2180 *Macromolecules* **1999,** *32,* 2180−2187

Analysis of Diblock Copolymers of Poly(α-methylstyrene)-*block*-polystyrene by Mass Spectrometry

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Received October 10, 1998; Revised Manuscript Received February 2, 1999

ABSTRACT: The individual block length distributions of a series of diblock copolymers, polystyrene-*b*-poly(α-methylstyrene), were determined by the MAC MALDI/TOF MS method of analysis of copolymers which combines matrix-assisted laser desorption/ionization time-of-flight mass spectrometry with computational data treatment. The robustness of the calculation technique was evaluated. The presence of unreacted homopolymer was observed as well bimodal and trimodal distributions for the poly(α-methylstyrene) segments. A new method to verify the random coupling hypothesis has been proposed. The hypothesis was verified to hold within the experimental error of the technique for all the correct assignments of polymers studied. The experimental distributions have been compared with the Poisson, Schulz−Zimm, Tung, and logarithmic-normal models, modified to account for the change of variables. The equations of the Tung model, which was found to have the best predictive capability for the PαMS blocks, were transformed into the analytical form. Overall, the Schulz−Zimm model remains the most flexible of all models.

Introduction

In the past three decades, block copolymers have been of scientific and technological interest, due to their phase behavior as well as actual and potential applications.[1,2] The properties of block copolymers are determined by the chain length of the individual segments and their distribution. For example, it has been shown that dimensions of aggregates of the smaller block in phase-separated systems are a function of both the average block length and the block length distribution.[3] Furthermore, it can be anticipated that brush density profiles will be very much a function of the individual block length distribution. The field of brush formation has received considerable attention recently.[4]

Block copolymers are prepared most frequently by anionic polymerization, which gives chemists a very powerful tool for the control of architecture, molecular weight, and polydispersity of the block copolymers.[5] When a block copolymer is prepared through a sequential anionic polymerization of two monomers, the length distributions of both segments reflect the mechanistic aspects of both the initiation and the propagation steps of the polymerization. Therefore, to understand better the block copolymerization process for two monomers, it is essential to know the detailed structural parameters of the resulting block copolymers.

Recently, a general method of independent determination of the chain lengths distribution by MALDI-TOF mass spectrometry was developed for both constituent parts of a block copolymer.[6] The proposed method gives the possibility of directly obtaining the experimental composition distribution for block copolymers, formed from two precursors. Using this technique, it was possible to verify experimentally the random coupling hypothesis. It was also feasible to confirm that block copolymers with narrow molecular weight distributions may have broad, complex, and even bimodal composition distributions. The polydispersity factors observed for individual parts were higher than those for the whole polymer.

The polymers first studied[6] were of the type ABA, where A corresponds to a poly(α-methylstyrene) chain and B to a polystyrene chain. As in the past, for the present work, the PS−PαMS block system is an ideal candidate for a study of molecular weight distribution in individual blocks because of the great chemical similarity of the two components. Thus, no unusual problems are to be expected due to differing kinetics of initiation and propagation, as is sometimes encountered in diblocks involving two very different monomers.

In the previous study,[6] PS−PαMS block copolymers, prepared under conditions where the PαMS was the first block to be polymerized with a *sec*-butyllithium initiator, were investigated. Because of the proximity to the ceiling temperature,[7,8] the α-methylstyrene did not polymerize completely in the first step. As a result, the remaining αMS had an opportunity to polymerize further after the styrene was completely polymerized. Thus, an asymmetric triblock resulted. While this type of polymerization was interesting in itself, it did not answer the general question of individual block length distribution in diblocks. Furthermore, a number of additional questions were of interest. Since the method used involves the preparation of families of diblocks with an identical first block, but varying second block lengths, it was of interest to see to what extent collateral termination accompanying the sequential second monomer addition could be detected.

Each new analytical method needs to be extensively tested to explore its potential and limitations. In this work, which is a continuation of a former study,[6] we

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10.1021/ma981594h CCC: $18.00 © 1999 American Chemical Society
Published on Web 03/17/1999

analyze again the series of polystyrene-*b*-poly(α-methylstyrene) block copolymers. This time, however, the polymer series consists strictly of diblocks, with an identical length of the first segment, and various lengths of the second block. As before,[6] the experimental distributions were determined by MALDI-TOF mass spectrometry, using the data treatment described previously.[6] For brevity, the whole procedure is called in this paper the MAC MALDI/TOF MS technique (method of analysis of copolymers by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry). To evaluate the error introduced by the computation part of the method, we evaluated the robustness of the peak assessment procedure and the calculation technique.

It has been established that MALDI-TOF MS measurements can provide correct molecular weight averages for samples with narrow MW distribution ($M_w/M_n \leq 1.20$). For polydisperse polymers different laboratories report a different level of success.[9−14] Therefore, we have limited our study to block copolymers with a low polydispersity index. As it is known that degradation and selective desorption of polymer can cause uncertainty in MALDI measurements,[9,12,15,16] the results are compared with the SEC and with the NMR data.

Unexpectedly, the unimodal experimental number distribution of segments of poly(α-methylstyrene) was not satisfactorily described by either Schulz−Zimm[17−19] or Poisson[20] models. Therefore, two additional models, Tung[21] and normal logarithmic,[19,20] were tested. It was necessary to modify the existing equations, to make them readily applicable to block copolymers. To facilitate calculations, the nonanalytical Tung model was transformed into an analytical form. The correlation capability of the four models was studied and compared. Random coupling hypothesis was verified again using a new more realistic statistical approach.

