Further Studies on the Composition and Microstructure of Copolymers by Statistical Modeling of Their Mass Spectra

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ABSTRACT: Statistical modeling of the mass spectral intensities of copolymers has been used to derive information on the distribution of monomers along the copolymer chain, and an automated procedure to find the composition and the sequence of the copolymers analyzed has been developed. A deconvolution method to determine the microstructure of copolymers when different chemical species contribute to the same mass spectral peak (that is, when a mass spectroscopic peak has an equivocal structural assignment) is presented. The effect of the partial degradation process on the mass spectra of copolymers is discussed, and a theory is given for the interpretation of the mass spectra of copolymers when the cleavage of the copolymer chain occurs by a selective or nonselective mechanism. A method is also reported to obtain the copolymer composition by direct analysis of the mass spectra. All these theories have been applied to determine the composition and microstructure of several copolymers (both addition and condensation types) whose mass spectra have been reported in the most recent literature.

1. Introduction

Although polymers often possess molecular dimensions too large to be revealed by high-resolution mass spectrometers (which usually have cut-offs below 10 000 Da), mass spectrometry (MS) has been successfully used to identify the mixture of oligomers formed in the partial degradation of synthetic and biological copolymers[1-7] or of the oligomers contained in low molecular weight polymers.[8,9]

We have recently found that decoding of the information contained in the mass spectral intensities leads to the determination of composition and microstructure in copolymers, and this represented significant progress, since only the mass numbers corresponding to MS peaks had been used in previous work on the structural elucidation of copolymers by MS.[10-12] Mass spectrometry is a powerful and rapid analytical method and, because it is able to look at the masses of individual molecules in a mixture of homologues, is particularly suitable for the detection of a series of oligomers. However, mass spectra have not been exploited to estimate oligomer distributions, due to the idea[1,2] that a lack of correlation existed between EI (electron impact) peak intensities and concentration of the oligomers in the mixture. The introduction of soft ionization techniques, such as chemical ionization (CI), fast atom bombardment (FAB), secondary ion mass spectroscopy (SIMS), laser desorption (LD), field desorption and field ionization (FD and FI), etc., has largely eliminated this problem, and much evidence has now accumulated showing that in many cases peak intensities of molecular ions appearing in the mass spectra reflect the relative amounts of oligomers present in the mixture.[1-9] Although this point now appears well established, one should always bear in mind that two major assumptions are being made when correlating MS peak intensities with the actual oligomer concentrations: (a) that the extent of fragmentation of molecular ions deriving from a series of homologous oligomers is not a function of the chain length and (b) that the detection efficiency is the same for all of the oligomers. If that is the case, in order to extract information about the composition and sequence of copolymers, one still has to learn how to exploit MS peak intensities, which depend on the relative abundances of the oligomers present in the spectrum and are directly related to the composition and microstructure of copolymers.

The statistical analysis of copolymers makes use of Bernoullian and Markovian models to characterize the microstructure of copolymer samples.[13-15] Assuming a theoretical distribution and then fitting the calculated oligomer abundances with the experimental peak intensities (see the example in Figure 1), one can determine the sequence and composition of the copolymer.[10-12] In our first approach to the problem,[10-12] we analyzed some microbial copolyesters having Bernoullian distributions, which were subjected to partial methanolysis to reduce their molecular weights. It was assumed that the chain cleavage was a nonselective process. This introduced a limitation in our approach, since the intensity of mass peaks actually depends both on the distribution of comonomers along the chain and on the cleavage process. We found that, from the analysis of the mass spectra, it is possible to ascertain if the cleavage of a copolymer chain occurs by a selective or a nonselective process, therefore removing the above ambiguity, as discussed in detail below.

In addition, we have extended our computations to determine the composition and microstructure of several copolymers whose mass spectra have been recently reported by various authors.[8,11,16-21] These spectra have been recorded using different ionization techniques such as LD, FAB, FI, and EI and refer both to low molecular weight copolymers[8,19] (which can be analyzed directly without subjecting the copolymer sample to partial cleavage to reduce their molecular weight) and to high copolymers.[11,16-21] The copolymers analyzed are of both the addition and the condensation type, thus removing another limitation in our previous studies, confined only to condensation copolymers.[10-12] Finally, one of the great advantages of NMR is that one may immediately get an estimate of the copolymer composition from the ratio of suitable peaks in the NMR spectrum, without performing the statistical calculations necessary to get the sequence information (from which the composition can also be derived).[13,14] Mass spectra may provide direct composition estimates as well, and we have now derived simple mathematical formulas that allow us to estimate the copolymer composition, independent of the statistical

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Table I
Number of Peaks Corresponding to Oligomers Expected in the Mass Spectra of a Two-Component Copolymer

highest oligomer[a]	peaks[b]	peaks[c]	peaks[d]
dimers	3	1	6
trimers	7	3	14
tetramers	12	6	24
pentamers	18	10	36
hexamers	25	15	50
heptamers	33	21	66
octamers	42	28	84
nonamers	52	36	104
decamers	63	45	126
11-mers	75	55	150
12-mers	88	66	176
13-mers	104	78	208
14-mers	119	91	238
15-mers	135	105	270
16-mers	152	120	304

[a] Highest oligomer group detected in the mass spectrum. [b] Peaks present in low molecular weight polymers or generated by partially-selective or nonselective cleavage processes (see section 3). [c] Peaks generated by totally-selective cleavage processes (see section 3). [d] Peaks present in low molecular weight polymers or generated by partially-selective or nonselective cleavage processes in the case of two mass series (see section 6).

calculations, by direct analysis of the mass spectra. The latter analysis allows us also to ascertain if the process used to cleave the copolymer chain has been selective or nonselective. Therefore, MS can now be used to provide direct estimates of copolymer composition, analogous to NMR. Statistical modeling of mass spectra of copolymers has thus reached a certain level of generalization, and it can be used to complement NMR analysis,[13,14] which has been so far the only technique available for sequencing copolymers.

2. Calculations

Mass spectrometry reveals mixtures of oligomers of relatively high molecular weight,[1-12] and in our simulation work we have selected examples of mass spectra showing peaks corresponding to oligomers ranging from dimers to 12-, 14-, and 16-mers in some cases. The number of MS peaks corresponding to each oligomer group (dimers, trimers, tetramers, etc.) for an AB copolymer is $(n + 1)$, where n represents the number of units. Table I, column 2, reports the total number of MS peaks that can be seen in the mass spectra of AB copolymers. For instance, if the mass spectrum reveals mixtures of oligomers from dimers up to 16-mers, the detection of 152 peaks (all belonging to the same mass number series) might be expected. The high number of MS peaks on which the simulation can be performed defines the microstructure of copolymers with great accuracy.

To perform numerical calculations, all the formulas reported later in the text have been incorporated in a computer program, MACO 4, written in Standard ANSI Fortran that runs on a Microvax computer. MACO 4 represents an improved and extended version of MACO 3;[10] for a detailed illustration of the program structure we refer the reader to the original description.[10] All of the mass spectra of the copolymers that appear in the text have been analyzed employing MACO 4. This work has required a number of improvements both in the theory and in the computer programs (MACO 3) used previously.[10] The present version of the computer program (MACO 4)[22] can deal with all the cases which have appeared in the literature independent of the method by which the partial degradation was performed (methanolysis, aminolysis, photolysis, or pyrolysis).[11,16-21]

MACO 4 accepts as input (a) the experimental mass spectrum, (b) the mathematical model that defines the distribution of comonomers along the chain, and (c) the process by which the oligomers subjected to MS were obtained (i.e., if they are preformed or obtained in a nonselective or selective cleavage process (see below)). The program generates the theoretical mass spectrum (see Figure 1), and, if a best fit is requested, the computer code varies the parameters associated with the selected mathematical model until it finds the best match between the observed and calculated data. For this purpose the minimization subroutine MINPACK1-LMDIF1 (belonging to the Argonne Library) is used.[10] MACO 4 yields as output the parameters that give the best agreement and the corresponding theoretical spectrum. The difference between the observed and calculated values is expressed by means of the Hamilton agreement factor[10,11] (AF):

$$\mathrm{AF} = (q_{\mathrm{tot}})^{-1}\left(\sum_i (I_i^{\mathrm{exptl}} - I_i^{\mathrm{calcd}})^2\right)^{1/2}$$

$$q_{\mathrm{tot}} = \left(\sum_i (I_i^{\mathrm{exptl}})^2\right)^{1/2} \qquad (1)$$

where I_i^{exptl} and I_i^{calcd} are the normalized experimental and calculated abundances of the oligomers. An average AF value is usually given by MACO 4 (see tables below). However, the program also calculates separate AF values for each group of oligomers, which can be used[10,11] to check the accuracy of the experimental data and the self-consistency of the calculations. Furthermore, MACO 4 provides an estimate of the composition of the copolymer, independent of that deriving from the statistical modeling calculations.

