

Determination of the Compositional Distribution and Compositional Drift in Styrene/Maleic Anhydride Copolymers

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ABSTRACT: A generally applicable method is used here to measure the weight of copolymer chains which possess a given mass and composition, i.e., to determine the bivariate distribution of chain sizes and composition in copolymers. The method consists of three steps. The copolymer is initially fractionated using size exclusion chromatography (SEC) and fractions are collected. The SEC fractions are analyzed by ^1H NMR to determine both the copolymer abundance and composition, and then by matrix-assisted laser desorption ionization mass spectrometry (MALDI) to determine the molar mass of each fraction. In the third step, bivariate distribution of chain sizes and composition maps are derived from knowledge of the molar mass, weight and composition of the copolymer fractions. The compositional distribution is obtained by summation of the sections of the bivariate distribution which belong to a narrow compositional range. The method was applied to two random copolymer samples containing units of styrene (St) and of maleic anhydride (MAH) reacted up to high conversion. Both samples had a strong compositional drift. At low masses, chains were rich in maleic anhydride, whereas at high masses chains were rich in styrene. The bivariate distribution was a smooth surface with a single maximum for both samples. Integration of the surface over narrow compositional ranges yielded the compositional distribution histogram. For one of the two samples, the histogram was relatively smooth and almost flat, whereas for the other sample the histogram was triangle-shaped with a discontinuity in the styrene-rich region.

Introduction

The structural and molecular analysis of copolymers is complex, as compared to homopolymers, since one has to determine the average copolymer composition, the variation of composition as the mass of the macromolecular chain grows (usually called the “compositional drift”) and the weight of copolymer chains at each composition (the compositional distribution).

The compositional distribution histogram of some copolymer samples is smooth,¹ although others may display swift changes.¹ In the case of mixtures of a copolymer and a homopolymer, the histogram rises steeply in the homosequence region.¹

Full copolymer characterization can be achieved by measuring the “bivariate distribution” with respect to masses and composition.^{1–3} Information on the bivariate distribution is particularly important in high conversion copolymers, since the rates of consumption of monomers A and B during the reaction often change with one of the two monomers preferentially incorporated into the copolymer chain. This implies that the spread in composition increases with conversion. Furthermore, the average length (λ) of the chains produced at high conversion may be higher than the λ produced at low conversion. This may happen when autoacceleration takes place and also when the amount of initiator decreases exponentially with polymerization time. This implies that high conversion copolymers display a compositional heterogeneity.^{3,4}

One of the methods developed for measuring the bivariate distribution employs a “chromatographic cross fractionation” apparatus (also referred to as “two-dimensional chromatography” and “orthogonal chromatography”), where macromolecules having different compositions are first separated in a chromatographic column, and a second column is used to elute macro-

molecules having different sizes.^{5–8} However this approach has not been used frequently due to huge instrumental requirements. In principle, the method can yield the compositional drift; it is not derived in practice, probably due to difficulties in data reduction).⁸

Another method developed for measuring the bivariate distribution employs SEC coupled with light scattering (LS).^{9,10} However, the intensity of the scattered light falls when the dimensions of the scattering particle shrink, which decreases the sensitivity when the mass of the molecules decreases. Furthermore, the use of a light scattering detector for copolymers may cause an error in the determination of the copolymer concentration in samples having a sizable compositional spread, where the chain dimensions of copolymers may not depend on the molar mass in a linear way.^{9,10} This error is reflected on the bivariate distribution measurement.

An alternative to the above methods is SEC/NMR.^{11–13} Recently this method has been used to measure the compositional drift in low molar mass copolymers.¹⁴ However, the error in determining the macromolecular size by measuring the NMR signal due to the terminal chemical group becomes large as the chain size increases.

