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Bivariate Distribution in PMMA/PBA Copolymers by Combined SEC/NMR and SEC/MALDI Measurements

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ABSTRACT: High conversion copolymers may experience a strong variation in composition as a function of monomer conversion, and since the compositional heterogeneity of copolymers varies as the size of the chains grows, this poses a problem in determining the bivariate distribution of masses and composition in copolymers. Although several methods have been proposed to determine bivariate distributions, relatively little data are available on this important aspect of copolymer characterization, perhaps because of the complexity of the methods available up to the present time. We propose here a generally applicable method to determine bivariate distribution of masses and composition in copolymers. SEC fractionation of two random copolymers, poly(methyl methacrylate)/polybutyl acrylate (PMMA/PBA) obtained at high and low conversions, respectively, was used to collect nearly monodisperse fractions that allowed the computation of the corresponding molar masses (by matrix-assisted laser desorption ionization mass spectrometry, MALDI, measurements) and of compositions (by NMR measurements) for the two copolymers. Bivariate distribution maps were derived by combining SEC/NMR and SEC/MALDI data with Stockmayer's theoretical distribution to estimate the composition distribution of each fraction.

Introduction

The structural and molecular analysis of copolymers is a difficult problem that often cannot be easily dealt with by analyzing the intact copolymer, and therefore much effort has been put into the task of converting the SEC traces into molar masses (MM) of copolymers.[1−7]

Multiple detectors and SEC/light-scattering techniques may provide a solution to the problem, but difficulties remain.[2,3,5]

In fact, the multiple detector approach requires 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 non homogeneous materials, where the chain dimensions of copolymers may not depend on the molar mass in a linear way.[2,3]

Being able to discriminate among different masses and possessing a remarkably high sensitivity, the matrix-assisted laser desorption ionization mass spectrometry (MALDI) detector does not suffer these limitations[8−10] and, coupled with analytical size exclusion chromatography (SEC), MALDI was found to give mass spectra with average MM values in excellent agreement with those obtained by conventional techniques.[8−10]

When MALDI was used as the detector in the SEC fractionation of polydisperse copolymer samples, it became possible to determine the molar mass distributions and the hydrodynamic interactions in copolymers,[11] and this method might also lead to an estimate of the molecular dimensions in copolymers.

Furthermore, the composition of copolymers varies as the size of the chains grows, and this poses the problem to determine the so-called "bivariate distribution" with respect to masses and composition.[12−15]

Information on the bivariate distribution is particularly important in high conversion copolymers, which may experience a strong variation in composition as a function of monomers conversion.

Various methods have been proposed to determine their compositional heterogeneity.

One possibility is to use a multiple detectors SEC apparatus,[6] modifying the classical SEC configuration by adding, for instance, an UV detector in series after the standard refractive index (RI) detector. Thus, it has been shown that it is possible to measure the variation of composition in styrene/butadiene copolymers.[6]

However, this method cannot be applied when both components possess UV absorption (or both do not absorb in the UV).

Another method uses a "chromatographic cross fractionation" apparatus,[16−20] where macromolecules having different composition are separated in a first chromatographic column, and a second column elutes, at different times, macromolecules having different sizes.[16−20]

Using an FTIR detector coupled to the SEC apparatus, it has been possible to measure the variation of composition in ethylene/vinyl acetate copolymers.[17]

However, scant data on bivariate distributions are available in the literature,[20,21] most likely because the protocols developed to this purpose are rather complex.

More recently SEC/NMR, for which an ample literature exists,[22−24] has been used to gain information on size and composition for low MM copolymers.[25]

Even more attractive (since both NMR and MS instruments are nowdays widely available) is the present attempt to combine data from SEC/NMR and from SEC/

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MALDI, leading to a direct measure of the bivariate distribution in copolymers.

NMR is always able to determine the composition of a copolymer fraction, independent from its molar mass value, but it provides reliable molar mass estimates only up to 10 000–20 000 Da.

On the other side, MALDI mass spectra enable to measure molar masses up to very high values (10^6 Da), but lose resolution above 30 000–50 000 Da, and therefore, the composition of high molar mass copolymers cannot be determined.

Therefore, if NMR and mass spectrometry (MS) are separately coupled to SEC to analyze copolymer fractions, they reveal some intrinsic limitations.

Instead, if they are used in parallel to determine the composition (NMR) and molar mass (MALDI) of the SEC fractions of a copolymer, the determination of the bivariate distribution becomes possible.

