode was achieved by means of a HIMAS detector, which provides a very wide dynamic range, but with a low temporal resolution. This detector is very sensitive to high molar mass ions (≥500 000 Da)[6] with respect to normal microchannel detectors which undergo saturation with ions with molar mass higher than 15 000 Da.

The accelerating voltage was 30 kV. The laser irradiance was slightly above threshold (ca. 10^6 W/cm^2). Ions below m/z 350 were removed with pulsed deflection, and 100 transients were summed.

2-(4-Hydroxyphenylazo)benzoic acid (HABA), 0.1 M in a THF/$CHCl_3$ 1:1 mixture, was used as a matrix. The sample for MALDI analysis was prepared as follows: 0.2 mL of the HABA solution was mixed with about 0.1 mL of each collected fraction and 2 μL of the resulting solution was placed on the probe tip and slowly dried.

The MALDI mass spectra of the SEC fractions were processed with the XMASS program from Bruker. The program uses mass spectral intensities to compute the quantities known as most-probable molar mass, number-average molar mass, weight-average molar mass, and polydispersity index (denoted as M_p, M_n, M_w, and M_w/M_n, respectively). Data obtained for some selected fractions are reported in Tables 1S and 2S (Supporting Information).

Molar Mass Calculations. The molar mass of the unfractionated polymer samples were calculated from the SEC curves by the Polymer Lab Caliber software using the absolute calibration curves obtained by plotting log M_w (calculated from the MALDI−TOF spectra) as a function of the elution volume of each SEC selected fraction. The molar mass distribution data obtained for the copolymers are reported in Table 1, whereas the results for homopolymers are as follows: PBSu ($M_w = 15400$, $M_n = 9200$, $M_w/M_n = 1.67$), PBA ($M_w = 14000$, $M_n = 8000$, $M_w/M_n = 1.75$), PBSe ($M_w = 17000$, $M_n = 10000$, $M_w/M_n = 1.7$).

The molar masses of the unfractionated polymer samples were also calculated with the universal calibration curve which was obtained using a set of 12 polymethylmathacrylate and fourteen polystyrene well characterized samples (purchased from Polymer Lab) having a narrow molar mass distribution ($M_w/M_n < 1.1$).[2,6] We measured the viscosity (η) and the elution volume at which the GPC trace takes its tallest value (V_R) and plotted the log(ηM) vs V_R. The resulting line was the Universal Calibration line for our set of SEC columns and it fits with the following equation:[6] $\log(\eta M) = 0.016(V_R)^2 - 1.76V_e + 22.7$. Molar mass data (Table 1) were calculated by considering the viscosity of unfractionated copolymer samples and the elution volume at the maximum of the SEC curves.

NMR Analysis. The ^{1}H and ^{13}C NMR characterizations were performed by on a Brucker A-CF 200 spectrometer at room temperature using deuterated chloroform as solvent and tetramethylsilane as standard.

Viscosimetry. Inherent viscosities ($\eta_{inh} = (\ln \eta_r)/C$; $C = 0.5$ g/dL) were measured in a Desreux-Bishoff suspended-level viscometer at 30 ± 01 °C. The solvents were $CHCl_3$ or THF depending on the specific solubility of the polymers. Inherent viscosity values of homopolymers and copolymers are given in Table 1.

Results and Discussion

In Table 1 are listed the structure and properties of the homo- and co-polyesters studied, which contain butylene adipate (BA), butylene succinate (BSu), and butylene sebacate, (BSe) units. These copolyesters have flexible chains and do possess a homogeneous composition, since they were synthesized by condensation polymerization. The synthesis was performed starting from a mixture of the dimethyl esters and stoichiometric amount of 1,4-butanediol (see Experimental Section), producing random copolymers.

All the polymerization reactions were conducted to completion, and therefore the copolyesters compositions are given by the monomer ratio in the feed, as checked by NMR analysis.

Only some homopolyesters and copolyesters are soluble in THF, but all are soluble in $CHCl_3$. SEC fractionation was performed in these solvents, and the fractions collected were used for the MALDI analysis.

The methodology consists of the analytical SEC fractionation of polydisperse samples and the collection of numerous fractions per run.