3. Effect of the Partial Degradation Process on the Mass Spectra of Copolymers

When a copolymer sample is subjected to partial degradation, a mixture of oligomers is formed and the intensity of each peak in the mass spectrum of a two-component (AB) copolymer is the sum of contributions due to oligomers having the same overall formula but different comonomer sequences. For instance, the intensity of MS peaks associated with the tetramers A_2B_2 and A_3B is

$$I_{A_2B_2} = I_{AABB} + I_{ABAB} + I_{ABBA} + I_{BAAB} + I_{BABA} + I_{BBAA}$$

$$I_{A_3B} = I_{AABB} + I_{AABA} + I_{ABAA} + I_{BAAA} \qquad (2)$$

where I_{XXXX} is the probability of finding the comonomer sequence XXXX (where X may be A or B) in the mixture of oligomers. The experimental intensities must therefore be pointwise deconvoluted to obtain the quantities I_{XXXX}, which are directly proportional to R^{∞}_{XXXX}, the probability of finding the sequence of comonomers XXXX in the nondegraded copolymer chain:

$$I_A = \sigma_1 R^{\infty}_A \qquad I_B = \sigma_2 R^{\infty}_B \qquad I_{AA} = \sigma_3 R^{\infty}_{AA}$$
$$I_{AB} = \sigma_4 R^{\infty}_{AB} \qquad I_{BB} = \sigma_5 R^{\infty}_{BB} \qquad (3)$$

where σ are proportionality factors which depend on the cleavage mechanism. Equation 3 implies that the mass spectral peak intensity depends on the distribution of comonomers along the copolymer chain. The initial assumption on which we developed[10-12] algorithms to match the experimental mass spectra to those theoretically calculated was that the partial degradation of the copol-

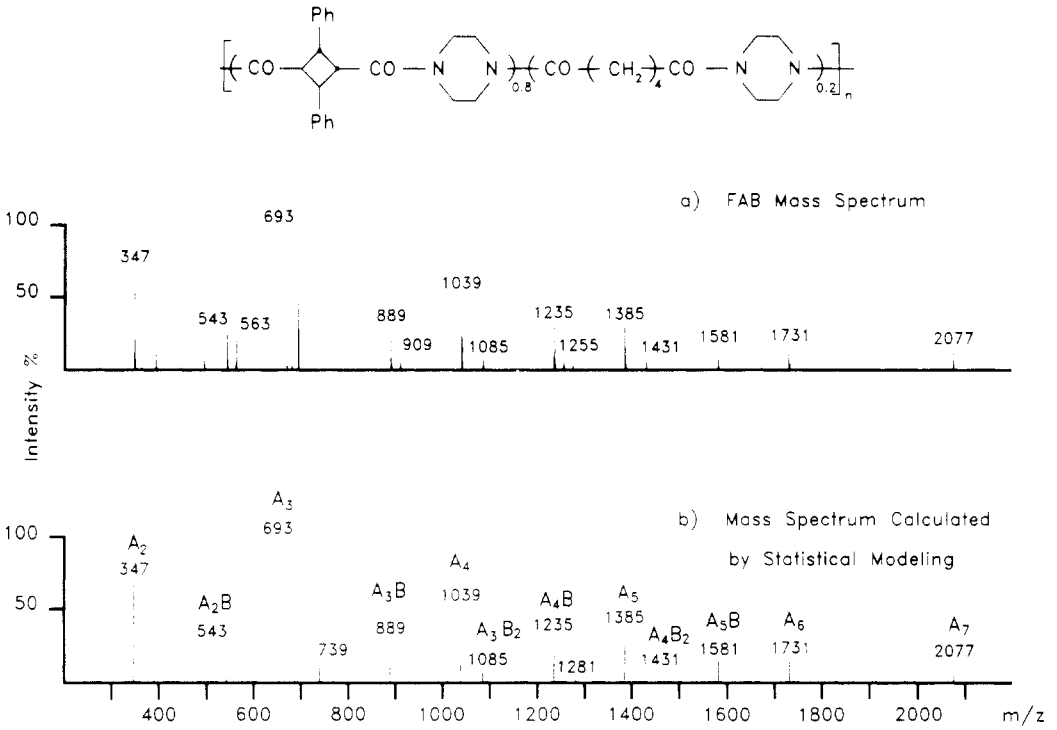


Figure 1. (a) Positive-ion FAB mass spectrum of the oligomers generated in the photolysis of copolyamide III.[17] (b) Theoretical mass spectrum generated by statistical modeling.

ymer chain occurs by a rigorously nonselective cleavage process. If all σ values in eq 3 are equal to 1, the relationship

$$I_{XXXX} = R^{\infty}_{XXXX} \tag{4}$$

holds for each sequence XXXX. Nonselective cleavage may occur in the pyrolysis of olefin and vinyl copolymers[2,16] and has been actually observed when a condensation copolymer is subjected to methanolysis,[11,12] hydrolysis,[19] and aminolysis.[18] Instead, a selective cleavage may occur in condensation copolymers bearing two different functional groups in the chain (for instance, amide and ester groups). Furthermore, thermal,[21] photolytic,[17] and ozone[20] cleavage may produce totally selective degradation processes along the copolymer chain. In fact, as illustrated in Figure 2, the cleavage process splits in two parts one of the comonomers, leaving intact the other. In the latter case, the probability ($R^{\infty}_{AABABBB}$) of finding the sequence of comonomers AABABBB in an infinite copolymer chain and the probability ($I_{AABABBB}$) of finding the sequence AABABBB in a heptamer are not the same (even the total number of MS peaks in the mixtures of oligomers is different from the case of nonselective cleavage, as shown in Table I, column 3), and a relationship between the two quantities has to be found for each specific case. In the following sections we shall derive equations for the probability of finding an oligomer sequence in the infinite copolymer chain and then we shall see how to modify them to match the conditions defined by the occurrence of a selective cleavage process.

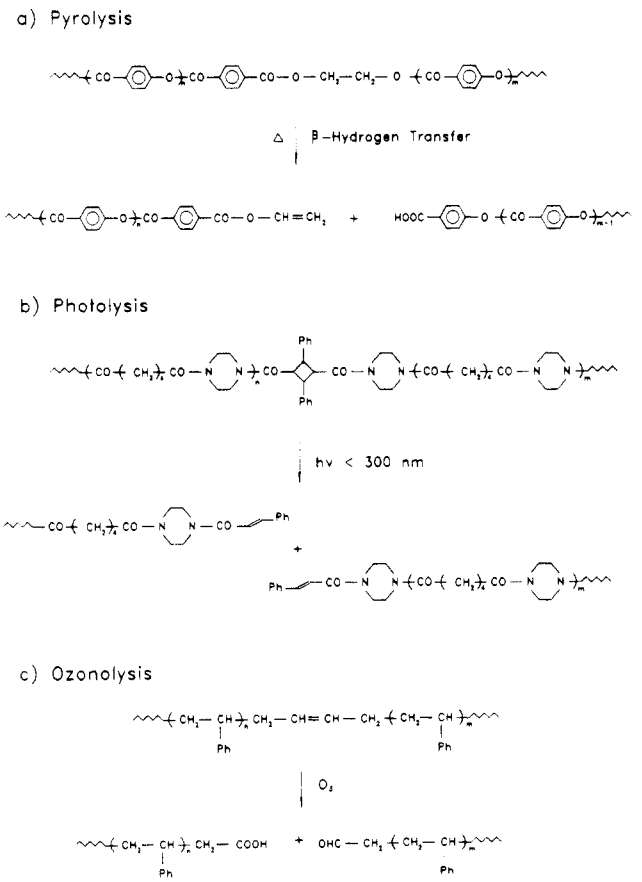


Figure 2. Examples of totally-selective chain cleavage processes.

4. Sequence Distributions in an Infinite Copolymer Chain

In our analysis we consider three different distributions of monomers along the copolymer chain, namely, first-order Markovian, Bernoullian, and sequential. We compute for each distribution R^{∞}_{XXXX}, the probability of finding the sequence of comonomers XXXX in the infinite chain. A Markov distribution is completely defined when the transition probability matrix (**P** matrix) is given. The **P** matrix is a square matrix of dimension N, where N is the number of different components that occur in the chain. Each matrix element P_{ij} describes the probability of finding the component i after the component j. For example, a Markov distribution for a two-component copolymer (AB) is defined when the four **P** matrix elements P_{AA}, P_{AB}, P_{BA}, and P_{BB} are given. The **P** matrix elements P_{ij} cannot assume arbitrary values. In fact, they must be positive

and they must satisfy the following property:

$$P_{AA} + P_{AB} = 1 \quad P_{BA} + P_{BB} = 1 \tag{5}$$

The probability of finding the hypothetical monomer sequences AABBA, AABAB, and BABBA is given by

$$R^{\infty}_{AABBA} = R^{\infty}_{A} P_{AA} P_{AB} P_{BB} P_{BA}$$

$$R^{\infty}_{AABAB} = R^{\infty}_{A} P_{AA} P_{AB} P_{BA} P_{AB}$$

$$R^{\infty}_{BABBA} = R^{\infty}_{B} P_{BA} P_{AB} P_{BB} P_{BA} \tag{6}$$

The quantities R^{∞}_{A} and R^{∞}_{B} (the probability of finding the sequence A or B in the infinite chain) in eq 6 are given by

$$R^{\infty}_{A} = P_{BA}/(P_{AB} + P_{BA}) \quad R^{\infty}_{B} = P_{AB}/(P_{AB} + P_{BA}) \tag{7}$$

R^{∞}_{A} was called S_A in the previous paper,[10] since R^{∞}_{A} also represents the probability that the chain starts with A.

We now compute R^{∞}_{XXXX} for a Bernoullian distribution. A Bernoullian distribution is completely defined when the molar fraction of A, $\rho(A)$, and the molar fraction of B, $\rho(B)$, are given. The probability of finding the hypothetical monomer sequences AABBA, AABAB, BABBA, A, and B is given by

$$R^{\infty}_{AABBA} = \rho(A)\rho(A)\rho(B)\rho(B)\rho(A)$$

$$R^{\infty}_{AABAB} = \rho(A)\rho(A)\rho(B)\rho(A)\rho(B)$$

$$R^{\infty}_{BABBA} = \rho(B)\rho(A)\rho(B)\rho(B)\rho(A)$$

$$R^{\infty}_{A} = \rho(A)$$

$$R^{\infty}_{B} = \rho(B) \tag{8}$$

We now compute R^{∞}_{XXXX} for a sequential distribution. This distribution is defined when the repeating sequence (G_{00}) is given. In a first approximation, R^{∞}_{XXXX} can be computed generating an artificial chain by repeating a large number of times the given sequence G_{00} and then using a "search-substring-in-string" procedure[23] to compute the number of times, N_{XXXX}, that a given sequence XXXX occurs in the chain. We shall refer to this method for deriving R^{∞} values for a sequential distribution as the "rate-of-occurrence" method. Accordingly, the probability of finding the sequence XXXX in the artificial chain is given by

$$R^{\infty}_{XXXX} = N_{XXXX}/L \tag{9}$$

(here L is the length of the artificial chain expressed in number of comonomer units present). Another quantity related to the sequence distribution of an infinite chain is the number-average length of like monomers,[13] which is a measure of the degree of "blockiness" of a copolymer chain. In the two-component copolymer example the number-average lengths of component A, $\langle n_A \rangle$, and of component B, $\langle n_B \rangle$, are defined by

$$\langle n_A \rangle = (\sum_i i R^{\infty}_{(A)_i})/(\sum_i R^{\infty}_{(A)_i})$$
$$\langle n_B \rangle = (\sum_i i R^{\infty}_{(B)_i})/(\sum_i R^{\infty}_{(B)_i}) \tag{10}$$

If the distribution of comonomers along the copolymer chain is Markovian, eqs 6 and 7 can be used to rewrite eq 10 as

$$\langle n_A \rangle = (1 - P_{AA})^{-1} \quad \langle n_B \rangle = (1 - P_{BB})^{-1} \tag{11}$$

If the chain follows a Bernoullian distribution, substituting eq 8 into eq 10 one obtains

$$\langle n_A \rangle = (1 - \rho(A))^{-1} \quad \langle n_B \rangle = (1 - \rho(B))^{-1} \tag{12}$$

If the chain follows a sequential distribution, number-average lengths can be evaluated using the definition in eq 10.