Two random poly(methyl methacrylate)/polybutyl acrylate (PMMA/PBA) copolyesters obtained at high and low conversions, respectively, were investigated here. SEC/NMR data allowed the computation of the fractional composition, whereas SEC/MALDI data provided the molar mass estimates, respectively. From the knowledge of mass and composition of the copolymer fractions, combined with Stockmayer's theoretical distribution to estimate the composition distribution of each fraction, bivariate distribution maps were derived.

Experimental Section

Materials. Copolymer samples S1 and S2 are PMMA/PBA copolymers. Sample S1 was polymeryzed in ethyl acetate using azobisdiethyl isobutyrate as an initiator. The monomers conversion amounts to about 4%, and the average molar fraction of MMA in the copolymer is 0.25, as measured by NMR. Sample S2 was polymerized in ethyl acetate using *tert*-butyl perpivalate as initiator. The monomer conversion amounts to about 100% and the average molar fraction of MMA in the copolymer is 0.41, as measured by NMR.

SEC Fractionation. The analyses were performed on a Polymer Lab apparatus, equipped with four UltraStyragel Waters columns (in the order 1000, 500, 10000, and 100 Å pore size) attached in series, using a Polymer Lab differential refractometer. A 60 μL aliquot of polymeric solution (15 mg/mL in THF) was injected. The flow rate was 1 mL/min, and 50–60 fractions of 0.24 mL were collected.

NMR. NMR analyses were performed on a Varian Unity Inova 500 spectrometer at room temperature using $CDCl_3$ as a solvent and tetramethylsilane as internal standard. The ^1H NMR spectra were acquired with the following acquisition parameters: spectral width of 4722.3 Hz, 131 072 data points, 700 accumulations, and an acquisition time of 3.47 s.

The copolymer composition of each fraction was determined by taking the ratio between the area in the region 4.16–3.92 ppm, corresponding to MMA units, and the area in the region 3.66–3.51 ppm, corresponding to butyl acrylate units. The results are reported in Table 1. The signal-to noise ratio (S/N) for fraction 61 of sample S2 (the least abundant of the fractions analyzed) was about 170:1.

MALDI Sample Preparation. A 0.02 mL aliquot of the chromatographic eluate in each fraction was added to 0.02 mL of a 0.7 M solution of 2-(4-hydroxyphenylazo)benzoic acid (HABA) matrix. Probe tips were loaded with 10^{-3} mL of the resulting solution, and the solvent was slowly evaporated off.

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), a flash ADC (time base of 4 ns), and a HIMAS detector. 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. 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 D, respectively) of each selected fraction.

Table 1. SEC/MALDI and SEC/NMR Data for Copolymers S1[a] and S2[b]

sample	fraction	V_e[c],	C_{MMA}[d]	M_n[e]	M_w[f]	D[g]	weight[h]
S1	38	28.36		90000	92000	1.02	0.174
	41	29.02	0.25	63000	64000	1.01	0.239
	47	30.34		35000	36000	1.03	0.318
	51	31.22	0.25	20000	21000	1.05	0.265
	53	31.66		18000	19000	1.06	0.212
	57	32.54		11000	11550	1.05	0.118
	61	33.42	0.25	7000	7700	1.10	0.066
S2	30	27.75		173000	175000	1.01	0.157
	31	28.25		133000	135000	1.03	0.234
	36	29.11	0.39	89000	90000	1.01	0.282
	40	30.01		72000	73500	1.02	0.298
	41	30.25	0.35	64000	67000	1.04	0.291
	42	30.52		55000	57000	1.04	0.274
	43	30.75		50000	51500	1.03	0.252
	44	31.01		45000	47700	1.06	0.223
	45	31.25		39000	41400	1.06	0.194
	46	31.52	0.42	34000	35400	1.04	0.164
	47	31.75		31000	32860	1.06	0.139
	48	32.01		28000	29400	1.05	0.107
	49	32.25		25000	26000	1.04	0.099
	50	32.51		23000	23920	1.04	0.084
	51	32.75	0.42	21000	21840	1.04	0.073
	54	33.51		17000	17900	1.05	0.046
	56	34.01	0.65	13500	13800	1.02	0.036
	58	34.51		11000	11400	1.03	0.031
	61	35.25	0.78	7200	7800	1.08	0.024
	62	35.51		6700	7250	1.08	0.022
	65	36.25		5000	5400	1.08	0.018

[a] For sample S1 the average molar fraction of MMA in the copolymer is 0.25, the average M_n is 22 000, and the average M_w is 38 000. [b] For sample S2 the average molar fraction of MMA in the copolymer is 0.41, the average M_n is 43 000, and the average M_w is 91 000. [c] SEC elution volume (mL). [d] Molar fraction of MMA in the copolymer fraction (as determined by NMR). [e] M_n of the SEC fraction as determined by MALDI. [f] M_w of the SEC fraction as determined by MALDI. [g] M_w/M_n ratio of the SEC fraction as determined by MALDI. [h] Weight fraction, as derived from the SEC trace.