Typically, injecting about 0.5−1 mg of polymer in the GPC system and collecting about 25−100 fractions, the amount of sample present in each fraction (about 5 μg, on average) exceeded many times the quantity needed for a MALDI spectrum. Selected fractions were then analyzed by MALDI−TOF, and the mass spectra of these nearly monodisperse samples allowed the computation of reliable values of the molar masses corresponding to the fractions. The calibrated SEC trace could then be used to compute average MM and MMD of the unfractionated sample.

In Figure 1 is shown an illustrative example of the SEC trace, together with some MALDI spectra of fractions 5, 7, 9, and 12, taken at different elution times (32.6, 34, 35.5, and 37.6 mL, respectively).

In Tables 1S and 2S are reported the average molar masses and molar mass distributions obtained by the analysis of the MALDI−TOF spectra of selected SEC fractions of each copolymer in Table 1. The three

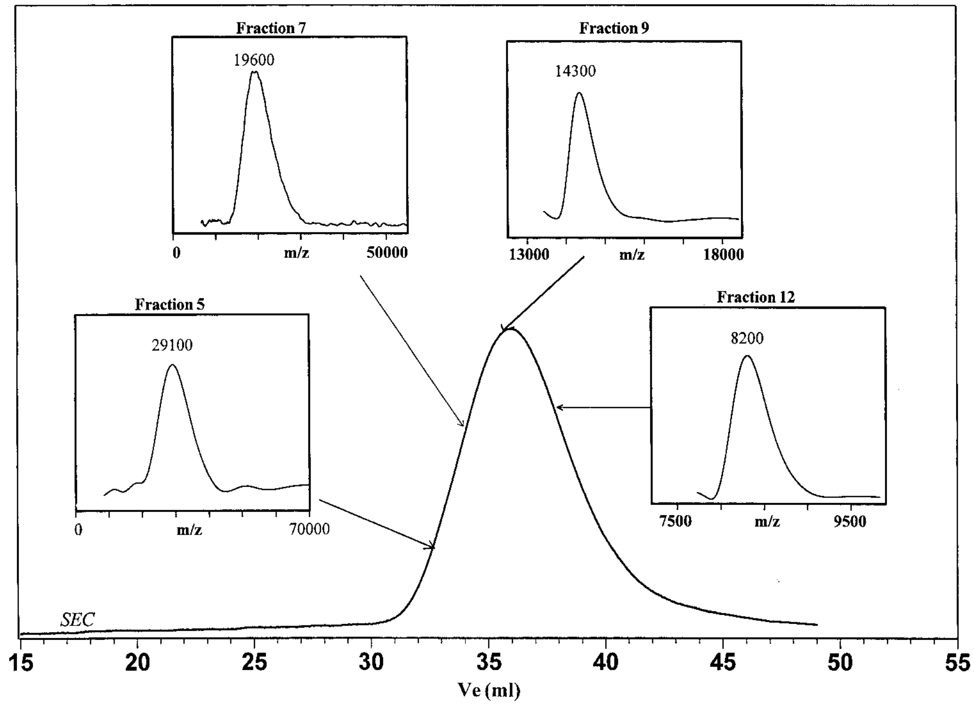

Figure 1. GPC trace of PBA/PBSe copolymer (solvent THF). The insets display the MALDI−TOF spectra of fractions 5, 7, 9, and 12.

homopolymers (PBA, PBSu, and PBSe, respectively), were subject to SEC fractionation too (Tables 1S and 2S).

Data in Tables 1S and 2S show that narrow MMD were obtained for each fraction. These data were used to build absolute calibration plots (log M vs V_e) corresponding to the polymers investigated. The calibrated SEC tracings against absolute molar masses were then used to compute average molar masses and molar mass distributions corresponding to the homo- and copolyesters (see Experimental).

The results of these calculations (M_w, M_n, and M_w/M_n) are reported in Table 1 together with the estimates computed from the SEC universal calibration curve for the weight average molar mass.

As expected, the universal calibration method provides only rough estimates of the weight average molar mass, with errors that can amount to a factor of 2 (Table 1). Average M_n values for the copolymers in Table 1 indicate conversions in the range of 0.97, and therefore the polydispersity indexes (M_n/M_w) measured (1.5−1.8) appear lower than expected. This fact can be due to purification procedures that strip the low masses from the crude sample.