Sequence Distributions in a Finite Chain (Oligomers). In the case of low molecular weight copolymers and in cases where the copolymer chain cleavages occur by a nonselective process, the σ factors in eq 3 are equal to 1 and the identity in eq 4 holds for each sequence XXXX. This means that, in the cases specified above, eqs 6–9 can be directly applied to predict the MS peak intensities for copolymers that follow Bernoullian and Markovian distributions. We report here the pertinent equations in the final form actually used in our computations (MACO 4).

In the case of Bernoullian distributions,[10] from eqs 8, 2, and 4 it follows

$$I_A = \rho(A)$$

$$I_B = \rho(B)$$

$$I_{A_2} = \rho(A)\rho(A)$$

$$I_{AB} = 2\rho(A)\rho(B)$$

$$I_{B_2} = \rho(B)\rho(B)$$

$$I_{A_3} = \rho(A)\rho(A)\rho(A)$$

$$I_{A_2B} = 3\rho(A)\rho(A)\rho(B)$$

$$I_{AB_2} = 3\rho(A)\rho(B)\rho(B)$$

$$I_{B_3} = \rho(B)\rho(B)\rho(B) \tag{13}$$

In the csae of Markovian distributions,[10] from eqs 6, 7, 2, and 4 it follows

$$I_A = R^{\infty}_{A}$$

$$I_B = R^{\infty}_{B}$$

$$I_{A_2} = R^{\infty}_{A} P_{AA}$$

$$I_{AB} = R^{\infty}_{A} P_{AB} + R^{\infty}_{B} P_{BA}$$

$$I_{B_2} = R^{\infty}_{B} P_{BB}$$

$$I_{A_3} = R^{\infty}_{A} P_{AA} P_{AA}$$

$$I_{A_2B} = R^{\infty}_{A} P_{AA} P_{AB} + R^{\infty}_{A} P_{AB} P_{BA} + R^{\infty}_{B} P_{BA} P_{AA}$$

$$I_{AB_2} = R^{\infty}_{A} P_{AB} P_{BB} + R^{\infty}_{B} P_{BA} P_{AB} + R^{\infty}_{B} P_{BB} P_{BA}$$

$$I_{B_3} = R^{\infty}_{B} P_{BB} P_{BB} \tag{14}$$

The theory can be extended to the case of sequential copolymers. In fact, from eqs 9, 2, and 4 it follows

$$I_A = N_A/L$$

$$I_B = N_B/L$$

$$I_{A_2} = N_{AA}/L$$

$$I_{AB} = N_{AB}/L + N_{BA}/L$$

$$I_{B_2} = N_{BB}/L$$

$$I_{A_3} = N_{AAA}/L$$

$$I_{A_2B} = N_{AAB}/L + N_{ABA}/L + N_{BAA}/L$$

$$I_{AB_2} = N_{ABB}/L + N_{BAB}/L + N_{BBA}/L$$

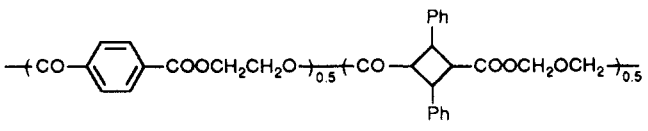
$$I_{B_3} = N_{BBB}/L \qquad (15)$$

Equations 13, 14, and 15 constitute a complete group of equations, valid in the case of nonselective cleavage, which can be used to compute the theoretical mass spectrum of a copolymer that follows Bernoullian, Markovian, or sequential distributions. Before going further with the theory, it seems appropriate to illustrate (in the following sections) a few examples where the equations derived up to now are used to model the experimental mass spectra.

5. Microstructure Determination in Low Molecular Weight Copolymers

The analysis of low molecular weight copolymers by MS is simpler than that of high molecular weight copolymers since their low weight avoids the necessity to subject the sample to partial degradation prior to the MS analysis. Furthermore, their mass spectra depend solely on the variables that describe the distribution of monomers along the chain and not on the cleavage process, rendering the simulation procedure straightforward. In many copolymerization processes, low molecular weight copolymers are formed together with high molecular weight copolymers (bimodal distributions) and both species have the same microstructure[9,19] (Bernoullian, Markovian, sequential, etc.). Therefore, the analysis of (performed) low molecular weight species by MS allows the determination of copolymer microstructure. We report here two examples[8,19] of microstructure determination from preformed oligomers. The structure of oligomers can be easily assigned in the original mass spectra[8,19] and, starting from the experimental intensities, eqs 13–15 can be directly applied.

In the first example, mixtures of low molecular weight oligomers of a copolyester containing ethylene terephthalate units (ET) and ethylene truxillate units (TX) (structure I) were analyzed by means of FAB-MS.[19]



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To proceed to the microstructure determination, the observed[19] MS peak intensities of the 15 mass peaks corresponding to oligomers ranging from dimers up to hexamers (shown in Table II) were given as input to MACO 4. Since the copolyester composition is known[19] to be $\rho(ET) = 0.50$, $\rho(TX) = 0.50$, theoretical mass spectra were generated for four different chain models, H1, H2, H3, and H4, which all correspond to the above composition (Table II). Model H1 is a pure Bernoullian distribution defined by $\rho(ET) = 0.50$, $\rho(TX) = 0.50$ with associated number-average lengths $\langle n_{ET} \rangle = 2$ and $\langle n_{TX} \rangle = 2$. Model H2 is a pure alternating $(ET\text{–}TX)_n$ distribution with associated number-average lengths $\langle n_{ET} \rangle = 1$ and $\langle n_{TX} \rangle = 1$. Model H3 is a pure Markovian distribution having **P** matrix elements $P_{ET,ET} = 0.20$, $P_{ET,TX} = 0.80$, $P_{TX,ET} = 0.80$, and $P_{TX,TX} = 0.20$ with associated number-average lengths $\langle n_{ET} \rangle = 1.25$ and $\langle n_{TX} \rangle = 1.25$. Model H4 is a pure Markovian distribution having **P** matrix elements $P_{ET,ET} = 0.80$, $P_{ET,TX} = 0.20$, $P_{TX,ET} = 0.20$, and $P_{TX,TX} = 0.80$ with associated number-average lengths $\langle n_{ET} \rangle = 5$ and $\langle n_{TX} \rangle = 5$.

Table II
Experimental[a] and Calculated[b–e] Relative Amounts of Preformed ET–TX Oligomers (ET = Ethylene Terephthalate, TX = Ethylene Truxillate)[19]

oligomer	m/z	obsd[a]	calcd[b] H1	calcd[c] H2	calcd[d] H3	calcd[e] H4
$(ET)_2$	401	10.6	12.1	0	4.8	19.4
(ET)(TX)	531	26.6	24.2	48.4	38.7	9.6
$(ET)_3$	593	3.4	3.1	0	0.5	8.0
$(TX)_2$	661	11.2	12.1	0	4.8	19.4
$(ET)_2(TX)$	723	8.8	9.5	12.6	12.1	4.5
$(ET)(TX)_2$	853	9.6	9.5	12.6	12.1	4.5
$(ET)_3(TX)$	915	3.9	4.4	0	2.6	3.5
$(TX)_3$	983	3.7	3.1	0	5.0	8.0
$(ET)_2(TX)_2$	1045	5.0	6.6	16.5	11.1	3.7
$(ET)(TX)_3$	1175	4.8	4.4	0	2.6	3.5
$(ET)_3(TX)_2$	1237	2.1	3.3	4.1	3.9	2.8
$(TX)_4$	1305	2.6	1.1	0	0.1	5.7
$(ET)_2(TX)_3$	1367	3.7	3.3	4.1	3.9	2.8
$(ET)(TX)_4$	1497	2.4	1.6	0	0.4	2.6
$(ET)_3(TX)_3$	1559	1.6	1.6	1.6	1.6	1.6
AF[f]			0.117	0.874	0.503	0.652

[a] Relative intensities of the (M^-) ions in the FAB mass spectrum taken from Table III, column 6 in ref 19. [b] Computed for model H1 using eq 13. [c] Computed for model H2 using eq 15. [d] Computed for model H3 using eq 14. [e] Computed for model H4 using eq 14. [f] Agreement factor computed using formula 1.