To cope with this problem, we¹⁵ proposed a generally applicable method to determine the bivariate distribution of masses and composition in copolymers. The copolymer is fractionated using SEC and the fractions are collected. The fractions are analyzed by NMR to determine the copolymer abundance and composition and then analyzed by matrix-assisted laser desorption ionization mass spectrometry (MALDI) to determine the molar mass (MM) of each fraction. Finally, NMR and MALDI data are combined with modeling of the compositional spread using Stockmayer’s theoretical distribution^{1,2} to yield the bivariate distribution maps. The method was applied to two copolymer samples contain-

Table 1. SEC/MALDI and SEC/NMR Data for Copolymer S91^a

fraction	V_e^b	C_{St}^c	M_n^d	M_w^e	D^f	weight ^g	weight ^h
7	23.8	0.97				27	27
10	24.7	0.89				33	35
14	25.9	0.99				34	37
16	26.5		92 000	97 000	1.05	32	
18	27.1	0.78	71 000	74 000	1.04	29	31
20	27.7		54 000	57 000	1.05	26	
22	28.3	0.81	42 000	45 000	1.07	22	20
24	28.9		32 000	34 000	1.06	19	
25	29.2		28 000	29 000	1.04	18	
26	29.5	0.70	25 000	26 000	1.04	16	14
27	29.8		22 000	23 000	1.04	15	
28	30.1		19 000	20 000	1.05	13	
29	30.4	0.58	16 700	17 000	1.02	12	9
30	30.7		14 700	15 300	1.04	11	
31	31		12 900	13 500	1.05	10	
32	31.3	0.66	11 300	11 600	1.03	9	5
33	31.6		9900	10 400	1.05	8	
34	31.9		8700	9200	1.06	7	
35	32.2	0.81	6600	7800	1.18	7	5
36	32.5		5700	6900	1.21	6	
37	32.8		5900	6200	1.05	6	

^a For sample S91 the average molar fraction of St in the copolymer is 0.91, \bar{M}_n is 151 000, \bar{M}_w is 345 000. ^b SEC elution volume (mL). ^c Molar fraction of St in the copolymer fraction. ^d \bar{M}_n of the SEC fraction as determined by MALDI. ^e \bar{M}_w of the SEC fraction as determined by MALDI. ^f \bar{M}_w/\bar{M}_n ratio of the SEC fraction as determined by MALDI. ^g Weight fraction, derived from the RI detector of the SEC apparatus without dn/dc correction for both monomers. ^h Weight fraction, derived from NMR data using eq 2.

ing units of methyl methacrylate (MMA) and butyl acrylate (BA), one obtained at low conversion and the other obtained at high conversion.¹⁵

Here, the above method was used to determine the bivariate distribution of two random copolymers containing units of styrene (St) and of maleic anhydride (MAH) obtained at high conversion. The overall molar fraction of styrene in these copolymers was 0.78 for sample S78 and 0.91 for sample S91.

SEC/NMR data allow the computation of the fractions composition, whereas SEC/MALDI data provide the molar masses estimates. The bivariate distribution maps were derived from the mass and composition of the copolymers fractions.

Experimental Section

Materials. Copolymer samples S91 and S78 were purchased from MPDAJAC (Feasterville, PA). They are random copolymer samples of styrene (St) and maleic anhydride (MAH) obtained at high conversion from solution polymerization using AIBN (*N,N*-azobis(isobutyronitrile)) as the initiator. The average molar fraction of St in the copolymer is 0.78 for sample S78 and 0.91 for sample S91.

SEC Fractionation. The analyses were performed on a Polymer Lab apparatus, equipped with five ultra-Styrigel Waters columns (in the order 1000, 500, 10000, 100, and 100000 Å pore size) attached in series, using a Polymer Lab differential refractometer (kept at room temperature). In practice, 60 μ L of polymeric solution (15 mg/mL in THF) were injected. The flow rate was 1 mL/min and 50–60 fractions of 0.24 mL were collected. The chromatograph was calibrated using the result of the analysis of MALDI–TOF spectra of selected fractions (see column 5 of Tables 1 and 2). The calibration lines for S91 and for S78 are $\log(M) = 9.7 - 0.168 V_e$ and $\log(M) = 10 - 0.188 V_e$. The average molar masses (\bar{M}_n and \bar{M}_w) of the copolymer were measured using the Caliber software distributed by Polymer Lab. The type of calibration selected by us was a “narrow standards”; the calibration function was “polynomial of order 1”, and the calculation