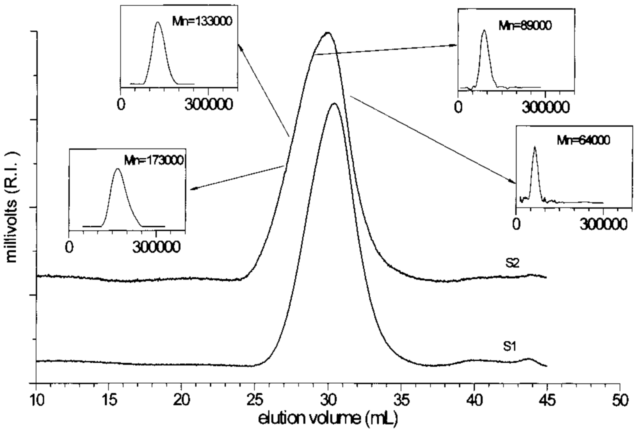

Figure 1. SEC trace for sample S1 (lower trace) and for sample S2 (upper trace). The insets display the MALDI mass spectra of selected SEC fractions of sample S2.

Calculations. The SEC traces (see Figure 1) show the weight fraction of copolymer, W, as a function of V_e, the elution volume. W is simply the RI detector response, since it was assumed that the refractive index increments (dn/dc) for MMA and BA in chloroform are the same (it is known[26] that in

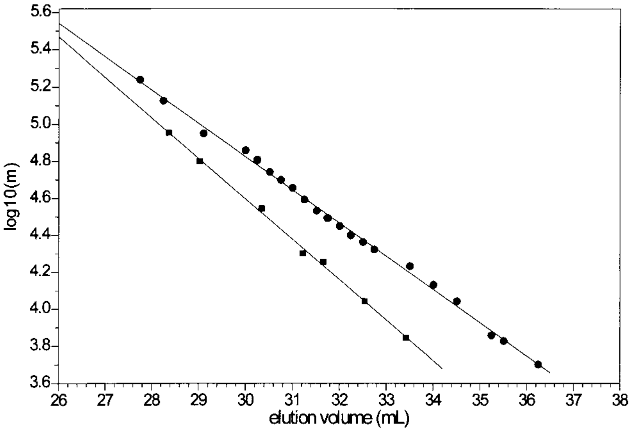

Figure 2. Mass calibrated SEC lines for sample S1 (circles) and for sample S2 (squares): the graph reports MALDI−TOF molar masses vs elution volume for each SEC fraction

acetone the d*n*/d*c* value for MMA and for BA are 0.112 and 0.113 mL/g, respectively, and thus the difference in sensitivity is lower than 1%).

SEC calibration lines in Figure 2 were used to convert eluted volumes in molar masses. Authentic GPC calibration plots for samples S1 and S2 were obtained by the correlation of log M_w, obtained by MALDI spectra, of each fraction with the corresponding eluted volume (Figure 2).

The calibrated SEC traces were used to compute average molar mass and dispersion of the unfractionated copolymers using the Caliber software distributed by Polymer Lab. The type of calibration selected by us was “narrow standards”; the calibration function was “polynomial of order 1”, and the calculation method was “area based”, since the distributor claims that the cited calculation method yields more accurate results than the “height based” method. The results were as follows: sample S_1, (M_w = 38 000, M_n = 22 000, D = 1.7; sample S_2, M_w = 91 000, M_n = 43 000, D = 2.1.

Data in columns 4, 5, and 8 of Table 1 and the SEC traces in Figure 1 were used to compute the bivariate distribution of chain composition and sizes for samples S1 and S2. These figures were grouped in triplets, reporting the weight fraction of macromolecular chains having mass M and an average copolymer composition (C_{av}).

Each mass value corresponds to a single average copolymer composition, as measured by NMR spectra. This average value would be satisfactory in the case of a narrow composition distribution in the SEC fraction. However, for heterogeneous copolymers, such as high conversion samples, copolymers having different compositions may be eluted at the same SEC volumes.[1,2]

To cope with this problem, we estimated the weight of macromolecular chains that possess a composition, C_{MMA}, which may be different from the average value, C_{av}.

More specifically, we computed the weight of macromolecular chains in which C_{MMA} takes all the values between 0 and 1 by assuming that the composition spread, β, is given by Stockmayer's theoretical distribution:[12,13]

$$\beta = \exp(-0.5(C_{av} - C_{MMA})^2/(0.001\sigma^2)) \qquad (1)$$

where σ^2 is the variance and it is given by $C_{av}(1 - C_{av})/s$, where s is the number of repeating units in the chain. Using the above equation, we generated the compositional distribution for sample S1 and for sample S2, which were used to produce the 3D-mesh plots in Figures 4−6.