In Table II the theoretical peak intensities are reported for the four selected models. Model H1 gives the best agreement (AF = 11.7%; Table II), and, it is therefore concluded that the TE–TX copolyester is best described by a pure Bernoullian distribution with $\langle n_{ET} \rangle = 2$ and $\langle n_{TX} \rangle = 2$, as would be expected from the method used in the synthesis.[19]

In another case,[8] low molecular weight oligomers, formed during ther synthesis of a copolymer containing units of methyl methacrylates (MA) and units of butyl methacrylate (BA), were analyzed by laser desorption Fourier transform MS.[8] To find the distribution of MA and BA units along the chain, the observed intensities[8] of the 58 mass peaks corresponding to oligomers ranging from nonamers up to 15-mers (reported in Table 1S) were given as input to MACO 4 and three different chain models, K1, K2, and K3, were considered (Table 1S). Model K1 is a pure sequential distribution having a ten-monomer repeating unit: $(MA\text{–}MA\text{–}BA\text{–}MA\text{–}MA\text{–}BA\text{–}MA\text{–}MA\text{–}MA\text{–}BA)_n$. This particular sequence was selected because its associated composition ($\rho(MA) = 0.70$, $\rho(BA) = 0.30$) coincides with the composition given by the copolymer's manufacturer.[8] Model K2 is a pure Bernoullian distribution defined by $\rho(MA) = 0.74$, $\rho(BA) = 0.26$, which gave the

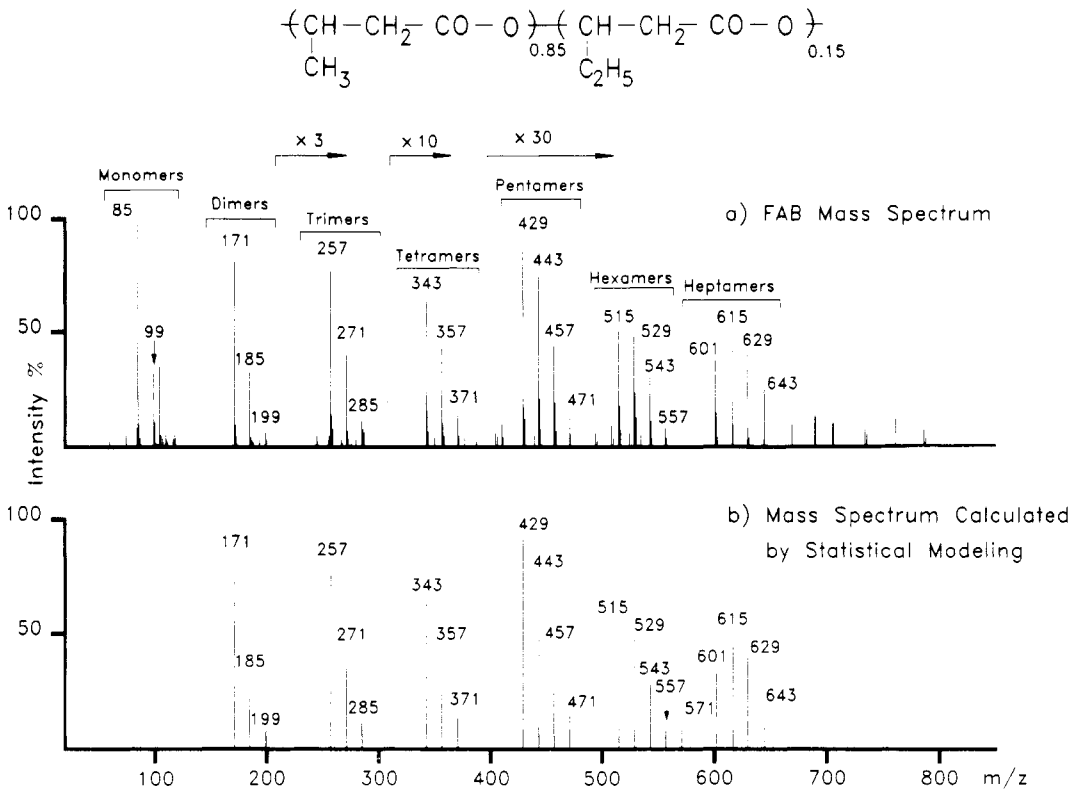


Figure 3. (a) Negative-ion FAB mass spectrum of the oligomers generated in the partial pyrolysis of P(HB-*co*-15%HV).[11] (b) Theoretical mass spectrum generated by statistical modeling.

best agreement factor in the minimization process among pure Markovian distributions. Model K3 is a pure Markovian distribution having **P** matrix elements $P_{MA,MA} = 0.78$, $P_{MA,BA} = 0.22$, $P_{BA,MA} = 0.50$, and $P_{BA,BA} = 0.50$ (with an associated composition $\rho(MA) = 0.69$ and $\rho(BA) = 0.31$) which gave the best agreement factor in the minimization process among pure Markovian distributions.

Considering that a radical copolymerization process was used to synthesize this MA/BA copolymer,[8] some qualitative predictions can be made based on copolymerization theory:[15] the pure Markovian distribution (model K3) is expected to yield the best agreement factor, while the agreement with experimental intensity data for the pure sequential (model K1) and for the pure Bernoullian (model K2) distributions is expected to be poor. These predictions are thoroughly confirmed by our computations (Table 1S), which yielded the following values: for model K1, AF = 1.273; for model K2, AF = 0.241; for model K3, AF = 0.092 ($\langle n_{MA} \rangle = 4.5$, $\langle n_{BA} \rangle = 2$).

6. Oligomers Generated by Nonselective Chain Cleavage Processes

In the case of oligomers generated by nonselective chain cleavages of copolymers, eqs 13–15 can be directly applied to obtain the microstructure. Some examples of analysis of mixtures of oligomers generated by methanolysis and pyrolysis of microbial copolyesters (both nonselective chain processes in these specific cases) have been previously reported.[10-12] However, the best fit copolymer compositions were calculated separately for each group of oligomers. As a matter of fact, previous computer programs (MACO 1[11] and MACO 3[10]) do not allow display of the full mass spectra calculated by statistical modeling. In Figure 3a is reported the negative ion FAB mass spectrum of the partial pyrolysis residue of P(HB-*co*-15%HV) (ref 11, sample 3), and in Figure 3b is displayed the mass spectrum calculated for a Bernoullian distribution (eq 13) by MACO 4. We may notice that the observed intensities of MS peaks corresponding to monomers in Figure 3a were not included in the simulation. In fact, for all the other groups of oligomers (from dimers to heptamers), the volatility difference in the MS is negligible. Instead, for the two monomers HB and HV the difference in volatility cannot be neglected, and thus the ratio of their peak intensities ($I_{HB}/I_{HV} = 75/25$) does not reflect the copolymer composition ($I_{HB}/I_{HV} = 85/15$).[11] Also, peaks beyond $m/z = 643$ in Figure 3a were not included in the calculation because they are known[11] to be scarcely reproducible.

Besides these straightforward examples, in some instances it is necessary to consider more complex models such as the case of binary mixtures of copolymers and/or the case of uncertainties in the structural assignment of MS peaks. Therefore, prior to discussing these cases, we shall derive the theory necessary to analyze these systems.

If the sample to analyze is a binary mixture of two copolymers, say C1 and C2, having the same comonomers but different sequence distributions along the two chains, the resulting MS peak intensities shall be the weighted sum of the contributions due to C1 and C2, and, therefore, eq 2 cannot be directly applied. If we call X the molar fraction of copolymer C1 in the mixture and $(1 - X)$ the molar fraction of copolymer C2, we can rewrite eq 2 as

$$I_{A_2B_2} = X(I^1_{AABB} + I^1_{ABAB} + I^1_{ABBA} + I^1_{BAAB} + I^1_{BABA} + I^1_{BBAA}) + (1 - X)(I^2_{AABB} + I^2_{ABAB} + I^2_{ABBA} + I^2_{BAAB} + I^2_{BABA} + I^2_{BBAA})$$

$$I_{A_3B} = X(I^1_{AAAB} + I^1_{AABA} + I^1_{ABAA} + I^1_{BAAA}) + (1 - X)(I^2_{AAAB} + I^2_{AABA} + I^2_{ABAA} + I^2_{BAAA}) \quad (16)$$

where I^1_{XXXX} and I^2_{XXXX} are the contributions to the MS peak intensities deriving from copolymer C1 and from copolymer C2. To derive some explicit expressions from eq 16, we must specify the type of distribution followed

by chains C1 and C2. If copolymer C1 follows a Bernoullian distribution defined by molar fractions $\rho_1(A)$ and $\rho_1(B)$ and copolymer C2 follows a sequential distribution, then, inserting eqs 8, 4, and 9 into eq 16, one obtains

$$I_A = X\rho_1(A) + (1 - X)(N_A/L)$$

$$I_B = X\rho_1(B) + (1 - X)(N_B/L)$$

$$I_{A_2} = X\rho_1(A)\rho_1(A) + (1 - X)(N_{AA}/L)$$

$$I_{AB} = 2X\rho_1(A)\rho_1(B) + (1 - X)(N_{AB}/L + N_{BA}/L)$$

$$I_{B_2} = X\rho_1(B)\rho_1(B) + (1 - X)(N_{BB}/L)$$

$$I_{A_3} = X\rho_1(A)\rho_1(A)\rho_1(A) + (1 - X)(N_{AAA}/L)$$

$$I_{A_2B} = 3X\rho_1(A)\rho_1(A)\rho_1(B) + (1 - X)(N_{AAB}/L + N_{ABA}/L + N_{BAA}/L)$$

$$I_{AB_2} = 3X\rho_1(A)\rho_1(B)\rho_1(B) + (1 - X)(N_{ABB}/L + N_{BAB}/L + N_{BBA}/L)$$

$$I_{B_3} = X\rho_1(B)\rho_1(B)\rho_1(B) + (1 - X)(N_{AAA}/L) \quad (17)$$

If copolymer C1 follows a sequential distribution with repeating sequence G_{01} and also copolymer C2 is described by a sequential distribution with repeating sequence G_{02}, then, using eq 9, eq 16 becomes

$$I_A = XN_A^{(1)}/L + (1 - X)N_A^{(2)}/L$$

$$I_B = XN_B^{(1)}/L + (1 - X)N_B^{(2)}/L$$

$$I_{A_2} = XN_{AA}^{(1)}/L + (1 - X)N_{AA}^{(2)}/L$$

$$I_{AB} = X(N_{AB}^{(1)} + N_{BA}^{(1)})/L + (1 - X)(N_{AB}^{(2)} + N_{AB}^{(2)})/L$$

$$I_{B_2} = XN_{BB}^{(1)}/L + (1 - X)N_{BB}^{(2)}/L$$

$$I_{A_3} = XN_{AAA}^{(1)}/L + (1 - X)N_{AAA}^{(2)}/L$$

$$I_{A_2B} = X(2N_{AAB}^{(1)} + N_{ABA}^{(1)})/L + (1 - X)(2N_{AAB}^{(2)} + N_{ABA}^{(2)})/L$$

$$I_{AB_2} = X(2N_{ABB}^{(1)} + N_{BAB}^{(1)})/L + (1 - X)(2N_{ABB}^{(2)} + N_{BAB}^{(2)})/L$$

$$I_{B_3} = XN_{BBB}^{(1)}/L + (1 - X)N_{BBB}^{(2)}/L \quad (18)$$

where $N_{XXXX}^{(1)}$ and $N_{XXXX}^{(2)}$ are the number of times that the given sequence XXX occurs in the chains C1 and C2. If copolymer C1 follows a Bernoullian distribution defined by molar fractions $\rho_1(A)$ and $\rho_1(B)$ and copolymer C2 follows a Bernoullian distribution defined by molar fractions $\rho_2(A)$ and $\rho_2(B)$, eq 16 takes the well-known[11] form