Table 2. SEC/MALDI and SEC/NMR Data for Copolymer S78^a

fraction	V_e^b	C_{St}^c	M_n^d	M_w^e	D^f	weight ^g	weight ^h
32	25.3	0.885				16	22
35	26.2	0.842	105 000	108 000	1.03	17	24
36	26.5	0.828	92 000	96 000	1.04	17	26
37	26.8	0.820	80 000	83 000	1.04	17	24
38	27.1		71 000	74 000	1.04	16	
39	27.4	0.697	62 000	64 000	1.03	16	22
40	27.7		54 600	56 000	1.02	15	
41	28.0		47 900	49 200	1.03	14	
42	28.3	0.661	42 000	43 500	1.03	14	18
43	28.6		37 000	40 000	1.08	13	
44	28.9		32 000	34 000	1.06	12	
45	29.2	0.605	28 300	30 100	1.06	11	14
46	29.5		25 000	26 000	1.04	11	
47	29.8		22 000	22 700	1.03	10	
48	30.1	0.531	19 100	20 400	1.07	9	10
49	30.4		17 700	18 400	1.04	8	8
50	30.7		14 700	15 000	1.02	8	
51	31	0.743	12 900	13 400	1.04	7	7
52	31.3		11 300	11 700	1.03	7	
53	31.6	0.753	9900	10 400	1.05	6	4
54	31.9		8700	9200	1.06	6	
55	32.2	0.78	6700	7700	1.15	5	2

^a For sample S78 the average molar fraction of St in the copolymer is 0.78, \bar{M}_n is 99 000, \bar{M}_w is 240 000. ^b SEC elution volume (mL). ^c Molar fraction of St in the copolymer fraction. ^d \bar{M}_n of the SEC fraction as determined by MALDI. ^e \bar{M}_w of the SEC fraction as determined by MALDI. ^f \bar{M}_w/\bar{M}_n ratio of the SEC fraction as determined by MALDI. ^g Weight fraction, derived from the RI detector of the SEC apparatus without dn/dc correction for both monomers. ^h Weight fraction, derived from NMR data using eq 2.

method was “area based”. The result was as follows: sample S91 ($\bar{M}_n = 151000$, $\bar{M}_w = 345000$, $D = 2.28$), sample S78 ($\bar{M}_n = 99000$, $\bar{M}_w = 240000$, $D = 2.42$).

NMR. NMR analyses were performed on a Varian Unity Inova 500 spectrometer at room temperature using $CDCl_3$ or acetone- d_6 as solvent and tetramethylsilane as internal standard. Experiments on the unfractionated samples were performed using a recycle time of 2 s and a J -modulation time of 3.7 ms. 1H and ^{13}C $\pi/2$ pulse times were 22 and 15 μ s, respectively. DEPT subspectra were generated using the following combination¹⁶ of the $\pi/4$ and $3\pi/4$ experiments: $CH_2 = (\pi/4) + 1.15 (3\pi/4)$.

The overall variance of compositional distribution for styrene, σ^2 , was computed from the areas under the SSS, SSM+MSS, and MSM resonances, I_{SSS} , $I_{SSM+MSS}$, I_{MSM} , using the formula

$$\sigma^2 = \{(3I_{SSS} - k)^2 + (2I_{SSM+MSS} - k)^2 + (I_{MSM} - k)^2\} / 3 \quad (1)$$

where $k = F_{st}DP_n$, DP_n is the number-average degree of polymerization, and F_{st} is the molar fraction of styrene in the copolymer.