In Figure 2 are shown the calibration lines for the SEC traces in chloroform of the three homopolymers PBSe, PBA, and PBSu. Apparently, the hydrodynamic volumes of the three polyesters lay in the order PBSe > PBA > PBSU, showing a correlation with their chemical structure.

In Figure 3 are reported the calibration lines for the SEC traces of the two homopolymers PBSe and PBA and also the one corresponding to the copolymer PBA/PBSe in THF as eluent.

The dotted line is the calibration line for the SEC trace of the copolymer PBA/PBSe calculated by means of eq 1.

This picture allows one to perceive immediately that the copolymer PBA/PBSe deviates, nearly over its entire molar mass range, from the additivity of hydrodynamic volumes predicted by eq 1.

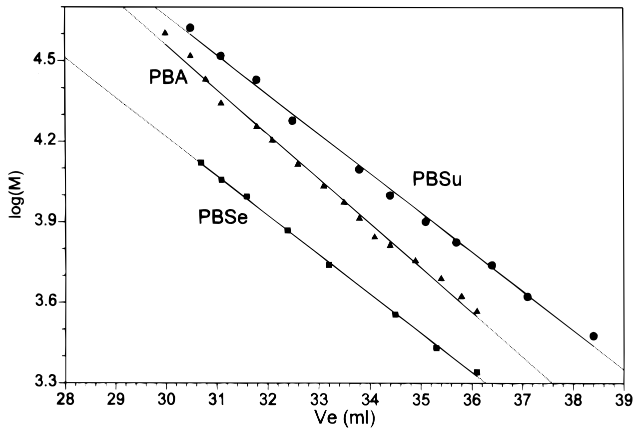

Figure 2. Calibration lines for the SEC trace of PBA, PBSu, and PBSe copolymer using $CHCl_3$ as solvent.

However, the values of the hydrodynamic interaction parameter β, listed in Table 2, appear to decrease significantly toward higher masses, showing the tendency to become nearly negligible for masses over 30 000.

In Figure 4 is reported a similar picture corresponding to the copolymer PBSu/PBA in $CHCl_3$ as eluent. The same behavior is observed; i.e., values of the hydrodynamic interaction parameter β, listed in Table 2, appear to decrease significantly toward higher masses, showing the tendency to become nearly negligible for masses over 30 000.

These results might be interpreted as indicating that, for flexible-chain random copolymers, the deviations of the molar masses from the simple additivity rule assumed in eq 1 are quite sensible for copolymer molecules of low molar masses, whereas at higher masses these deviations tend to disappear. It might appear that, provided the molar mass of a monodisperse

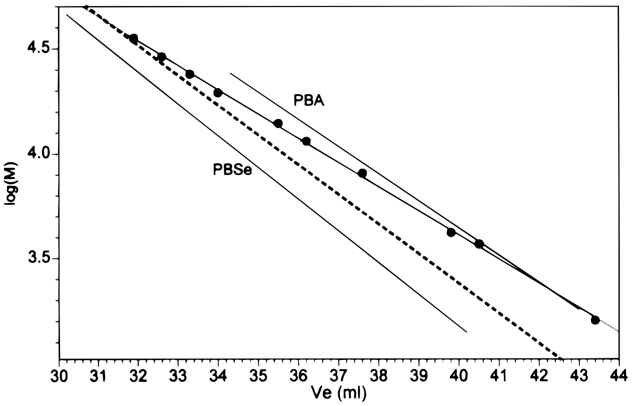

Figure 3. Calibration lines for the SEC trace of PBA, PBSe and PBA/PBSe copolymer (●) using THF as solvent. The dotted line is the calibration line for the GPC trace of PBA/PBSe copolymer, calculated by means of eq 1.