$$I_A = X\rho_1(A) + (1 - X)\rho_2(A)$$

$$I_B = X\rho_1(B) + (1 - X)\rho_2(B)$$

$$I_{A_2} = X\rho_1(A)\rho_1(A) + (1 - X)\rho_2(A)\rho_2(A)$$

$$I_{AB} = 2X\rho_1(A)\rho_1(B) + 2(1 - X)\rho_2(A)\rho_2(B)$$

$$I_{B_2} = X\rho_1(B)\rho_1(B) + (1 - X)\rho_2(B)\rho_2(B) \quad (19)$$

Number-average lengths $\langle n_A \rangle$ and $\langle n_B \rangle$ for a binary mixture of copolymers are the weighted sum of number-average lengths for the two pure copolymers. Therefore, to evaluate $\langle n_A \rangle$ and $\langle n_B \rangle$, one must first compute the number-average lengths $\langle n_A^{(1)} \rangle$, $\langle n_B^{(1)} \rangle$, $\langle n_A^{(2)} \rangle$, and $\langle n_B^{(2)} \rangle$ for copolymers C1 and C2 making use of eq 12, 10, or 11 and then combine these quantities according to the formulas

$$\langle n_A \rangle = X\langle n_A^{(1)} \rangle + (1 - X)\langle n_A^{(2)} \rangle$$
$$\langle n_B \rangle = X\langle n_B^{(1)} \rangle + (1 - X)\langle n_B^{(2)} \rangle \quad (20)$$

The molar fractions of comonomers A and B in the binary mixture are computed by inserting the values for I_A and I_B obtained from eq 19, 17, or 18 in the expressions

$$\rho(A) = \frac{I_A}{I_A + I_B} \qquad \rho(B) = \frac{I_B}{I_A + I_B} \quad (21)$$

The theoretical MS peak intensities obtained using eqs 13–19 are valid when all peaks in the mass spectrum belong to the same mass number series, i.e., when all peaks correspond to oligomers A_mB_n, which start and end with the same chemical groups. Therefore, once a theoretical MS spectrum (I^{calcd}) is generated using eqs 13–19, a comparison between theoretical and measured MS intensities can be readily done by computing the agreement factor (eq 1). However, often the mass spectrum displays peaks associated with two different mass series, say S1 and S2, which correspond to the same oligomer but have different end groups. Therefore, the total number of MS peaks that can be seen in the mass spectra of AB copolymers increases as $2(n + 1)$ (Table I, column 4). In these cases, one must first compute the theoretical MS intensities $I^{S1,calcd}$ and $I^{S2,calcd}$ for the two series and then evaluate separately the agreement factors AF^{S1} and AF^{S2} for the two series using eq 1. The total agreement factor is obtained as a combination of AF^{S1} and AF^{S2}:

$$AF = (1/q_{tot})[q_1AF^{S1} + q_2AF^{S2}]$$
$$q_1 = (\sum_i (I_i^{S1,exptl})^2)^{1/2} \qquad q_2 = (\sum_i (I_i^{S1,exptl})^2)^{1/2} \quad (22)$$

where $I^{S1,exptl}$ and $I^{S2,exptl}$ are the intensities of MS peaks belonging to the series S1 and S2. In Table 2S is reported an example of this type (discussed below). Copolymer mass spectra displaying two different mass series may show a further complication. In fact, it can happen that the MS peak seen at mass number μ has an *uncertain* structural assignment since it can be associated with the oligomer A_pB_q belonging to series S1 or associated with

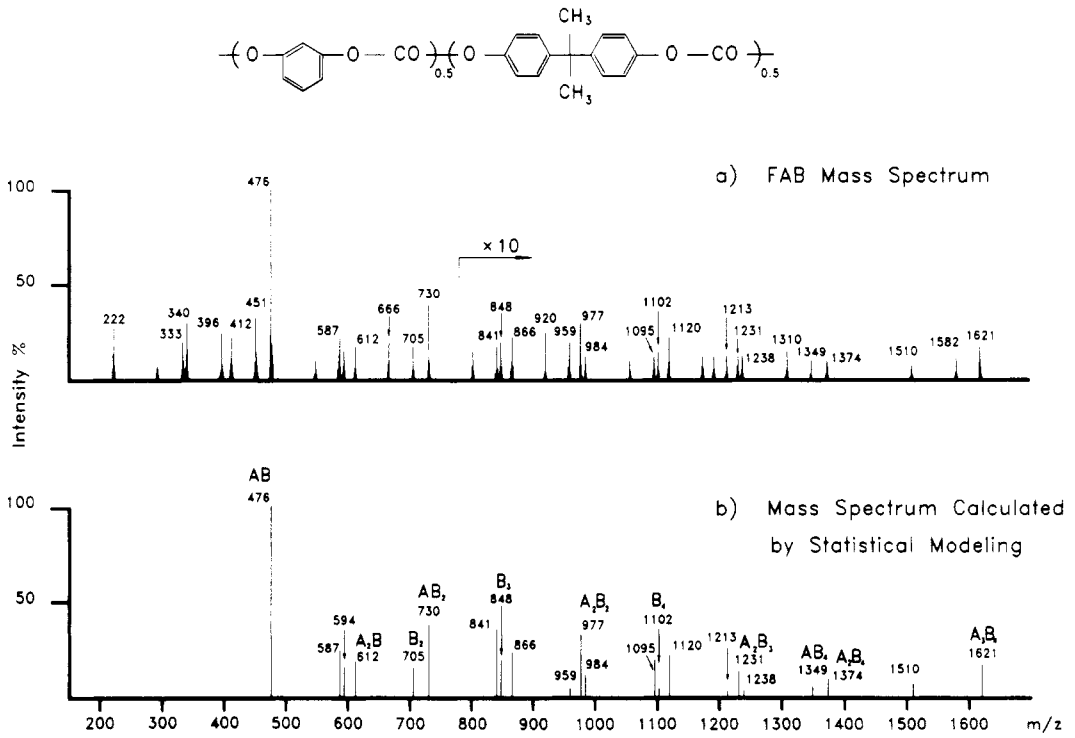


Figure 4. (a) Positive-ion FAB mass spectrum of the oligomers generated in the partial aminolysis of RE–BP copolycarbonate IIa.[18] (b) Theoretical mass spectrum generated by statistical modeling.

the oligomer A_rB_s belonging to series S2. A deconvolution procedure must be applied in these cases, since the intensity of the peak associated with mass number μ is the weighted sum of the contribution from the isobaric oligomers A_pB_q and A_rB_s. Therefore, one must compute the theoretical intensities $I^{S1,calcd}$ and $I^{S2,calcd}$ for series S1 and S2 and then combine the intensities of isobaric oligomers using the formula

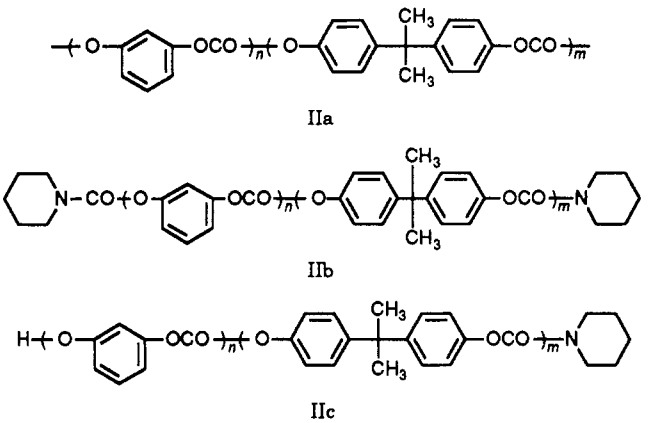
$$I^{S1+S2,calcd} = tI^{S1,calcd} + (1-t)I^{S2,calcd} \qquad (23)$$

where t is an unknown parameter. In this case, the copolymer composition will be a linear combination of the compositions associated with $I^{S1+S2,calcd}$, $I^{S1,calcd}$, and $I^{S2,calcd}$, and it is also necessary to modify eq 22 for the agreement factor in the following way:

$$AF = (q_{12}/q_{tot})AF^{S1+S2} + (q_1/q_{tot})AF^{S1} + (q_2/q_{tot})AF^{S2}$$
$$q_{12} = (\sum_i (I_i^{S1+S2,exptl})^2)^{1/2} \qquad (24)$$

where $I^{S1+S2,exptl}$ are the intensities of MS peaks belonging to both series S1 and S2 and where AF^{S1+S2} is obtained by inserting $I^{S1+S2,exptl}$ and $I^{S1+S2,calcd}$ in eq 1.

To illustrate some complex systems, we have selected an aromatic copolycarbonate (structure IIa) containing resorcinol units (RE) and Bisphenol A units (BP). The copolymer was synthesized by interfacial polymerization[18] with the purpose of obtaining an (exactly) alternating copolymer. to check its microstructure, the copolycarbonate was amminolyzed using piperidine, and the FAB mass spectrum of the mixture of products obtained was recorded. Experimental MS data[18] are reported in Figure 4a and in Table 2S, and, from inspection of these data, it appears that several peaks do correspond to sequences containing blocks of two, three, and four consecutive BP units, thus demonstrating that the copolymer is not exactly alternating.[18] Peaks in the MS spectrum can be grouped[18] in two mass series: series S1 (structure IIc) has one piperidine end group and series S2 (structure IIb) has two piperidine end groups.