In the case of the mass spectra of high conversion PMMA/PBA copolymer samples taken from Nuwaysir et al.,[27] the composition spread was measured directly from the spectra.

The formula[28−30] which relates the spread to experimental MS intensities is

$$\sigma^2 = 1000 \sum \sum (C_s - m^2 I_{exp})^2 \delta_s \qquad (2)$$

where I_{exp} is the intensity of mass spectral peak corresponding to the oligomer A_mB_n, C_s is the average molar fraction of MMA in chains which possess s of repeating units, δ_s is equal to 1/s when $m + n = s$ and is zero otherwise and where the summations are extended to all nonnegative values of n and m.

Results and Discussion

SEC fractionation was used to obtain a series of fractions from two high molar mass, random, polymethyl methacrylate/polybutyl acrylate (PMMA/PBA) copolymers produced by radical initiation.

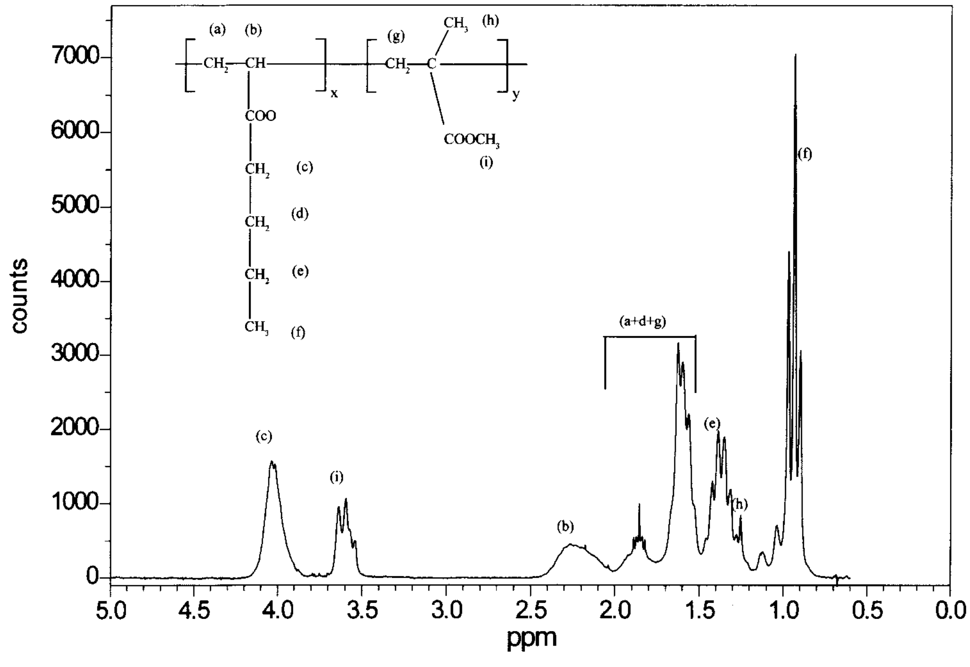

Figure 3. 500 MHz ^{1}H NMR spectrum of fraction 41 of sample S1.