The 1H NMR spectra of the SEC fractions were acquired with the following acquisition parameters: spectral width 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 using the formula $F_{st} = 0.2 I_{arom} / (0.5 I_{alif} - 0.1 I_{arom})^{-1}$ where F_{st} is the molar fraction of styrene in the copolymer, I_{arom} is the area in the region 6–8 ppm, corresponding to styrene units, and I_{alif} is the area in the region 1–3 ppm. The result was $F_{st} = 0.78$ for sample S78 and $F_{st} = 0.91$ for sample S91.

The weight of copolymer in each fraction, w_{cupo} , was determined using the formula

$$w_{cupo} = (w_{TMS}/I_{TMS})k_1 I_{cupo}/M_{fra} \quad (2)$$

where M_{fra} is the number-average molar mass of the fraction, I_{cupo} is $I_{alif} + I_{arom}$, I_{TMS} is the area under the peak at 0 ppm, corresponding to tetramethylsilane (briefly TMS), and w_{TMS}

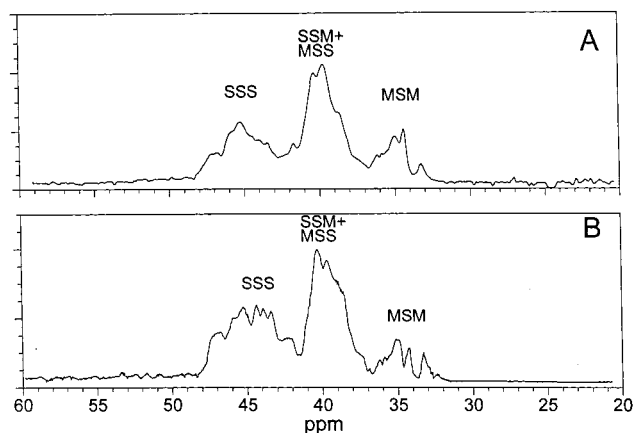


Figure 1. Combination of DEPT NMR spectra for samples S78 (A) and S91 (B).

is the weight of TMS in the NMR tube (0.136 mg) and where k_1 is a dimensionless constant equal to 1466.2, which arises from the fact that St and MAH repeat unit possess eight and two protons, respectively, whereas TMS possesses 16 protons.

The resulting values for F_{St} and w_{copo} are reported in Table 1.

MALDI Sample Preparation. The chromatographic elute in each fraction was 0.02 mL and it 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.

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 was 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/cm²). Ions below m/z 2000 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 , \bar{M}_n , \bar{M}_w and D , respectively) of each selected fraction.

Results and Discussion

The St-MAH copolymerization has a strong alternating tendency and the terminal model does not accurately predict the sequence distribution, not even at low conversions.¹⁷ In particular, the fraction of exactly alternating triads is underestimated when the feed is close to equimolar and it is overestimated when the feed is rich in St.¹⁷ Furthermore, it is not known if the conversion may affect the sequence of the copolymer. Since theoretical predictions on the sequence are unreliable, it must be determined experimentally.

Copolymer samples S91 and S78 were analyzed by ¹³C NMR. The ¹³C 125 MHz spectrum (omitted for brevity) does not yield sequence information because the signals due to methine and methylene carbons are partially overlapped. However, sequence information can be obtained from DEPT experiments, by recording the spectra at $\pi/4$ and at $3\pi/4$ and then combining them together.¹⁶ Figure 1A shows the resulting combination of NMR spectra for sample S78. The areas under the SSS, SSM + MSS, and MSM resonances are 0.32, 0.50, and 0.18, respectively. In a similar manner, the areas under the SSS, SSM + MSS, and MSM resonances for sample S91 (see Figure 1B) were 0.39, 0.47 and 0.13, respectively. Inserting the three values for the SSS,