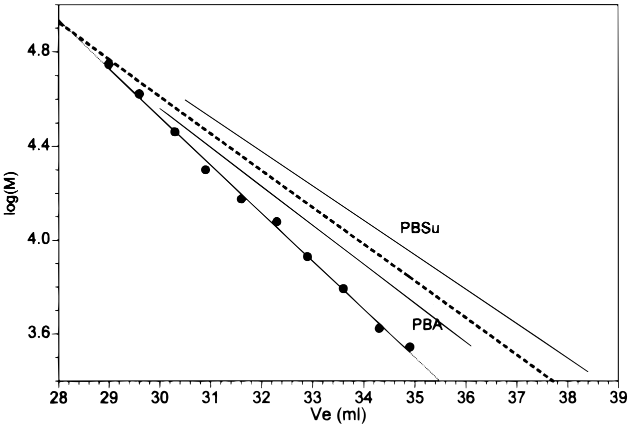

Figure 4. Calibration lines for the SEC trace of PBA, PBSu, and PBSu/PBA copolymer (●) using $CHCl_3$ as solvent. The dotted line is the calibration line for the GPC trace of PBSu/PBA copolymer, calculated by means of eq 1.

copolymer is sufficiently high, the presence of two comonomer units along the copolymer chain does not induce sensible changes in the overall chain dimensions with respect to those expected for a mixture of the two homopolymers.

In general, however, this happens not to be the case for all the random copolyesters investigated. In fact, for the systems PBSu/PBSe and PBA/PBSe, reported respectively in Figures 5 and 6, the SEC calibration traces of the copolymer calculated by means of eq 1, deviate from the experimental line for all the measured MM values.

This is also true for the terpolymer PBSu/PBA/PBSe (Figure 7), where the SEC calibration traces of the copolymer calculated by means of eq 8 (for $\gamma = 0$), deviate from the experimental line for all the measured MM values.

In $CHCl_3$, apparently, the presence of butylene sebacate units in the copolymer chain is capable of inducing a sensible increment of the hydrodynamic volume.

For the copolymer PBA/PBSe the SEC/MALDI data are available both in THF and $CHCl_3$ (in Figures 3 and 6, respectively), allowing an estimate of the changes in the value of β due to solvent effects (Table 2).

Therefore, in all the cases investigated it has been found that the molar mass of a random copolyester molecule cannot be estimated by averaging the molar masses of the homopolymers measured at the same elution volume of the copolymer. Instead, the more complex eqs 5 and 8 provide an estimate of the β hydrodynamic interaction parameter, showing that sensible errors (up to 50−100%; Table 2) can be made if the molar masses are calculated by simple averaging.

Table 2. Hydrodynamic Interaction Factor for the Copolymer Samples

sample	solvent	V_e[a]	HIF[b]	M_{exp}[c]	M_{calc}[d]	Δ%[e]
PBA/PBSe	THF	43.4	0.331	1700	790	73
		40.5	0.257	3700	2050	58
		39.8	0.223	4300	2580	51
		37.6	0.211	8600	5280	48
		36.2	0.153	8350	8350	36
		35.5	0.145	10500	10500	34
		34.0	0.081	17150	17150	16
		33.3	0.054	21600	21600	13
		32.4	0.037	27100	27100	9
		31.9	0.021	35900	34100	6
PBSu/PBA	$CHCl_3$	34.9	−0.274	3700	6950	60
		34.3	−0.303	4300	8650	66
		33.6	−0.234	6500	11100	52
		32.9	−0.207	8900	14300	46
		32.3	−0.147	12700	17800	33
		31.6	−0.179	15200	22950	40
		30.9	−0.157	20600	29550	35
		30.3	−0.093	29700	36700	21
		29.6	−0.037	43500	46300	8
		29.0	−0.015	56900	58800	3
PBSu/PBSe	$CHCl_3$	35.8	−0.189	2300	3550	42
		35.0	−0.191	3000	4650	43
		33.7	−0.206	4500	7200	46
		32.9	−0.198	6000	9450	44
		32.0	−0.205	8000	12800	46
		31.2	−0.201	10600	16800	45
		30.4	−0.264	12000	22000	58
PBA/PBSe	$CHCl_3$	35.4	−0.137	2500	3400	31
		34.9	−0.147	2900	4070	33
		34.4	−0.156	3400	4860	35
		33.8	−0.178	4000	6050	40
		33.3	−0.177	4800	7200	40
		32.8	−0.172	5800	8600	39
		32.2	−0.184	7000	10700	41
		31.7	−0.182	8400	12750	41
		31.2	−0.171	10300	15250	38
		30.7	−0.175	12200	18250	39
		30.1	−0.188	14700	22600	42
		29.6	−0.182	17800	27000	41
		29.1	−0.168	22000	32300	37
		28.5	−0.164	27500	40050	37
PBSu/PBA/PBSe	$CHCl_3$	34.7	−0.133	4000	5400	30
		34.1	−0.141	4850	6700	31
		33.2	−0.165	6300	9200	37
		32.7	−0.248	6200	10950	55
		32.3	−0.212	7750	12600	47
		31.8	−0.183	9900	15050	41
		31.4	−0.202	10900	17300	45
		31.2	−0.217	11300	18570	48
		31.1	−0.206	12000	19250	46
		30.7	−0.216	13500	22150	48
		30.3	−0.203	16000	25500	45
		29.8	−0.205	19000	30400	46