Experimental Section

Chemicals. Tetrahydrofuran (THF) (Aldrich) was dried by refluxing over sodium benzophenone complex under nitrogen atmosphere. A blue-violet color indicating an oxygen and moisture-free solvent was observed. The THF was further distilled under dry nitrogen over poly(styryllithium). Styrene (Aldrich) and α-methylstyrene (Aldrich) were dried over calcium hydride for 24 h, distilled under vacuum, and stored under nitrogen at −20 °C. Styrene and α-methylstyrene were subsequently treated with fluorenyllithium for 30 min and distilled under vacuum just before polymerization. *sec*-Butyllithium (Aldrich) was used as received.

Anionic Synthesis of Polystyrene-*b*-poly(α-methylstyrene) Diblock Copolymers. The anionic block copolymerization of styrene and α-methylstyrene was performed under a nitrogen atmosphere in a previously flamed glass reactor. THF was added into the glass reactor, followed by the proper amount of *sec*-butyllithium. After the solution was cooled to −78 °C, the calculated amount of styrene needed for a specific molecular weight of PS was added dropwise by means of a stainless steel capillary. During this addition, the reacting mixture was stirred vigorously. The deep orange-yellow color, characteristic of the poly(styryllithium), developed quickly upon addition of the first drop of styrene. Ten minutes after the last drop of styrene was added, an aliquot of the reaction mixture was withdrawn for analysis by SEC in order to determine the degree of polymerization of the polystyrene block.

α-Methylstyrene was then added to the polymerization medium. Upon addition of a few drops of the α-methylstyrene, the deep orange-yellow color of living poly(styryllithium) anions changed instantaneously to the deep red color, characteristic of the poly(α-methylstyryllithium). After 10 min, an aliquot of the reaction medium was withdrawn. This was the first diblock copolymer with the shortest poly(α-methylstyrene) chain attached to the polystyrene block. This procedure was repeated two times to obtain three different polystyrene-*b*-poly(α-methylstyrene) diblock copolymers having the same length of the polystyrene block but a varying length of the poly(α-methylstyrene) segment. The polymers were recovered by precipitation in methanol and dried under vacuum at 80 °C for 48 h.

Table 1. Chemical Composition of PS-*b*-PαMS Diblock Copolymers

sample no.	n_{PS}-*b*-$n_{PαMS}$: theoretical composition[a]	n_{PS}-*b*-$n_{PαMS}$: composition determined by SEC	polydispersity index
PS1	6-*b*-6	5.6-*b*-5.7	1.15
PS2	6-*b*-12	5.6-*b*-12.2	1.07
PS3	6-*b*-24	5.6-*b*-22.4	1.07

[a] Calculated from monomers ratios.

Size-Exclusion Chromatography. Size-exclusion chromatography (SEC) measurements were carried out with THF as a solvent on a Varian 5010 liquid chromatography apparatus, equipped with a refractive index detector. THF was used for elution at a flow rate of 1 mL/min. The column was a progel-TSK G4000 HXL from Supelco, Inc. The system was calibrated with "monodisperse" polystyrene. The concentration of the injected polymer solution was about 2 mg/mL. The solution was filtered through membrane filters before injection. The molecular weight and distribution of the polymers were calculated by a Varian DS-604 computer with SEC application software.

Mass Spectrometry. MALDI-TOF measurements were performed with the PerSeptive Biosystems Voyager-DE and Voyager-DE STR mass spectrometers, using linear mode. For all cases, 20 kV acceleration was used with delayed extraction. The nitrogen laser (337 nm, 3 ns pulse width) operating at 5 Hz produced spectra by summing 250 shots. The spectra were externally calibrated (with two points) using peptide standards. All spectra were baseline corrected and smoothed. Samples were prepared with a dithranol (10 mg/mL) matrix with silver trifluoroacetate (AgTFA) (1 mg/mL). The polymer sample (1 mg/mL) was mixed 20:20:1 v/v (matrix:polymer: AgTFA). Approximately 0.5 μL of this solution in tetrahydrofuran was applied to the sample plate.

Results and Discussion

Polymer Samples. In the previous paper,[6] two PαMS-*b*-PS-*b*-PαMS triblock copolymers were analyzed by the MAC MALDI/TOF MS technique. The length distributions of both PαMS (in total) and PS blocks were determined, but the individual lengths of PαMS blocks at each end of the polymer chains were not known since the method of preparation involved the addition of styrene monomer to the monofunctional living PαMS solution above its ceiling temperature. Thus, an αMS segment was added to the chain at the end of the polymerization after all the PS had polymerized. In the present study, the lengths of both PαMS and PS blocks in the diblock are well-defined.

Table 1 reports the characteristic features of the PS-*b*-PαMS diblock copolymers used in the present study. The number of units in the PS block was assumed to be constant for all the samples. All the block copolymers have a narrow molecular weight distribution determined by SEC. The experimentally determined compositions were in good agreement with the values calculated from the monomer/initiator ratios. All three samples are thus expected to have the same length of PS block. The mole ratio of PαMS/PS changes from 1 to 4.