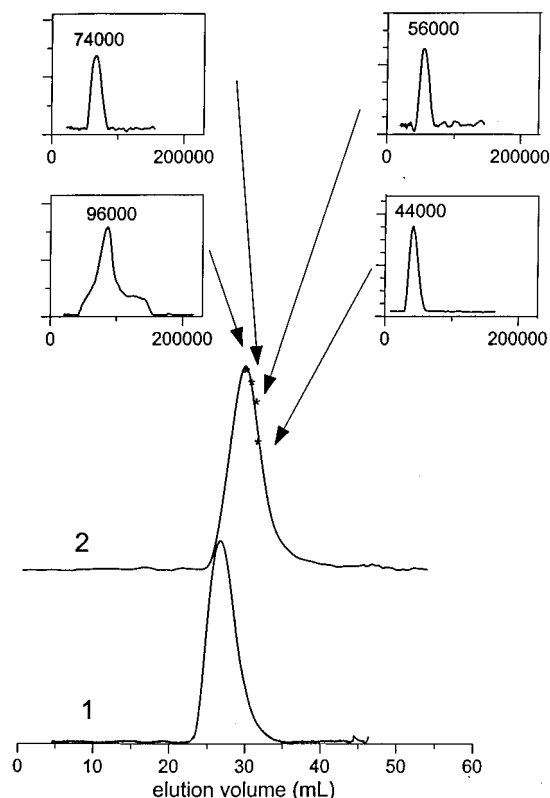


Figure 2. SEC traces for samples S91 (1) and S78 (2). The insets report the MALDI-TOF mass spectra for fractions 36, 38, 40, and 42 of sample S78.

SSM + MSS, and MSM resonances in eq 1, the overall variance of compositional distribution was found to be $\sigma^2 = 0.0844$ for sample S78 and $\sigma^2 = 0.0676$ for sample S91. The theoretical variances for S78 and S91 are $\sigma^2 = 0.015$ and $\sigma^2 = 0.0097$ respectively, which are lower than the former ones. Knowledge of the average composition and of the variance around the average may give some hints on the abundance of chains which possess a composition that differs from the average, although this is not sufficient to reconstruct the compositional distribution. For this reason, it is necessary to adopt a different approach, based on fractionation. Copolymers S91 and S78 were fractionated by SEC, and 50–60 fractions were collected for each copolymer. Figure 2 shows the SEC trace for sample S91 (trace 1), which has its maximum at about 27 mL. It also reports the SEC trace for sample S78 (trace 2), where the maximum is shifted to about 30 mL. Figure 2 also insets the MALDI-TOF mass spectrum for fractions 36, 38, 40, and 42 of sample S78. The insets demonstrate that the SEC fractions yield excellent MALDI-TOF spectra with narrow distributions (the \bar{M}_w/\bar{M}_n ratio is often smaller than 1.1, as reported in Tables 1 and 2) up to high molar masses (up to 96 kDa, Figure 2). After that value, MALDI spectra became very weak and molar mass could not be estimated.

The copolymer fractions were also analyzed by ¹H NMR. As an example, Figure 3 shows the ¹H NMR spectrum of fraction 39 of sample S78. The copolymer composition of each fraction was determined measuring I_{arom} (the area in the region 6–8 ppm) and I_{alif} (the area in the region 1–3 ppm) and combining them together (see Experimental Section). The composition values obtained by this procedure (see Tables 1 and 2) imply that the molar fraction of styrene in both copolymer

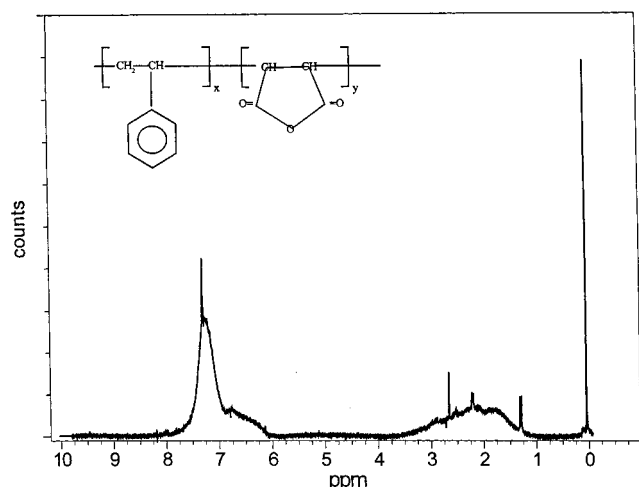


Figure 3. 500 MHz ^1H NMR spectrum of SEC fraction 39 of sample S78.