[a] Elution volume (in mL) at which the fraction was collected. [b] Hydrodynamic interaction factor computed using eq 5 or eq 8. [c] Measured mass of the copolymer as resulting by MALDI MS. [d] Calculated mass of the copolymer, computed using eq 5 (for $\beta = 0$) or eq 8 (for $\gamma = 0$). [e] Values of the ratio $|M_{calc} - M_{exp}|100/(0.5(M_{calc} + M_{exp}))$, as resulting from the values of M_{calc} and M_{exp} in columns 4 and 5.

Conclusions

The combination of SEC with MALDI mass spectrometry, an absolute method for the determination of molar masses, brings new possibilities to copolymer analysis.

Only scant data have appeared in the literature on MM determination of copolymers by SEC because the

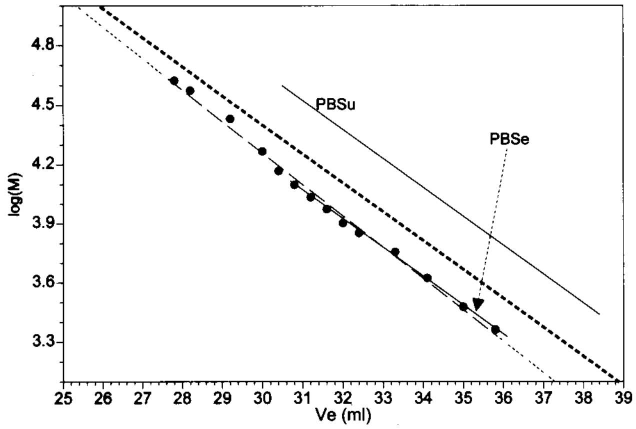

Figure 5. Calibration lines for the SEC trace of PBSe, PBSu, and PBSu/PBSe copolymer (●) using $CHCl_3$ as solvent. The dotted line is the calibration line for the GPC trace of PBSu/PBSe copolymer, calculated by means of eq 1.

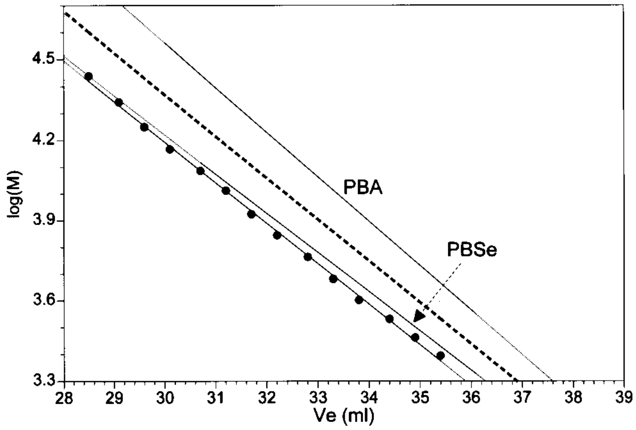

Figure 6. Calibration lines for the SEC trace of PBA, PBSe, and PBA/PBSe copolymer (●) using $CHCl_3$ as solvent. The dotted line is the calibration line for the GPC trace of PBSu/PBSe copolymer, calculated by means of eq 1.