Table 2. Characteristic Parameters of MALDI/TOF Spectra

sample no.	min value of *m*/*z*[a]	max value of *m*/*z*[a]	no. of peaks	no. of peak clusters	position of strongest peak
PS1	819	2354	107	15	1397
PS2	1216	3302	141	19	2107
PS3	1347	5197	248	32	3187

[a] The *m*/*z* values include the copolymer, butyl group, proton, and silver ion. See eq 1.

The molecular weights of individual blocks within each polymer were determined by SEC, assuming that the methyl group in PαMS has only a minor effect on the elution time as compared to the case of PS. The precision and accuracy of the SEC method had been estimated in a separate study. It was found that the precision of determination of the molecular weight was better than 2.5%. The average molecular weight obtained was not significantly different from the molecular weight of the PS standard. The polydispersity index was reproducible within 0.5%.

Robustness of the Calculation Technique. The precision and accuracy of any property determined by an experimental technique depends on the experimental procedure and the instruments used. In addition, the data treatment itself can be the source of an easy to overlook error. In the following sections each computational step of the the "MAC MALDI/TOF MS" method is discussed in terms of its possible contribution to the final error of determination.

Peak Assignment Procedure. Mass spectra of diblock copolymers consist of multiple peaks grouped in numerous clusters.[6] The number and complexity of these clusters increase with molecular weight of a sample. The most basic properties of the MALDI/TOF spectra of samples studied in this work are summarized in Table 2.

Molecular weight distributions of polymers made by anionic technique are generally narrower relative to those made by other polymerization procedures, such as free radical polymerization or polycondensation. Even so, the mass spectrum of such polymers consists of multiple peaks, each of which represents a particular combination of the two monomers.

As explained elsewhere,[6] every molecule of the diblock copolymer, AB, initiated by *sec*-butyllithium consists of one butyl group at one end, a number of A-type and B-type units in the middle, and one proton on the other end of the chain. In the course of ionization for MALDI-TOF measurements, an oligomeric ion is formed by attachment of one silver cation to the molecular chain. For a molecule with n_A number of A units and n_B number of B units, of corresponding molecular weights M_A^0 and M_B^0, the following equation can be used to calculate the value of *m*/*z*:

$$(m/z)_{\mathrm{calc}} = n_A M_A^0 + n_B M_B^0 + (M_{\mathrm{butyl}}^0 + M_{\mathrm{Ag}} + M_{\mathrm{H}}) \quad (1)$$

In this work, the index A corresponds to PS and B represents PαMS. The molecular weights used in calculations are $M_{\mathrm{PS}}^0 = 104.15$, $M_{\mathrm{P\alpha MS}}^0 = 118.18$, $M_{\mathrm{butyl}}^0 = 57.115$, $M_{\mathrm{Ag}} = 107.868$, and $M_{\mathrm{H}} = 1.008$ mass units. As the silver doublet was not resolved, the average molecular weight of silver was used.

The MAC MALDI/TOF MS method of assigning chemical composition to particular peaks has been described previously.[6] The key problem is to find a combination of n_A and n_B values that would match the experimental value of *m*/*z*. As only one equation (eq 1) relates two variables, n_A and n_B, many solutions are possible. Therefore, to find the right pair of values, additional information is needed on the chemical composition of the sample. This information can come from the knowledge of the monomer ratios used for the synthesis or from an experimental technique that allows to independently determine the chemical composition of a sample (for example, SEC coupled with NMR).

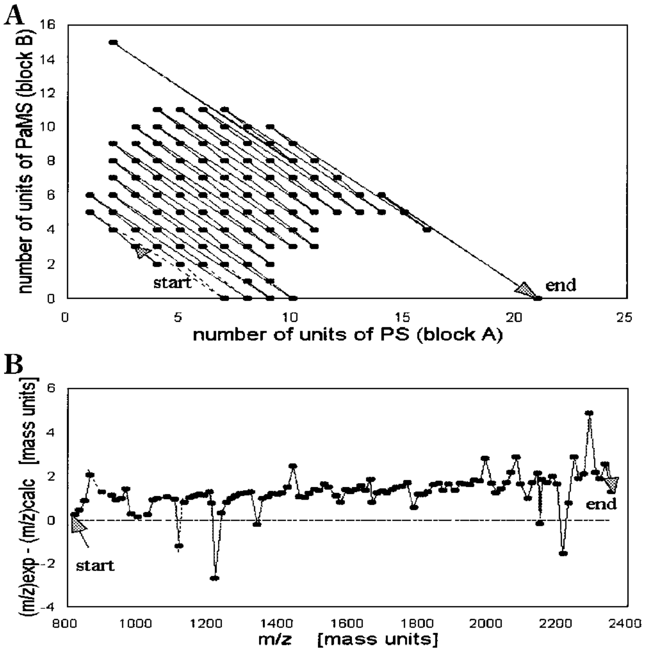

Figure 1. Assignment of chemical composition in the sample PS1. (A) The map of the assigned pairs of number of units of PS and PαMS. "Start" denotes the first peak of the spectrum with the lowest value of *m*/*z*, and "end" represents the last peak. (B) Difference between the experimental and calculated values of *m*/*z*.

After this step, the chemical composition of other peaks can be assigned as described previously.[6] Two properties of the MS spectrum are used: (1) When shifting from one of the strongest peaks to another, one of the coordinates n_A or n_B is constant, while the other increases by one unit when passing from a group of lower values of *m*/*z* to a group with higher values of *m*/*z*. (2) Within a group of peaks, the numbers of segments of the heavier monomer are increasing with increasing mass, while the numbers of segments of the lighter monomer are decreasing. The above rules are more general than those presented in the previous paper.