samples varies as the mass of the chain grows. In the case of sample S91, the average molar fraction of styrene is in the range 0.58–0.99. Sample S78 displays a more limited compositional heterogeneity since the average molar fraction of styrene is in the range 0.53–0.89.

The SEC data in Tables 1 and 2 indicate that the copolymer fractions have a composition close to alternating (50%) for a molar mass of about 17–19 kDa. We hypothesize that this molar mass corresponds to the kinetic chain length of the alternating copolymer and that lower and higher molar masses are subjected to higher percent of styrene inclusion. Thereafter, we used ^1H NMR data to measure the amount of copolymer contained in each fraction by measuring I_{TMS} (the area under the peak at 0 ppm, corresponding to tetramethylsilane) and combining it with I_{arom} and I_{alif} using eq 2 (see above). The resulting weight values are reported in Tables 1 and 2 (column 8).

To measure the amount of copolymer, one may rely on the SEC detector, which is a differential refractometer, and assume that the detector's response reflects the amount of copolymer. Tables 1 and 2 (column 7) report the amount of copolymer estimated using the latter method.

There are some discrepancies between the cited (R.I.) values and the values obtained by ^1H NMR. The discrepancies between the two measurements are often small; however, in some cases they become large and cannot be neglected. For instance, the two values for the amount of copolymer in fraction 36 are 17 and 26 which implies a difference larger than 30%. This difference is due to the fact that we are dealing with compositionally heterogeneous copolymers; the response to styrene units and to maleic anhydride units may be different and the refractometer's response is therefore unreliable. An UV detector is commonly added to the apparatus and used to correct for the different values of the quantity dn/dc for the two monomers. However the time lag estimation between the two detectors is cumbersome.¹⁸

The average molar mass and dispersion of the unfractionated copolymers were then computed. The software for such calculations needs the calibration lines for the two samples and the abundances. The calibration data were taken from Tables 1 and 2 (column 5), which reports the MALDI–TOF analysis of each fraction. The

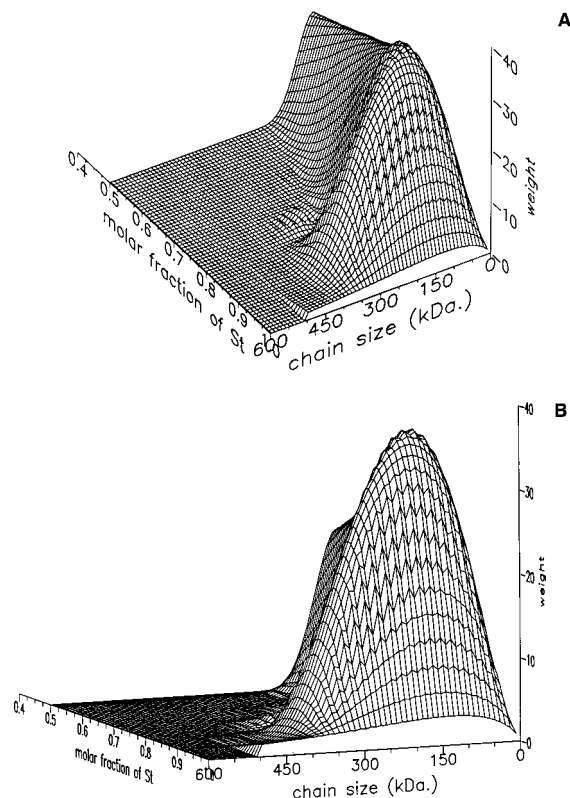


Figure 4. Bivariate distribution of chain sizes and compositions for sample S91: (A) first view; (B) second view.

result was: sample S91 ($\bar{M}_n = 151\,000$, $\bar{M}_w = 345\,000$, $D = 2.28$), sample S78 ($\bar{M}_n = 99\,000$, $\bar{M}_w = 240\,000$, $D = 2.42$).