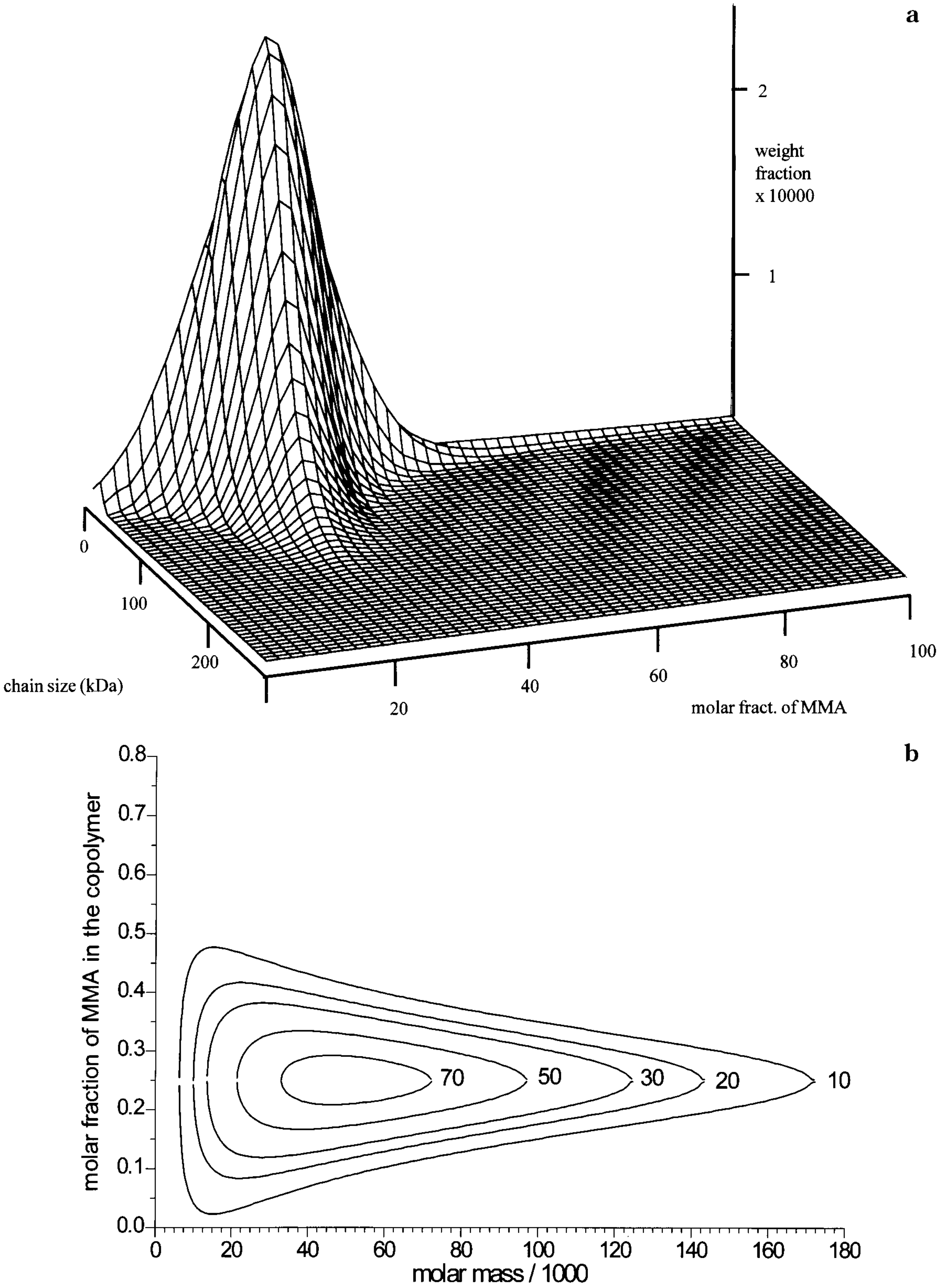

Figure 4. (a) Bivariate distribution of chain sizes and compositions for sample S1. (b) Contour map of the bivariate distribution of chain sizes and compositions for sample S1.

One copolymer sample (S1) is a low conversion (4%) and the other (S2) is a high conversion (100%) copolymer.

Figures 1a and 1b show the SEC traces for samples S1 and S2, respectively. The trace corresponding to S2 displays a broader peak than the trace corresponding to S1.

Samples S_1 and S_2 were separately injected into the SEC apparatus, and about 50 fractions were collected from each eluate. Several SEC fractions were then subjected to off-line MALDI and NMR analysis, respectively (Table 1).

The SEC fractions analyzed by MALDI−TOF yielded excellent spectra with narrow distributions up to high molar masses (170 000 Da, Figure 2), and the mass spectra of these nearly monodisperse samples allowed the computation of reliable values of the molar masses corresponding to the fractions.[8−10]