Sample PS1. After an initial assignment of $n_{\mathrm{PS}} = 5$ and $n_{\mathrm{P\alpha MS}} = 6$ to the strongest peak in the spectrum at (*m*/*z*) equal to 1397, the chemical composition of all the other peaks was uniquely determined. Figure 1 shows the assignment of chemical composition and the difference of the experimental and calculated *m*/*z* values of the sample PS1.

Figure 1A presents the coordinates (number of units of PαMS vs number of units of PS) of all but four peaks of the MS spectrum of the sample PS1. The points representing neighboring peaks are connected with a solid line. Four peaks (883, 914, 1021, 1123) could not be identified, and they are not shown in Figure 1A,B. The dotted lines in the plot mark these gaps between peaks. The possible assignments for these four peaks produced deviations from the experimental values of m/z more than 4 times greater than the average deviation obtained for the whole spectrum. Two of the unidentified peaks are the weakest peaks in their clusters. The omitted peaks contributed 1.7% to the sum of all the peak heights or 2.1% to the sum of all peak areas. Figure 1A also shows that five peaks belong to homopolystyrene (homo-PS). These peaks have their second coordinate equal to zero, as there is no PαMS present.

The coordinates of the peaks, shown in Figure 1A, were used to calculate the values of $(m/z)_{\mathrm{calc}}$ according to eq 1. Figure 1B presents the differences (Δ) between the experimental and calculated values of m/z for all but four MS peaks. These deviations are reasonably small and for most peaks within the range of experimental error (below 2 mass units). It is interesting to note that the absolute value of Δ increased with increasing m/z values. The same tendency can be observed in each group of peaks. Figure 1B also shows that occasionally the deviation between the calculated and experimental values is bigger than normal, particularly for some peaks at the beginning or at the end of a group of peaks. In general, the experimental values are slightly higher than the calculated ones.

Sample PS2. Multiple peaks of the sample PS2 were identified in the same way described above.

The calculated value of (m/z) equal to 2105, which corresponds to $n_{\mathrm{PS}} = 5$ and $n_{\mathrm{P\alpha MS}} = 12$, is the most probable assignment for the strongest peak of sample PS2. The length of polystyrene block in the sample PS2 is the same as that in the sample PS1 (five units), but the PαMS block is twice as long. Assignment of other peaks was performed as before. The differences between the experimental and calculated masses are greater than in sample PS1. Once again, the absolute value of Δ increases with increasing m/z values, and the same tendency can also be seen in each group of peaks. It is worth noting that homopolystyrene was not observed in sample PS2, which indicates that all the homopolystyrene in sample PS1 was still alive at the time of the second addition of the αMS monomer.

Sample PS3. Peak identification of the sample PS3 was more complicated. The calculated value of m/z equal to 3186 is the closest to the experimental value of 3187. However, this corresponds to $n_{\mathrm{PS}} = 29$ and $n_{\mathrm{P\alpha MS}} = 0$, which is too far from the real chemical composition as determined by other techniques. Two other pairs of values (12,15) and (20, 8) are not consistent with the chemical composition either. From the two pairs (3, 23) and (4, 22) the last one is the one that presents the best agreement with the ratios of monomers used for the synthesis. Additionally, as indicated by the results from the previous study,[6] the difference, Δ, between the experimental and calculated mass increases with the value of m/z. The approximate relation is $\Delta \approx 0.001m/z$. The deviation of 4.62 is of the right order of magnitude for the value of m/z equal to 3187. Therefore, the pair (4, 22) was chosen. After this step, other peaks were assigned.

Sample PS3, with the highest molecular weight, posed a new problem with the peak assignments that was not observed for two previous samples. It was noticed that, at the end of some groups of peaks (for m/z higher than 3100), two assignments were possible; thus, it was possible either to continue with the same group or to start a new one. The first cluster, in which this phenomenon was observed, starts at 3115 with the pair (9, 17), which corresponds to $n_{\mathrm{PS}} = 9$ and $n_{\mathrm{P\alpha MS}} = 17$. Then, as described before, the number of segments of the heavier monomer (αMS) is increasing with increasing mass, while the number of segments of the lighter monomer (S) is decreasing. For the last peak in the series (3216), there are two possible combinations: (2, 24) as the last member of this cluster or (10, 17) as the first member of the next group. The last combination gives a much smaller deviation from the experimental m/z value than the first one. Nevertheless, this small deviation is unusual for the whole series presented. Therefore, for further data processing, the (2, 24) assignment was chosen. Similarly, in all the subsequent peak groups, the coordinates of the last peak were selected as a continuation of the finishing cluster. The peaks that could be interpreted in two different ways contributed 8.1% to the total area. The alternative assignment shifts the calculated parameters for sample PS3 by about 0.5 for the number of units in the block and the polydispersity index by about 0.02. There is an increase in values of these parameters for the PS block and a decrease for the PαMS block.