Thereafter the bivariate distributions of masses and composition for the two samples were generated in a fashion similar to the one previously adopted.¹⁵ More specifically, data in columns 3, 5, and 8 of Table 1 were used to compute the weight of macromolecular chains in which C_{MAH} (the molar fraction of MAH in the chain) takes all the values between 0.5 and 1. We assumed that the compositional spread, β , at high conversion follows a Gaussian (similar to β at low conversion) and that it is given by

$$\beta = \exp(-0.5 (C_{\text{av}} - C_{\text{MAH}})^2 / \sigma^2) \quad (3)$$

where C_{av} is the average MAH molar fraction measured by SEC NMR (see Tables 1 and 2, column 5) and σ^2 represents the variance of the compositional distribution determined by the DEPT–NMR experiment (see above).

Parts A and B of Figure 4 show the bivariate distribution of masses and composition for sample S91, seen in two different perspectives. The surface displays a single maximum, which is located at $F_{\text{St}} = 0.85$ and molar mass 150 kDa. Parts A and B of Figure 5 show the bivariate distribution of masses and composition for sample S78 (again two different perspectives are shown). It displays a smooth surface, with an almost linear drift in the region 200–300 kDa. Again, the surface displays a single maximum, which is located at $F_{\text{St}} = 0.88$ and molar mass 100 kDa. As the mass increases, the weight of the chains falls more quickly with respect to S91. This is due to the fact that sample S78 possesses lower M_n and M_w than sample S91.

Once the bivariate distribution maps for the two samples are available, one can derive the compositional

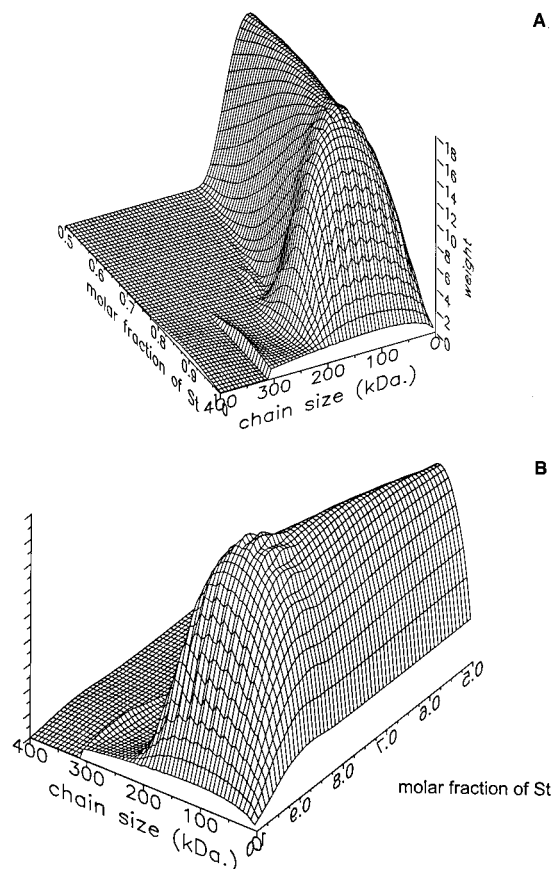


Figure 5. Bivariate distribution of chain sizes and compositions for sample S78: (A) first view; (B) second view.

distribution histogram. In fact, the bivariate distribution reports the weight, $W(s, F_{St})$, of chains that possess a given size (s) and a given composition (F_{St}). The compositional distribution histogram reports, instead, the weight $W(F_{St})$ of chains which possess a given composition and it is therefore obtained from $W(s, F_{St})$ by summation over all chain sizes. In formulas

$$W(F_{St}) = \sum W(s, F_{St}) \quad (4)$$

where the summation is over s and it goes from one to infinity.