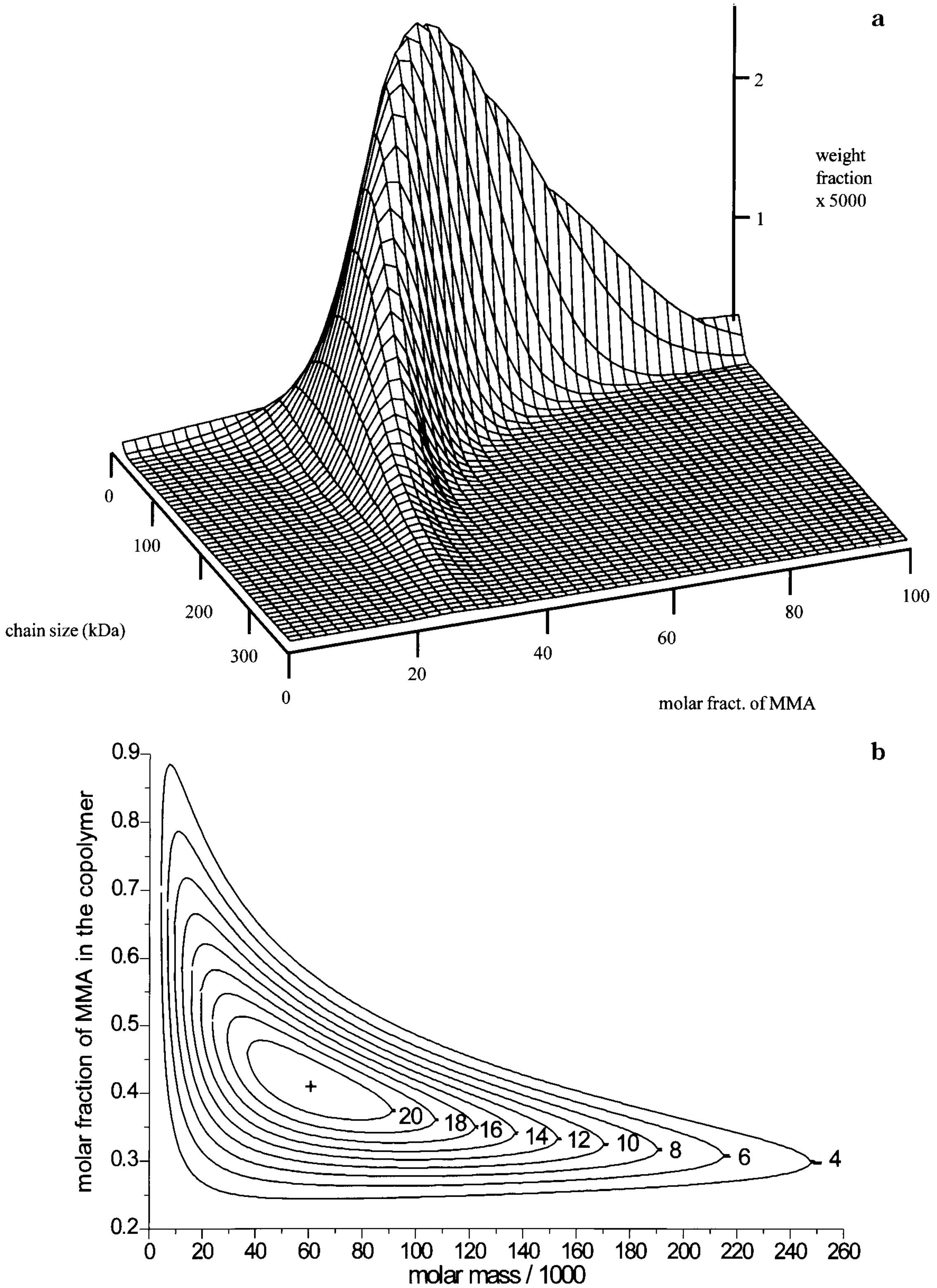

Figure 5. (a) Bivariate distribution of chain sizes and compositions for sample S2. (b) Contour map of the bivariate distribution of chain sizes and compositions for sample S2.

In Figure 1 (insets) are shown some MALDI spectra corresponding to selected fractions of copolymer sample S$_2$, taken at different elution times.

The log MM values of the fractions showed a linear correlation with the elution volume of each fraction and allowed the calibration of the SEC traces for samples S$_1$ and S$_2$ against MM (Figure 2), and the calibrated SEC trace could then be used to compute average molar mass and dispersion of the unfractionated copolymer sample S$_1$ (M_w = 38 000, M_n = 22 000, D = 1.7) and S$_2$ (M_w = 91 000 M_n = 43 000, D = 2.1).

Table 1 reports also the composition of the S$_1$ and S$_2$ fractions analyzed by 500 MHz ^{1}H NMR. The copolymer composition of each fraction was determined by taking the ratio between the area in the region 4.16−3.92 ppm, corresponding to MMA units, and the area in the region 3.66−3.51 ppm, corresponding to butyl acrylate units. (Figure 3).