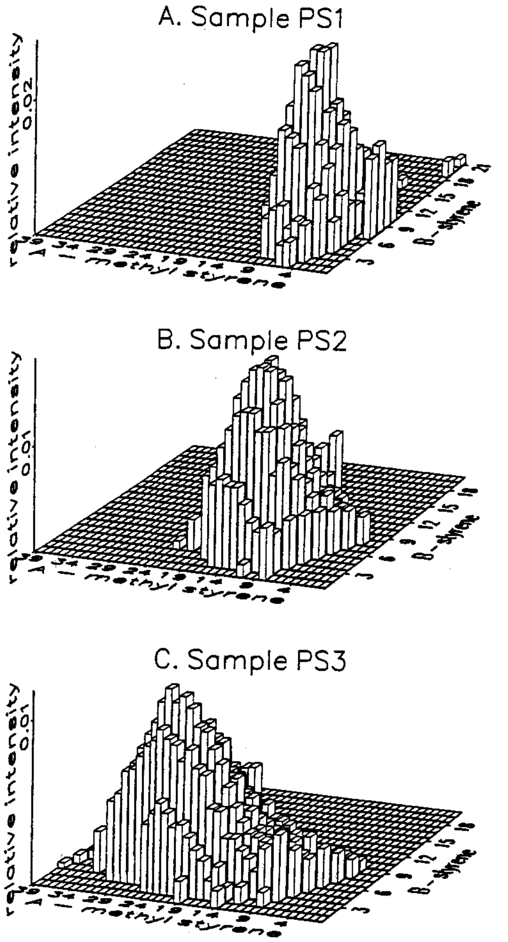

Figure 2. Experimental normalized distribution of units, $N_{\mathrm{exp}}(n_{i_A}^{A}, n_{i_B}^{B})$, for polystyrene-*b*-poly(α-methylstyrene) diblock copolymers: (A) sample PS1, (B) sample PS2, and (C) sample PS3.

3-D Distributions. After the assignment of (n_{PS}, $n_{\mathrm{PS\alpha MS}}$) pairs to all the peaks of the spectrum and the normalization of their intensities, it is possible to create a three-dimensional (3-D) image of the distribution of the number of units in each of the two blocks of the copolymer. Figure 2 shows such distributions for the PS−PαMS samples. The probability surfaces are all well-defined in the range of high intensities. The peripheral low-intensity parts of the surface are subject to experimental error and assignment ambiguity (for high molecular weight samples), and as such they carry less information.

Calculation of Polymer Properties. The next step, calculating the various properties of the samples, was performed according to the method described previously.[6] The explanations of symbols and all the defining equations are presented in the previous paper[6] or in part A of the Supporting Information. To test the robustness of the calculation technique, two questions had to be answered: (1) What is the difference in results caused by the use of the complete spectrum (including the PS homopolymer) as compared to the use of only the normalized peaks for the diblock copolymer? (2) What is the difference in results when the peak heights are used instead of the peak areas?

The presence of the polystyrene homopolymer has been detected in sample PS1. It contributed 5.5% to the total area of peaks. The removal of these peaks before further data processing shifted the average number of units in the PS block toward slightly lower values, 5.87 ± 0.02 vs 6.00 ± 0.01, while raising at the same time the average number of units in the PαMS block, 5.93 ± 0.02 vs 5.66 ± 0.02. The polydispersity index for polystyrene did not change, but for the PαMS it was reduced by about 6%. The properties of the PS homopolymer were calculated separately. The average number of segments was slightly higher than in the copolymer, 8.6 ± 0.1 vs 5.87 ± 0.02, while the polydispersity index was a little lower, 1.065 ± 0.003 vs 1.161 ± 0.001. To obtain full and undistorted information on the system, it is recommended to treat data belonging to the copolymer separately from data of the homopolymer. Both sets should be normalized before further data processing.

The difference between using the heights or areas of peaks, tested on all the samples studied, proved to be insignificant, resulting in the maximum discrepancy of less than 0.1 in the average number of monomer units per block. This gives the precision of the polydispersity ratios better than 0.01. The average molecular weights are precise within 10 mass units for individual blocks and up to 20 mass units for the whole polymer. In all cases the precision of calculations was better than 2%.

Table 3 summarizes the properties of all the diblock copolymers examined in this work. A brief comparison between Tables 1 and 3 reveals an excellent agreement between the properties calculated by the MAC MALDI/TOF MS method and the experimental properties obtained from the monomer ratios used for the synthesis and the SEC technique. The only major difference is observed between the calculated and experimental polydispersity index for the PS1 copolymer. However, the experimental value of 1.15 refers to the mixture of the copolymer and the PS homopolymer. The calculated value of 1.07 corresponds to the copolymer only.

Table 4 contains the comparison of chemical composition of the PS−PαMS diblock copolymers studied using different experimental techniques. All experimental methods agree within experimental error.

Table 3. Comparison of Properties of Samples PS1, PS2, and PS3 (PS-*b*-PαMS)

property	PS1	PS2	PS3
$\bar{n}_{\mathrm{PS}}$	5.8	5.6	5.6
$\bar{n}^{\mathrm{w}}_{\mathrm{PS}}$	6.8	6.5	6.5
$\bar{n}^{\mathrm{w}}_{\mathrm{PS}}/\bar{n}_{\mathrm{PS}}$	1.16	1.16	1.16
$\bar{n}_{\mathrm{P\alpha MS}}$	5.9	11.9	21.4
$\bar{n}^{\mathrm{w}}_{\mathrm{P\alpha MS}}$	6.7	13.0	23.3
$\bar{n}^{\mathrm{w}}_{\mathrm{P\alpha MS}}/\bar{n}_{\mathrm{P\alpha MS}}$	1.13	1.09	1.09
X_{PS}	0.46	0.29	0.19
$X_{\mathrm{P\alpha MS}}$	0.54	0.71	0.81
$M_{\mathrm{n}}{}^{\mathrm{PS}}$	610	585	585
$M_{\mathrm{w}}{}^{\mathrm{PS}}$	710	680	680
$M_{\mathrm{n}}{}^{\mathrm{P\alpha MS}}$	700	1410	2530
$M_{\mathrm{w}}{}^{\mathrm{P\alpha MS}}$	795	1535	2755
M_{n}	1312	1995	3120
M_{w}	1408	2110	3320
PI	1.07	1.06	1.06
P/M_{n}	0.0008	−0.003	−0.006
Q/M_{w}	0.0170	0.010	0.005
no. of peaks	98	141	248
av Δ[a]	1.29	1.52	3.83
std dev of Δ	0.87	1.30	2.13