The above formula was applied to the data in Figures 4 and 5. Data points corresponding to chains that have different sizes and possess a composition in a given range, (namely 0.5–0.52, 0.52–0.54, up to the range 0.98–1) are summed together. Figure 6A reports the compositional distribution histogram for sample S91. When the composition increases from 0.5 to 0.95, the weight increases; thereafter, it bends downward. Figure 6B reports the compositional distribution for sample S78. This histogram differs from the preceding one in that it is almost flat, especially in the region 0.7–0.9, which implies that the compositional distribution is broad. This agrees with the results of the DEPT–NMR experiment, which indicated that the overall variance of compositional distribution for sample S78 is large. These results can be understood since the MAH monomer is consumed in the first part of the copolymer forming reaction. Therefore, in the S91 copolymer sample, when the conversion is above 50%, the compositional distribution becomes very rich in styrene units, showing a neat maximum at 95% in styrene units

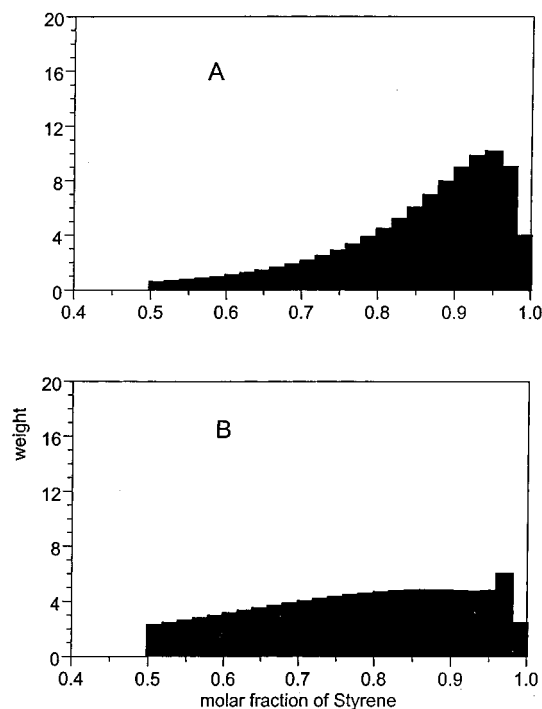


Figure 6. Compositional distribution histogram of samples S91 (A) and S78 (B).

(Figure 6A). In the S78 copolymer sample, instead, excess styrene is not sufficient to build up such large amount of styrene-rich copolymer units and the distribution is broad (Figure 6B).

The compositional distribution function derived here provides a detailed description of the amount of copolymer chains having a composition that deviates from the average. This kind of feature, up to the present, has not been extracted from the experimental data for any copolymer system (with the exception of an early study of styrene/2-vinylthiophene¹⁹ copolymers).

Conclusions

A method was developed to determine the bivariate distribution of masses and composition without fractionation of fractions and is therefore simpler than the standard “two-dimensional chromatography”.^{5–8} The method was applied to two random St/MAH copolymers obtained at high conversion. Some changes were introduced to the original formulation;¹⁵ namely the abundance of the fraction was derived from NMR (instead of using the differential refractometer signal) and the variance of the compositional distribution was measured experimentally (instead of using a theoretical estimate). SEC fractionation²⁰ was used to collect nearly monodisperse fractions and to compute the corresponding molar masses (by MALDI measurements) and compositions (by NMR measurements) for the two copolymers. The samples possessed a strong compositional drift and the molar fraction of Styrene grew as the chain size increased. bivariate distribution maps were derived by combining SEC/NMR and SEC/MALDI data with NMR data on the unfractionated sample.

A formula (eq 4), valid for all copolymers, is derived, which relates the bivariate distribution with the compositional distribution. This formula (which consists of an integration over chain length) was used to determine the compositional distribution for the two St/MAH copolymers.

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