IIa

IIb

IIc

To proceed to the microstructure determination, the observed[18] MS peak intensities of the 22 mass peaks corresponding to oligomers ranging from dimers up to heptamers (Table 2S), were given as input to MACO 4, and eq 22 was used to compute the agreement factor. Since the amminolysis cleavage is a nonselective process, eqs 13–19 were used to generate theoretical intensities and five different chain models, M1, M2, M3, M4, and M5, were considered. Model M1 is a pure alternating $(RE–BP)_n$ distribution, which implies a composition $\rho(RE) = 0.50$, $\rho(BP) = 0.50$. Model M2 is a pure sequential $(RE–BP–RE–BP–BP)_n$ distribution, with an associated composition $\rho(RE) = 0.40$, $\rho(BP) = 0.60$. Model M3 is a Markovian distribution having **P** matrix elements $P_{RE,RE} = 0.00$, $P_{RE,BP} = 1.00$, $P_{BP,RE} = 0.76$, and $P_{BP,BP} = 0.24$ (with an associated composition $\rho(RE) = 0.43$, $\rho(BP) = 0.57$), which gave the best agreement factor among pure Markovian distributions in the minimization process. Model M4 is a mixture of two pure sequential copolymers containing 86% alternating $(RE–BP)_n$ and 14% sequential $(RE–(BP)_{20})_n$ distribution with an associated composition $\rho(RE) = 0.44$, $\rho(BP) = 0.56$. This model takes into account spurious sequences containing consecutive BP units by introducing a second chain containing long $(BP)_n$ blocks. The value $X = 0.86$ gave the best agreement factor in the minimization

Table III
Experimental[a] and Calculated[b-e] Relative Amounts of the Partial Pyrolysis Products from an AN-ST Copolymer (AN = Acrylonitrile, ST = Styrene)[16]

oligomer	m/z	obsd[a]	calcd[b] G1	calcd[c] G2	calcd[d] G3	calcd[e] G4	oligomer	m/z	obsd[a]	calcd[b] G1	calcd[c] G2	calcd[d] G3	calcd[e] G4
$(AN)_3(ST)_2$	367	13.9	7.8	12.5	12.4	13.3	$(AN)_2(ST)_6$	730	0	1.2	0	0	0
$(AN)_5(ST)$	369	0	1.7	0	0	0	$(AN)_4(ST)_5$	732	2.8	1.7	3.5	3.4	2.8
$(AN)_7$	371	0	0.2	0	0	0	$(AN)_6(ST)_4$	734	1.8	1.9	0.1	1.1	2.0
$(AN)_2(ST)_3$	418	11.1	7.8	12.5	12.4	11.1	$(AN)_8(ST)_3$	736	0	0.7	0	0	0
$(AN)_4(ST)_2$	420	4.6	4.3	0.1	1.4	2.8	$(AN)_{10}(ST)_2$	738	0	0.1	0	0	0
$(AN)_6(ST)$	422	0	0.9	0	0	0	$(AN)(ST)_7$	781	0	0.3	0	0	0
$(AN)(ST)_4$	469	0	3.9	0	0	0	$(AN)_3(ST)_6$	783	0.1	1.1	0	0	0.1
$(AN)_3(ST)_3$	471	12.0	5.8	18.5	15.7	14.2	$(AN)_5(ST)_5$	785	6.9	2.2	9.1	7.0	6.1
$(AN)_5(ST)_2$	473	0.4	2.6	0	0	0.5	$(AN)_7(ST)_4$	787	0	1.3	0	0.1	0.5
$(ST)_5$	520	0	0.8	0	0	0	$(AN)_4(ST)_6$	836	0.4	1.9	0.1	1.0	1.0
$(AN)_2(ST)_4$	522	1.8	4.3	0.1	1.4	1.5	$(AN)_6(ST)_5$	838	3.7	1.9	4.2	4.0	4.4
$(AN)_4(ST)_3$	524	8.8	4.3	7.9	7.7	8.4	$(AN)_8(ST)_4$	840	0	0.7	0	0	0.1
$(AN)_6(ST)_2$	526	0.3	1.2	0	0	0	$(AN)(ST)_8$	885	0	0.1	0	0	0
$(AN)(ST)_5$	573	0	1.7	0	0	0	$(AN)_3(ST)_7$	887	0	1.1	0	0	0
$(AN)_3(ST)_4$	575	6.9	4.3	7.9	7.7	6.7	$(AN)_5(ST)_6$	889	4.6	1.9	4.2	4.0	3.2
$(AN)_5(ST)_3$	577	0.9	3.2	0.1	1.0	2.0	$(AN)_7(ST)_5$	891	0.9	1.1	0.1	0.7	1.3
$(AN)_2(ST)_5$	626	0	2.6	0	0.1	0.1	$(AN)_4(ST)_7$	940	0	1.3	0	0.1	0.1
$(AN)_4(ST)_4$	628	9.2	2.9	10.6	8.5	7.6	$(AN)_6(ST)_6$	942	4.2	1.2	5.5	4.1	3.5
$(AN)_6(ST)_3$	630	0.3	1.1	0	0.1	0.3	$(AN)(ST)_9$	989	0	0.1	0	0	0
$(AN)_8(ST)_2$	632	0	0.4	0	0	0	$(AN)_3(ST)_8$	991	0	0.7	0	0	0
$(AN)(ST)_6$	677	0	0.9	0	0	0	$(AN)_5(ST)_7$	993	0.5	1.1	0.1	0.7	0.6
$(AN)_2(ST)_5$	679	0.5	2.3	0.1	1.0	1.0							
$(AN)_4(ST)_4$	681	4.2	1.7	3.5	3.4	3.7	AF[f]			0.586	0.323	0.185	0.111
$(AN)_6(ST)_3$	683	0	1.1	0	0	0.1							

[a] Relative intensities of the (M^+) ions from the field ionization mass spectrum taken from Figure 3c in ref 16. [b] Computed for model G1 using eq 13. [c] Computed for model G2 using eq 15. [d] Computed for model G3 using eq 17. [e] Computed for model G4 using eq 14. [f] Agreement factor computed using formula 1.

process. Model M5 is a binary mixture of copolymers containing a 77% sequential $(RE-BP)_n$ and a 23% Bernoullian distribution with composition $p_2(RE) = 0.27$, $p_2(BP) = 0.73$. The overall composition of this mixture is $p(RE) = 0.45$, $p(BP) = 0.55$. The values $X = 0.77$ and $p_2(RE) = 0.27$ gave the best agreement factor in the minimization process.

The results of these calculations (Table 2S) specify that the distribution of monomers along the copolycarbonate chain is best described by a pure Markovian distribution (model M3; AF = 5.9%), which accounts for the presence of consecutive sequences of BP units found in the mass spectrum[18] by setting P_{BP-BP} (the probability of finding unit BP after unit BP) to a value different from zero. The number-average length of BP sequences is $\langle n_{BP} \rangle = 1.3$, and the average number of RE-BP bonds over 100 repeating units[24] in the chain is given by $100R^{\infty}_{RE-BP} = 43$. In Figure 4a is reported the FAB mass spectrum[18] of the partial aminolysis residue of copolymer IIa, and in Figure 4b is displayed the mass spectrum calculated by statistical modeling (Table 2S). As discussed above for P(HB-*co*-15%HV) (Figure 3), also in the present case the observed intensities of MS peaks corresponding to monomers in Figure 4a were not included in the simulation.

In another example, we analyzed a copolymer obtained by free-radical copolymerization, an AN-ST copolymer (AN = acrylonitrile, ST = styrene), studied by means of pyrolysis-field-ionization MS.[16] To proceed to the microstructure determination, the observed[16] MS peak intensities of the 45 mass peaks corresponding to oligomers ranging from pentamers up to 12-mers (shown in Table III) were given as input to program MACO 4. The pyrolysis cleavage was considered to be a nonselective process, and four different chain models, G1, G2, G3, and G4, were considered. Model G1 is a pure Bernoullian distribution defined by $p(AN) = 0.50$, $p(ST) = 0.50$, which gave the best agreement factor among Bernoullian distributions in the minimization process. Model G2 is a pure alternating $(AN-ST)_n$ distribution. This model was chosen because it predicts the systematic absence of MS signals at m/z = 422, 469, 520, 573, 632, 677, 991, which is a relevant feature of this mass spectrum[16] (Table III). Model G3 is a binary mixture of copolymers containing 96% of an alternating $(RE-BP)_n$ and 4% of a Bernoullian distribution with composition $p_2(AN) = 0.50$, $p_2(ST) = 0.50$. The value $X = 0.96$ gave the best agreement factor in the minimization process. Model G4 is the pure Markovian distribution having **P** matrix elements $P_{AN,AN} = 0.11$, $P_{AN,ST} = 0.89$, $P_{ST,ST} = 0.11$, and $P_{ST,AN} = 0.89$ (with an associated composition of $p(AN) = 0.50$, $p(ST) = 0.50$), which gave the best agreement factor among pure Markovian distributions in the minimization process.

Table III reports the theoretical mass spectra for the four models. The results show that the chain is best described by a Markovian distribution (model G4; AF = 11.1%). These results are in agreement with free-radical copolymerization kinetic theory,[15] which predicts that the microstructure of those copolymers is seldom described by a pure Bernoullian or sequential disrtibution but usually is first order Markovian (in fact, agreement factors for models G1, G2, and G3 are poor). The Markovian distribution predicted by the theory[15] has **P** matrix elements given by

$$P_{AA} = \frac{r_A f_A}{f_B + r_A f_A} \qquad P_{BB} = \frac{r_B f_B}{f_A + r_B f_B} \tag{25}$$

where r_A and r_B are the copolymerization reactivity ratios for radical A* and radical B* and f_A and f_B are the molar fractions of the two comonomers in the feed.