[a] $\Delta = (m/z)_{\mathrm{exp}} - (m/z)_{\mathrm{cal}}$.

Table 4. Comparison of the Chemical Composition of the Copolymers Obtained by Different Experimental Techniques

	mole fraction of PαMS as determined by			
sample	ratio of reagents	SEC	NMR	MAC MALDI/TOF MS
PS1	0.50	0.50	0.53	0.50
PS2	0.67	0.69	0.71	0.68
PS3	0.80	0.80	0.86	0.80

Marginal Probabilities and the Random Coupling Hypothesis. To verify the assumption of the random coupling hypothesis, which states that the molecular weights of individual parts are not correlated, the experimental marginal probabilities were calculated for all the polymers studied. This was done[6] by summing all the normalized intensities corresponding to the same value of n_{B} (or n_{A}) to obtain the vector of the marginal probability[22] for the part A (or B):

$$N^{\mathrm{A}}_{\mathrm{exp}}\,(n^{\mathrm{A}}_{i_{\mathrm{A}}}) = \sum_{i_{\mathrm{B}}=1}^{N_{\mathrm{B}}} N_{\mathrm{exp}}(n^{\mathrm{A}}_{i_{\mathrm{A}}},n^{\mathrm{B}}_{i_{\mathrm{B}}}) \tag{2A}$$

$$N^{\mathrm{B}}_{\mathrm{exp}}\,(n^{\mathrm{B}}_{i_{\mathrm{B}}}) = \sum_{i_{\mathrm{A}}=1}^{N_{\mathrm{A}}} N_{\mathrm{exp}}(n^{\mathrm{A}}_{i_{\mathrm{A}}},n^{\mathrm{B}}_{i_{\mathrm{B}}}) \tag{2B}$$

If a block copolymer of the (polyA−polyB) type has a structure described by the random coupling statistics, i.e., the distribution of molecular weight of part A is independent of the distribution of molecular weight of part B, then the distribution function $N_{\mathrm{exp}}(n^{\mathrm{A}}_{i_{\mathrm{A}}},n^{\mathrm{B}}_{i_{\mathrm{B}}})$ can be represented as a product of two marginal distributions:[22]

$$N^{\mathrm{calc}}_{\mathrm{exp}}(n^{\mathrm{A}}_{i_{\mathrm{A}}},n^{\mathrm{B}}_{i_{\mathrm{B}}}) = N^{\mathrm{A}}_{\mathrm{exp}}(n^{\mathrm{A}}_{i_{\mathrm{A}}})\; N^{\mathrm{B}}_{\mathrm{exp}}(n^{\mathrm{B}}_{i_{\mathrm{B}}}) \tag{3}$$

Table 5 presents the average absolute deviations between the experimental intensities and those calculated from the corresponding marginal probabilities. Analysis of these results shows that the average absolute deviations do not provide sufficient information to verify the hypothesis. Therefore, two other statistical parameters were determined and presented in Table 5: the correlation coefficient, r, between the experimental and calculated distribution functions and the percentage of unexplained variation, $1 - r^2$. In the case of a perfect agreement between the calculated and experimental

Table 5. Verification of the Random Coupling Hypothesis for Samples Studied in This Project

sample	av error[a]	corr coeff[b]	% of unexplained variance
PS1	0.0010	0.961	7.6
PS2	0.0010	0.958	8.2
PS3	0.0050	0.964	7.1
PS3[c]	0.0056	0.926	14.3

[a] $\Sigma(|N_{cal} - N_{exp}|)$/(no. of points). [b] Correlation coefficient between the experimental and calculated number distribution function. The expected value is 1. [c] Alternative option.

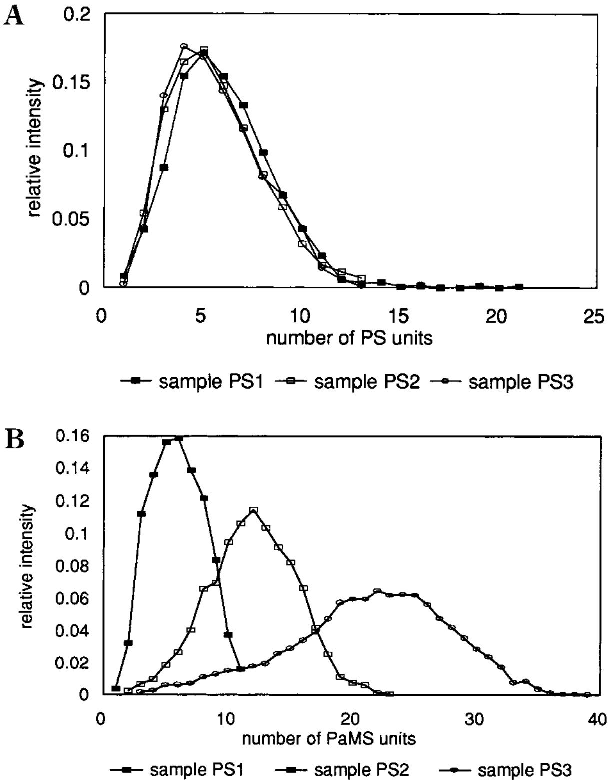

Figure 3. Comparison of experimental marginal distribution for polystyrene-*b*-poly(α-methylstyrene) diblock copolymers: (A) marginal distributions of polystyrene; (B) marginal distributions of poly(α-methylstyrene).