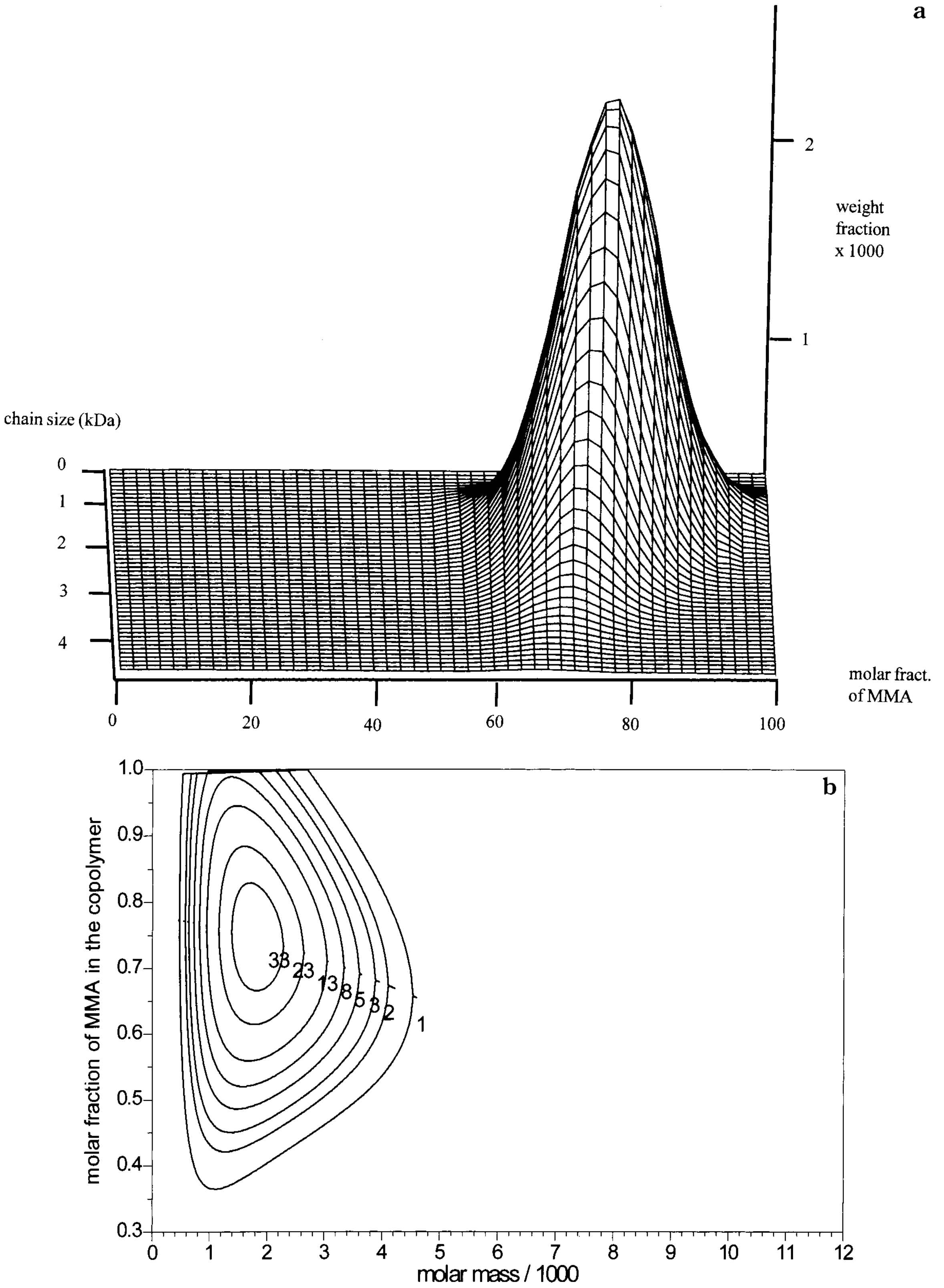

Figure 6. (a) Bivariate distribution of chain sizes and compositions for sample S3. (b) Contour map of the bivariate distribution of chain sizes and compositions for sample S3.

From data in Table 1, it can be seen that the for the low conversion copolymer S_1 the composition is constant throughout the sample (PMMA/PBA 24/76). Instead, for sample S2 the composition varies, and the fractions taken in the SEC region close to the peak elution volumes possess compositional values close to the average ones (PMMA/PBA 41/59). At higher masses the composition takes values up to 65% BA. At low masses, instead, the macromolecular chains are rich in MMA (about 78%, Table 1).

The NMR spectra yield exclusively the average copolymer composition of a fraction, but do not give information on its composition spread. We assumed here that the spread takes its theoretical value (see Experimental Section).

Using the above assumption, we computed the bivariate distribution of chain sizes and compositions.

Figure 4a shows the bivariate distribution for the low conversion sample S1, displaying the weight fraction of macromolecules as a function of size and MMA/BA ratio. In Figure 4b is shown a contour map, showing further details of the bivariate distribution corresponding to sample S1. The distribution is symmetric with respect to the molar fraction of comonomers and nicely shows the theoretically predicted[12,13] broadening of composition at low masses for low conversion copolymers.

In Figure 5a is shown the bivariate distribution for the high conversion sample S2, displaying the weight fraction of macromolecules as a function of size and MMA/BA ratio.