For the AN-ST 50:50 copolymer, the quantities r_{AN}, r_{ST}, f_{AN}, and f_{ST} are available from the literature.[25] Inserting these experimental values in eq 25, we obtain $P_{AN,AN} = 0.114$ and $P_{ST,ST} = 0.114$, which are in excellent agreement with the values $P_{AN,AN} = 0.11$ and $P_{ST,ST} = 0.11$ derived from the analysis of the mass spectrum (Table III). As mentioned above, uncertainties in the structural assignment of MS peaks increase the difficulty of mass

Table IV
Experimental[a] and Calculated[b-d] Relative Amounts of the Partial Pyrolysis Products from an AN-ST Copolymer (AN = Acrylonitrile, ST = Styrene)[16]

deprotonated oligomer	protonated oligomer	m/z	obsd[a]	calcd[b]	calcd[c]	deprotonated oligomer	protonated oligomer	m/z	obsd[a]	calcd[b]	calcd[c]
$(AN)_5$	$(AN)_3(ST)$	264	4.6	0.6	4.5	$(AN)_4(ST)_6$	$(AN)_2(ST)_7$	835	1.8	1.6	1.1
$(AN)_4(ST)$	$(AN)_4(ST)$	315	4.6	2.9	4.8	$(AN)_6(ST)_5$	$(AN)_4(ST)_6$	837	3.9	2.4	4.0
$(AN)_3(ST)_2$	$(AN)(ST)_3$	366	3.5	5.8	3.4	$(AN)_8(ST)_4$	$(AN)_6(ST)_5$	839	3.9	1.6	3.7
$(AN)_5(ST)$	$(AN)_3(ST)_2$	368	3.8	1.2	3.8	$(AN)_{10}(ST)_3$	$(AN)_8(ST)_4$	841	0.3	0.3	1.0
$(AN)_7$	$(AN)_5(ST)$	370	0.2	0.1	0.1	$(AN)_3(ST)_7$	$(AN)(ST)_8$	886	0.01	0.9	0.1
$(AN)_2(ST)_3$	$(ST)_4$	417	2.7	5.9	2.8	$(AN)_5(ST)_6$	$(AN)_3(ST)_7$	888	3.3	2.4	3.4
$(AN)_4(ST)_2$	$(AN)_2(ST)_3$	419	2.9	3.1	3.0	$(AN)_7(ST)_5$	$(AN)_5(ST)_6$	890	3.9	2.6	4.1
$(AN)_6(ST)$	$(AN)_4(ST)_2$	421	1.0	0.7	0.9	$(AN)_9(ST)_4$	$(AN)_7(ST)_5$	892	1.4	0.8	1.3
$(AN)_3(ST)_3$	$(AN)(ST)_4$	470	4.4	4.1	4.3	$(AN)_{11}(ST)_3$	$(AN)_9(ST)_4$	894	0.1	0.3	0.1
$(AN)_5(ST)_2$	$(AN)_3(ST)_3$	472	4.0	2.1	4.0	$(AN)_4(ST)_7$	$(AN)_2(ST)_8$	939	0.3	1.7	0.5
$(AN)_7(ST)$	$(AN)_5(ST)_2$	474	0.5	0.3	0.4	$(AN)_6(ST)_6$	$(AN)_4(ST)_7$	941	3.2	3.0	3.3
$(AN)_9$	$(AN)_7(ST)$	476	0.04	0.01	0.1	$(AN)_8(ST)_5$	$(AN)_6(ST)_6$	943	3.4	1.5	3.3
$(AN)_2(ST)_4$	$(ST)_5$	521	0.5	3.1	0.4	$(AN)_{10}(ST)_4$	$(AN)_8(ST)_5$	945	0.7	0.1	0.6
$(AN)_4(ST)_3$	$(AN)_2(ST)_4$	523	2.3	3.4	2.2	$(AN)_3(ST)_8$	$(AN)(ST)_9$	990	0.01	0.9	0.8
$(AN)_6(ST)_2$	$(AN)_4(ST)_3$	525	2.7	1.2	2.8	$(AN)_5(ST)_7$	$(AN)_3(ST)_8$	992	0.9	2.6	0.7
$(AN)_8(ST)$	$(AN)_6(ST)_2$	527	0.2	0.1	0.2	$(AN)_7(ST)_6$	$(AN)_5(ST)_7$	994	1.8	2.0	1.8
$(AN)_3(ST)_4$	$(AN)(ST)_5$	574	2.2	3.4	2.4	$(AN)_9(ST)_5$	$(AN)_7(ST)_6$	996	1.5	1.1	1.5
$(AN)_5(ST)_3$	$(AN)_3(ST)_4$	576	2.2	2.3	2.2	$(AN)_{11}(ST)_4$	$(AN)_9(ST)_5$	998	0.2	0.7	0.3
$(AN)_7(ST)_2$	$(AN)_5(ST)_3$	578	0.9	0.6	0.8	$(AN)_4(ST)_8$	$(AN)_2(ST)_9$	1043	0.01	1.62	0.01
$(AN)_4(ST)_4$	$(AN)_2(ST)_5$	627	2.8	2.9	2.9	$(AN)_6(ST)_7$	$(AN)_4(ST)_8$	1045	1.29	2.05	1.16
$(AN)_6(ST)_3$	$(AN)_4(ST)_4$	629	3.1	1.4	2.9	$(AN)_8(ST)_6$	$(AN)_6(ST)_7$	1047	1.82	1.33	2.01
$(AN)_8(ST)_2$	$(AN)_6(ST)_3$	631	0.5	0.3	0.5	$(AN)_{10}(ST)_5$	$(AN)_8(ST)_6$	1049	0.53	0.07	0.51
$(AN)_2(ST)_5$	$(AN)(ST)_6$	678	0.9	2.3	0.8	$(AN)_{12}(ST)_4$	$(AN)_{10}(ST)_5$	1051	0.06	0.12	0.01
$(AN)_4(ST)_4$	$(AN)_2(ST)_5$	680	1.7	2.0	1.8	$(AN)_5(ST)_8$	$(AN)_3(ST)_9$	1096	0.15	0.15	0.05
$(AN)_6(ST)_3$	$(AN)_4(ST)_4$	682	1.6	0.9	2.0	$(AN)_7(ST)_7$	$(AN)_5(ST)_8$	1098	1.14	0.91	1.10
$(AN)_8(ST)_2$	$(AN)_6(ST)_3$	684	0.2	0.3	0.1	$(AN)_9(ST)_6$	$(AN)_7(ST)_7$	1100	1.34	0.75	1.62
$(AN)_4(ST)_5$	$(AN)_2(ST)_6$	731	1.5	2.0	1.4	$(AN)_{11}(ST)_5$	$(AN)_9(ST)_6$	1102	0.03	0.17	0.02
$(AN)_6(ST)_4$	$(AN)_4(ST)_5$	733	1.5	1.6	1.5	$(AN)_6(ST)_8$	$(AN)_4(ST)_9$	1149	0.30	0.50	0.37
$(AN)_8(ST)_3$	$(AN)_6(ST)_4$	735	0.6	0.8	0.5	$(AN)_8(ST)_7$	$(AN)_6(ST)_8$	1151	0.58	0.65	0.57
$(AN)_3(ST)_6$	$(AN)(ST)_7$	782	0.1	1.4	0.4	$(AN)_{10}(ST)_6$	$(AN)_8(ST)_7$	1153	0.43	0.21	0.38
$(AN)_5(ST)_5$	$(AN)_3(ST)_6$	784	1.7	1.9	1.6	$(AN)_{12}(ST)_5$	$(AN)_{10}(ST)_6$	1155	0.12	0.11	0.10
$(AN)_7(ST)_4$	$(AN)_5(ST)_5$	786	1.9	1.7	1.9						
$(AN)_9(ST)_3$	$(AN)_7(ST)_4$	788	0.3	0.7	0.3	AF[d]				0.439	0.037

[a] Relative intensities of the ions from the electron impact mass spectrum taken from Figure 4 in ref 16. [b] Computed using eqs 14 and 26 with $X = 1.0$, $P_{AN,AN} = 0.12$, $P_{AN,ST} = 0.88$, $P_{ST,AN} = 0.92$, and $P_{ST,ST} = 0.08$. [c] Computed using eqs 14 and 26 with $X = 0.5$, $P_{AN,AN} = 0.12$, $P_{AN,ST} = 0.88$, $P_{ST,AN} = 0.92$, and $P_{ST,ST} = 0.08$. [d] Agreement factor computed using eq 24.

spectral interpretation because the contributions of all isobaric structures that determine the total peak intensity must be considered. Such equivocal structural assignment of MS peaks occurred when the above-discussed AN-ST copolymer was analyzed by means of direct pyrolysis-electron-impact (EI-MS).[16] The resulting EI-MS[16] shows signals up to 18-mers, which can be grouped in two series which correspond, respectively, to deprotonated and protonated AN-ST oligomers (Table IV). Most mass peaks can be assigned to both series (as shown in Table IV), and, therefore, these MS peaks have an uncertain structural assignment. Since the intensities of these MS peaks derive from two contributions, the calculation of theoretical MS intensities can be performed by computing the contribution due to deprotonated oligomers, I_{deprot}, and the contribution due to protonated oligomers, I_{prot}, and by combining these values using the formula

$$I_{tot} = XI_{deprot} + (1 - X)I_{prot} \quad (26)$$

Intensities I_{deprot} and I_{prot} in eq 26 depend on the distribution of comonomers along the AN-ST copolymer chain. The quantities X and $(1 - X)$ in eq 26 describe the probability of forming a deprotonated or protonated oligomer. These probabilities should be equal ($X = 0.5$), since both species derive (in the proposed[16] ion fragmentation reaction scheme) from the same homolytic scission.[16] To use eq 26 to simulate the AN-ST copolymer mass spectrum, the chain was assumed to follow Markovian statistics (according to the results of the previous analysis), and the thermal cleavage process was assumed to be nonselective. The observed[16] MS peak intensities of the 64 mass peaks corresponding to oligomers ranging from trimers up to 15-mers (shown in Table IV) were given as input to MACO 4, and a minimization was performed to search for the values of X, $P_{AN,AN}$, $P_{AN,ST}$, $P_{ST,AN}$, and $P_{ST,ST}$ which identify a minimum in the agreement factor (eq 24 was used to compute the AF). These values were found to be $X = 0.50$, $P_{AN,AN} = 0.12$, $P_{AN,ST} = 0.88$, $P_{ST,AN} = 0.92$, and $P_{ST,ST} = 0.08$ with an associated AF = 3.7% (Table IV). Comparing the **P** matrix elements obtained from the simulation of the EI mass spectrum in Table IV with those found for the same AN-ST copolymer analyzed by FI-MS (Table III), it can be noticed that the two sets of values are very close and that, furthermore, they are in excellent agreement with the values obtained from kinetics[25] through eq 25 (see above). Also, the value $X = 0.50$ found for this system (Table IV) indicates that the probabilities of forming a protonated and a deprotonated oligomer are equal, as required by the ion fragmentation process.[16] If a value $X = 1.0$ is selected for the simulation, a much worse agreement is obtained (Table IV, AF = 43.9%).