values, the expected value of the correlation coefficient is 1 and the value of the percentage of unexplained variation is 0.[23] The values shown in Table 5 are statistically different from those for perfect correlation at 95% CL. This indicates the need to evaluate the order of magnitude of the total error in the MAC MALDI/TOF MS method. According to our experience, a value of about 10% is appropriate. For all cases of the correct assignments, the deviations from the expected values of unexplained variation are of this order of magnitude. On the other hand, the erroneous assignment for the sample PS3 produces significantly higher values of the percentage of unexplained variation (14.3% for the alternative assignment of the sample PS3 vs 7.1% for the correct one). Therefore, the calculation of the percentage of unexplained variation provides additional means of distinguishing between erroneous and correct assignments.

Figure 3 shows the comparison of marginal distributions for the PS-*b*-PαMS diblock copolymer. The experimental distributions of the number of units of PS (Figure 3A) in the first block are within the experimental error all the same with the most probable number of PS units equal to about five. On the other hand, the distributions of PαMS (Figure 3B) change in a consistent way, as expected. The maxima of the curves shift toward higher values from around 5 PαMS units for the sample PS1, to 12 for the sample PS2, up to 22 segments for the sample PS3.

Table 6. Comparisons of the Predictive Capability and Flexibility of Different Distribution Models

		relative standard deviation (%)[a]				
sample	block	Schulz–Zimm	Tung	Poisson	log-normal	modality
		Predictive Capability[b]				
PS1	PαMS	6.8	4.1	4.8	10.1	1
	PS	2.0	4.6	2.9	4.9	1
PS2	PαMS	4.9	1.6	3.7	6.8	2
	PS	1.9	4.5	4.6	5.5	1
PS3	PαMS	5.6	2.4	7.6	7.0	3
	PS	4.2	6.3	6.1	6.5	1
av		4.2	3.9	5.0	6.8	
		Flexibility[c]				
PS1	PαMS	4.1	3.4	4.6	5.5	1
	PS	1.8	3.6	2.5	3.0	1
PS2	PαMS	3.3	1.6	3.0	4.4	2
	PS	1.1	3.5	3.9	2.6	1
PS3	PαMS	3.8	1.8	6.2	4.5	3
	PS	3.1	5.5	5.7	3.1	1
av		2.9	3.2	4.3	3.8	

[a] RSD (%) = $\sqrt{\Sigma(N_{exp}-N_{calc})^2/\Sigma N_{exp}} \times 100\%$. [b] Note: only the experimental values of parameters were used. [c] Note: the model parameters were optimized to obtain the best fit.

Models of Length Distribution of Individual Blocks. In the previous study[6] two mathematical models were used to describe the experimental marginal distributions of two blocks forming the copolymer, Schulz–Zimm (Gamma)[17,18] and Poisson.[20] The first model was suitable for all the cases studied. It came, therefore, as a surprise that neither of these models was able to follow with sufficient closeness the trend of the experimental points for the marginal distribution of PαMS in sample PS1. Thus, two other distributions, the Tung distribution[21] and the logarithmic-normal distribution,[19] were considered. Part B of the Supporting Information contains all the essential equations for the four models discussed in this paper. These models were modified for the case when the numbers of segments of parts A and B are used as independent variables, instead of using the molecular weight and the chemical composition. Additionally, the equation of the Tung distribution was transformed to the direct analytical form.

Results presented in Table 6 show that all the models tested are able to predict the marginal distributions of the systems studied with the average relative standard error of 5.0% (the maximum value was 10.1%). After the optimization of parameters, this average error decreased to 3.6% (the maximum error was 6.2%). This means that even the multimodal curves can be fairly well represented when only the most basic unimodal approach is used.

The Schulz–Zimm model has the best flexibility with the average standard error of fit below 3%. It is also clearly superior in the description of the marginal distributions of polystyrene. The Tung model has the best predictive capability for the PαMS blocks. The flexibility of this model is also good. The one-parameter Poisson model performed well for samples with lower molecular weight. The logarithmic-normal model was in most cases the worst of all in its predictive capability,