It appears clearly that this high conversion sample, having an average MMA/BA composition of 41/59, has instead a sensible composition heterogeneity, as can be noted also from the inspection of the contour map reported in Figure 5b.

It could be argued that for low conversion polymers, such as sample S1, eq 1 (Stockmayer's theoretical distribution[12,13]), may be acceptable, but in general the present method cannot be applied to high conversion copolymers, since conversion affects the composition distribution.

Actually, we have performed some controls in order to test the validity of the method in the case of high conversion copolymers, and we estimate that eventual distortions introduced by our modeling into the 3D mesh plots of high conversion copolymers are minor.

Let us recall that bivariate distributions[12] can be obtained directly from mass spectra of copolymers, provided that these copolymers have low molar masses. In fact, at low masses the mass spectra show mass resolved peaks, and therefore both mass and composition distribution can be extracted from such mass spectral data.[28−30]

The composition distribution is directly measured in this experiment, and is not merely an average value, so that no assumptions need to be made to estimate the sample composition distribution. The experimental variance of the Gaussian distribution corresponding to each discrete chain size can be then obtained and compared with that calculated by Stockmayer's theoretical distribution used in our modeling.

In a paper particularly relevant to the present one, Nuwaysir et al.[27] reported the analysis of three high conversion PMMA/PBA copolymer samples, by laser desorption fourier transform mass spectrometry (LD/FTMS).

We considered the LD/FTMS mass spectrum of the PMMA/PBA sample, which possesses an average composition[27] of 78.5/21.5, which we refer to as sample S3, a sample which possesses an average composition[27] of 83/17, which we refer to as sample S4, and a sample which possesses an average composition[27] of 88/12, which we refer to as sample S5.

The experimental mass spectral intensities for samples S3, S4, and S5 were inserted in eq 2 to yield the experimental variances. The variances (Table 2, columns 2, 4, and 6) decrease strongly with increasing size going from values of 23 to 2 for sample S3 and from 28 to 1 for sample S5.

Table 2, columns 3, 5, and 7, also reports the theoretical variances for samples S3, S4, and S5 computed applying Stockmayer's theoretical distribution (eq 1).

Table 2. Comparison between Experimental and Calculated Variance of the Gaussian Compositional Distribution for PMMA/PBA Copolymer Samples S3, S4, and S5

	sample S3		sample S4		sample S5	
oligomer size	measd[a]	calcd[b]	measd[c]	calcd[d]	measd[e]	calcd[f]
5					28	21
6	23	33	18	26	15	17
7	23	28	16	22	24	15
8	25	25	14	19	25	13
9	29	22	12	17	13	12
10	30	20	11	15	16	11
11	21	18	9	14	15	10
12	26	16	12	13	10	9
13	25	15	11	12	6	8
14	19	14	10	11	7	7
15	21	13	10	10	5	7
16	21	12	10	10	12	6
17	21	11	10	9	8	6
18	27	11	10	9	8	6
19	27	10	9	8	2	5
20	22	10	7	8	5	5
21	27	9	6	7	3	5
22	22	9	4	7	2	5
23	20	9			1	4
24	10	8				
25	13	8				
26	5	8				
27	2	7				

[a] Variance measured using eq 2 from the mass spectrum for sample S3.[27] [b] Variance calculated using eq 1 for sample S3. [c] Variance measured using eq 2 from the mass spectrum for sample S4.[27] [d] Variance calculated using eq 1 for sample S4. [e] Variance measured using eq 2 from the mass spectrum for sample S5.[27] [f] Variance calculated using eq 1 for sample S5.

The experimental variance values and those calculated applying Stockmayer's distribution are of the same order of magnitude as the theoretical ones (Table 2), and the ageement is fair enough to encourage using eq 1 for high conversion samples, as we have done in the present method.

In Figure 6a is reported the bivariate distribution for sample S3, and in Figure 6b is shown the corresponding contour map. Although the molar masses in Figure 6 reach only values of about 4000 Da (as compared to 300 000 Da in Figures 4 and 5), the compositional heterogeneity is detectable also for this sample.

Conclusions

Although several methods have been proposed to determine bivariate distributions, relatively little data[20,21] are available on this important aspect of copolymer characterization, perhaps because of the complexity of the methods available to the present.

We propose here a generally applicable method to determine bivariate distribution of masses and composition in copolymers.

SEC fractionation of two random copolyesters polymethyl methacrylate/ polybutyl acrylate (PMMA/PBA) obtained at high and low conversion, respectively, was used to collect nearly monodisperse fractions that allowed the computation of the corresponding molar masses (by MALDI measurements) and of compositions (by NMR measurements) for the two copolymers. Bivariate distribution maps were derived by combining SEC/NMR and SEC/MALDI data.

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