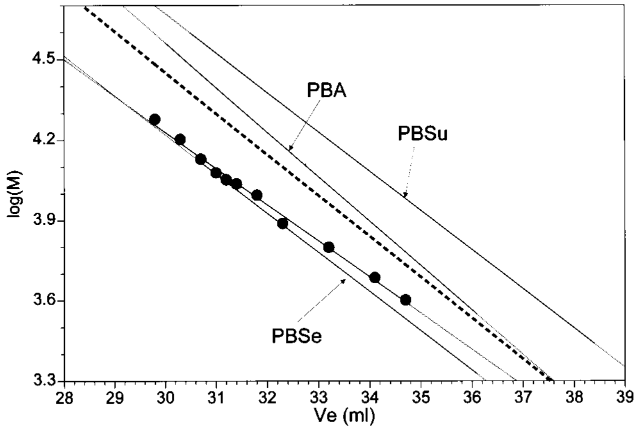

Figure 7. Calibration lines for the SEC trace of PBSu, PBA, PBSe, and PBSu/PBA/PBSe copolymer (●) using $CHCl_3$ as solvent. The dotted line is the calibration line for the GPC trace of PBSu/PBA/PBSe copolymer, calculated by means of eq 8 (for $\gamma = 0$).

conventional detectors (LALLS, viscosity) have too low sensitivity to be applied routinely in all the range of high and low MM.

SEC/MALDI instead can be applied routinely and reliably. Because of its unprecedented sensitivity, MALDI constitutes an excellent SEC detector and permitted us to accumulate a remarkable amount of high quality data on the series of aliphatic homo- and co-polyesters investigated.

The sensible deviations from the simple additivity found over nearly all the molar mass range of the copolymers studied imply that the presence of two comonomer units along the copolymer chain induces also changes in the overall chain dimensions with respect to those expected for a mixture of the two homopolymers.

Acknowledgment. The active collaboration of Sabrina Carroccio to this work is acknowledged. Partial financial support from the Italian Ministry for University and for Scientific and Technological Research (MURST), from Progetto Finalizzato Materiali per Tecnologie Avanzate (CNR, Rome), and from the National Council of Research (CNR, Rome) is gratefully acknowledged.

APPENDIX

In this appendix we derive the complete equation for the calibration curve of a copolymer. Equation 5 holds for one molar mass only, whereas the terms which contain $[\eta]_A$, $[\eta]_B$, and $[\eta]_C$ in β depend on the molar mass.

More specifically, if the viscosity of a polymer is assumed to increase with its mass with a law of the type kM^a, where k and a are two parameters, one has

$$\log([\eta]_A) = \log(k_A) + a_A \log(M_A) \tag{A1}$$

$$\log([\eta]_B) = \log(k_B) + a_B \log(M_B) \tag{A2}$$

$$\log([\eta]_C) = \log(k_C) + a_C \log(M_C) \tag{A3}$$

where k_A, k_B, k_C, a_A, a_B, and a_C are parameters. Using the above equations, the calibration curve for the copolymer becomes

$$\log(M_C) = z_A \log(M_A) + z_B \log(M_B) + z_C \tag{A4}$$

$$z_A = w_A(1 + a_A)/(1 + a_C) \tag{A5}$$

$$z_B = (1 - w_A)\,(1 + a_B)/(1 + a_C) \tag{A6}$$

$$z_C = (w_A \log(k_A) + (1 - w_A) \log(k_B) - \log(k_C))/(1 + a_C) \tag{A7}$$

To solve eq A4 (holding at any V_e), one needs to know the k and a values for the three samples.

Supporting Information Available: Table 1S, reporting the average molar masses and molar mass distributions obtained by the analysis of the MALDI–TOF spectra of SEC fractions of samples PBA, PBSe, and PBA\PBSe using THF as a solvent, Table 2S, reporting the average molar masses and molar mass distributions obtained by the analysis of the MALDI–TOF spectra of SEC fractions of samples PBSu, PBA,-PBSe, PBSu/PBA, PBSu/PBSe, PBA/PBSe, and PBSu/PBA/PBSe using $CHCl_3$ as a solvent, Figure 1S–3S, reporting the SEC traces for samples PBA, PBSe, and PBA\PBSe using THF as a solvent, and Figures 4S–10S reporting the SEC traces for samples PBSu, PBA,PBSe, PBSu/PBA, PBSu/PBSe, PBA/PBSe, and PBSu/PBA/PBSe using $CHCl_3$ as a solvent (17 pages). Ordering and Internet access information is given on any masthead page

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MA980019A