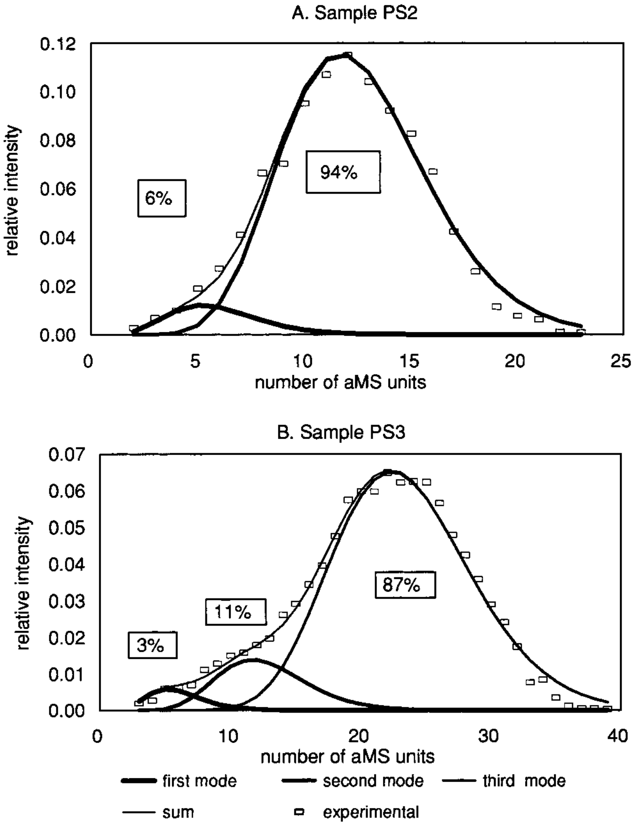

Figure 4. Comparison of the experimental marginal distribution of poly(α-methylstyrene) with the superimposition of Schulz–Zimm models. Markers, experimental data; lines, calculated values. A, sample PS2; B, sample PS3.

but having two adjustable parameters was able to outperform the Poisson equation in fitting samples with higher molecular weight.

Table 6 clearly demonstrates that despite the usual opinion[19] of virtual equivalence of the four models for low-polydispersity polymers, their predictive and descriptive power is different.

The results of the present and the previous study[6] show that polystyrene chain distributions are always unimodal. The poly(α-methylstyrene) blocks, on the other hand, show occasionally some bi- or trimodality (see Figure 4). The small humps at the beginning of the experimental marginal distribution curves in samples PS2 and PS3 can be easily attributed to termination accompanying the successive additions of monomer to the polymerization mixture.

To describe the multimodal curves, a combination of two (or three) Schulz–Zimm models was used[6] (see Figure 4). The characteristic parameters of the Schulz–Zimm equation are given in Table 7. The characteristic parameters for the first block are almost identical to the PαMS parameters presented in Table 3 for sample PS1. The average number of segments in the second block is naturally little higher than in sample PS2, the polydispersity index slightly lower. In general, there is a remarkable consistency between the parameters reported in Tables 3 and 7.

Summary and Conclusions

The series of polystyrene-*b*-poly(α-methylstyrene) diblock copolymers was successfully analyzed by the MAC MALDI/TOF MS method. Using this technique, it is possible to determine the individual length distribution of both chains forming a block copolymer. This provides detailed information on the system studied which would be impossible to obtain using any other method. The progress of the polymerization process was easily observed. The length distribution of the first block (PS) was practically the same for all the samples studied. The growth of the second block (PαMS) was very consistent from one sample to the other. The presence of a homopolymer and the killing of a small portion of the previous block at each step of monomer addition were also detected.

The robustness of the calculation technique was tested. The difference between the results obtained from the peak heights or the peak areas was negligible, less than 2%. To obtain meaningful parameters for the distribution of a copolymer, in the presence of a homopolymer, it is necessary to remove all the homopolymer peaks from the database before calculating the averages for the copolymer. On the basis of comparison of calculated diblock properties with those experimentally determined by the SEC and NMR techniques, the total error of the MAC MALDI/TOF MS method, for this series of polymers, is estimated to be around 10%. The estimate includes all the steps of the procedure, together with the MALDI-TOF measurements. This error is significantly better than results reported by other laboratories.[11,15,24]

The random coupling hypothesis was tested using a new statistical approach and was found to hold within experimental error for all the systems studied. The new approach provides additional information on the correctness of the technique of assignment of peaks.

Four models of differential number distributions of block length were examined. It was found that, even for systems with low polydispersity index, they differ significantly from each other. Overall, the commonly used Schulz–Zimm distribution model proved to be the most flexible of all. Nevertheless, the Tung model was superior for the PαMS system. The Poisson distribution model worked well only when polydispersity index and the chain lengths were low. The use of the logarithmic-normal model is not recommended.

For multimodal systems a linear combination of two or three Schulz–Zimm models was successfully used. The calculated parameters of the constituent parts of the combination are consistent with those experimentally determined for each of the three samples. The ability to see a diblock system in so much detail is unique for the MAC MALDI/TOF MS method and provides a very powerful tool in understanding the

Table 7. Calculated Parameters of the Schulz–Zimm Model for Multimodal PαMS Blocks

		first mode			second mode			third mode			
sample	block	$\bar{n}$	PI	contents (%)	$\bar{n}$	PI	contents (%)	$\bar{n}$	PI	contents (%)	RSD (%)[a]
PS2	PαMS	5.95	1.13	6	12.7	1.08	94				2.0
PS3	PαMS	5.95	1.13	3	12.7	1.08	11	23.6	1.05	87	1.5

[a] RSD (%) = $\sqrt{\Sigma(N_{\mathrm{exp}}-N_{\mathrm{calc}})^2/\Sigma N_{\mathrm{exp}}} \times 100\%$.

mechanism of the polymerization process and building of reliable theoretical models.

Supporting Information Available: Equations used to calculate the properties of the polymers presented in Table 3, as well as the equations for different differential distribution models from Table 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA981594H