Uncertainties in the structural assignment of MS peaks can also occur when, in a copolymer, molecular weights of the two comonomer units differ by one mass unit and both protonated and nonprotonated species are present. This is the case of a copolymer containing acrylonitrile (AN) and butadiene (BU) units studied[16] by direct pyrolysis-field ionization MS. In this system it happens that the BU units ($m/z = 54$) appear always as nonprotonated species, whereas the AN units ($m/z = 53$) may appear as protonated and nonprotonated species. Therefore, protonated AN species are isobaric with BU species (Table 3S). This copolymer produced a mass spectrum containing

peaks ranging from monomers up to 16-mers.[16] The inspection of the mass spectrum[16] reveals that the intensity of MS peaks corresponding to AN protonated oligomers (observed at m/z 107, 160, 213, 266, 319, and 372) are incompatible with the overall 2:1 molar ratio of comonomers in the copolymer,[16] and, therefore, it was inferred[16] that some AN homopolymer ought to be present, mixed with the copolymer. This means that the observed MS intensities derive from three contributions—the contribution of AN–BU nonprotonated oligomers (referred to as $I_{\text{nonprot}}^{\text{AN-BU}}$), the contribution of AN–BU protonated oligomers (refered to as $I_{\text{prot}}^{\text{AN-BU}}$), and the contribution of AN protonated homopolymer sequences (referred to as $I_{\text{prot}}^{\text{homo}}$)—and that the resulting mass spectrum, I_{tot}, is the weighted sum of the above three intensities:

$$I_{\text{tot}} = T_1 I_{\text{nonprot}}^{\text{AN-BU}} + T_2 I_{\text{prot}}^{\text{AN-BU}} + T_3 I_{\text{prot}}^{\text{homo}} \quad (27)$$

In eq 27 $T_1 + T_2$ is the molar fraction of AN–BU oligomers, T_3 is the molar fraction of AN homopolymer, and intensities $I_{\text{nonprot}}^{\text{AN-BU}}$ and $I_{\text{prot}}^{\text{AN-BU}}$ depend on the AN–BU chain model. For our numerical simulation we considered 101 peaks in the mass spectrum (Table 3S) corresponding to oligomers ranging from dimers up to 12-mers. The chain was assumed to follow the Markovian chain model, the cleavage process was assumed to be nonselective, and MACO 4 was used to find the values of T_1, T_2, T_3, $P_{\text{AN,BU}}$, and $P_{\text{BU,AN}}$ that gave the best agreement. These values are $T_1 = 0.55$, $T_2 = 0.37$, $T_3 = 0.08$, $P_{\text{AN,BU}} = 0.80$, and $P_{\text{BU,AN}} = 0.39$ and imply that the sample analyzed[16] is a binary mixture of a 92% Markovian AN–BU copolymer and an 8% AN homopolymer with a resulting overall Bu/AN molar ratio of 62:38. The agreement factor (AF = 8.9%), evaluated using eq 24, is reported in Table 3S together with the resulting mass spectrum. For comparison, other theoretical spectra, obtained using eq 27 with $T_1 = 1.0$, $T_2 = 0$, and $T_3 = 0$ and with $T_1 = 0.92$, $T_2 = 0$, and $T_3 = 0.08$, are also reported, but the AF obtained with these values is much poorer (Table 3S).

7. Composition of Copolymers by Direct Analysis of Their Mass Spectra

The peak intensities displayed by the mass spectra of copolymers contain direct information about the relative abundance of comonomers, and a copolymer composition estimate can be directly extracted from the analysis of the mass spectra[26] without making any hypothesis on the distribution of comonomer units present in the copolymer. In the case of a four-component copolymer (ABCD), it is possible to make an estimate of the copolymer composition $c_x^A c_x^B c_x^C c_x^D$ from a knowledge of the x-mer peak intensities, $I_{A_mB_nC_pD_q}$ using the formulas

$$c_x^A = \frac{1}{x\beta_x}\{\sum_{m=0}^{x} m[\sum_{n=0}^{x}\delta_{x,n+m} I_{A_mB_n} + \sum_{p=0}^{x}\delta_{x,p+m} I_{A_mC_p} + \sum_{q=0}^{x}\delta_{x,q+m} I_{A_mD_q}]\} \quad (28)$$

$$c_x^B = \frac{1}{x\beta_x}\{\sum_{n=0}^{x} n[\sum_{m=0}^{x}\delta_{x,m+n} I_{B_nA_m} + \sum_{p=0}^{x}\delta_{x,p+n} I_{B_nC_p} + \sum_{q=0}^{x}\delta_{x,q+n} I_{B_nD_q}]\} \quad (29)$$

$$c_x^C = \frac{1}{x\beta_x}\{\sum_{p=0}^{x} p[\sum_{m=0}^{x}\delta_{x,m+p} I_{C_pA_m} + \sum_{n=0}^{x}\delta_{x,n+p} I_{C_pB_n} + \sum_{q=0}^{x}\delta_{x,q+p} I_{C_pD_q}]\} \quad (30)$$

$$c_x^D = \frac{1}{x\beta_x}\{\sum_{q=0}^{x} q[\sum_{m=0}^{x}\delta_{x,m+q} I_{D_qA_m} + \sum_{n=0}^{x}\delta_{x,n+q} I_{D_qB_n} + \sum_{p=0}^{x}\delta_{x,p+q} I_{D_qC_p}]\} \quad (31)$$

where β_x is the sum of x-mer intensities and δ is the Kronecker symbol (defined by $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$). If we specialize eqs 28–31 for a two-component copolymer and for $x = 1$, $x = 2$, $x = 3$, and $x = 4$, we obtain

monomers $$c_1^A = (I_A)(I_A + I_B)^{-1}$$

dimers $$c_2^A = {}^1/_2(2I_{A_2} + I_{AB})(I_{A_2} + I_{AB} + I_{B_2})^{-1}$$

trimers $$c_3^A = {}^1/_3(3I_{A_3} + 2I_{A_2B} + I_{AB_2}) \times (I_{A_3} + I_{A_2B} + I_{AB_2} + I_{B_3})^{-1}$$

tetramers $$c_4^A = {}^1/_4(4I_{A_4} + 3I_{A_3B} + 2I_{A_2B_2} + I_{AB_3}) \times (I_{A_4} + I_{A_3B} + I_{A_2B_2} + I_{AB_3} + I_{B_4})^{-1} \quad (32)$$

Equation 32 implies that each oligomer group (i.e., dimers, trimers, tetramers, etc.) provides an independent estimate of the copolymer composition. Formulas in eq 32 have been used to compute the composition of the copolymer samples listed in Table V, starting from the peak intensities published in the original mass spectra of all the copolymers analyzed here.[8,11,12,16–21] From inspection of Table V two different behaviors can be noticed. In the cases where the reported mass spectrum refers to preformed cooligomers[8,19] (Table V, columns 11 and 15) and also in the cases of copolymer samples which have been subjected to partial degradation by means of a nonselective chain cleavage process[11,16,18] (Table V, columns 2–5, 8–10, 14), the estimated compositions are roughly the same (Figure 5c,d). In these cases, one can safely compute an average copolymer composition by means of eq 33, which provides a weighted average of the data appearing in Table V for each oligomer group:

$$\rho(A) = \{\sum \beta_x\}^{-1} \sum c_x^A \beta_x \quad (33)$$

However, there are a few cases in Table V (columns 6, 7, 12, 13, and 16) where the estimate provided by each oligomer group varies continuously (Figure 5a,b). This behavior distinguishes cases where the copolymer samples have been subjected to partial degradation by a selective chain cleavage process (Figure 2). Therefore eq 32 provides only a diagnostic test of whether the copolymer sample has been subjected to a selective cleavage process but does not allow a determination of copolymer composition. Instead, in this case, copolymer composition must be computed indirectly, by finding copolymer microstructure and calculating the associated composition (see below). As a matter of fact, a selective chain cleavage favors the production of oligomers with a certain type of end group. The resulting mass spectrum is no more a transparent image of copolymer microstructure, and the correspon-

dence with the sequences present in the nondegraded copolymer chain is altered. This effect is more pronounced in short oligomers so that the composition estimates associated with low c_x^A differ sensibly from the actual composition value.

8. Oligomer Distributions Generated by Totally-Selective Chain Cleavage Processes

The case of selective chain cleavage occurs when one or more than one σ factor in eq 3 takes a value different from 1 and, therefore, for the sequence, say XXXX, associated with that σ one has

$$I_{XXXX} \neq R^{\infty}_{XXXX} \tag{34}$$

As a consequence, the solutions of eq 3 given by eqs 13, 14, and 15 are not applicable and a new theory has to be developed.

An exact solution of eq 3 valid for all types of cleavages cannot be found (see section 9). However, an exact solution can be derived when copolymer chain cleavage is totally selective (e.g., when the mixture of oligomers is formed only by oligomers of the type AXXXXA, which start and end with the same comonomer). Assuming that only A units are cleaved (Figure 2), σ factors in eq 3 can take only two values, namely, 0 and 1, and, therefore, we may rewrite eq 2 as

$$I_{A_2B_2} = I_{ABBA}$$

$$I_{A_3B} = I_{AABA} + I_{ABAA} \tag{35}$$

In the case of Bernoullian distributions, from eqs 8, 35, and 34 it follows

$$I_{A_2} = \rho(A)\rho(A)$$

$$I_{AB} = 0$$

$$I_{B_2} = 0$$

$$I_{A_3} = \rho(A)\rho(A)\rho(A)$$

$$I_{A_2B} = \rho(A)\rho(B)\rho(A)$$

$$I_{AB_2} = 0$$

$$I_{B_3} = 0$$

$$I_{A_4} = \rho(A)\rho(A)\rho(A)\rho(A)$$

$$I_{A_3B} = \rho(A)\rho(B)\rho(A)\rho(A) + \rho(A)\rho(A)\rho(B)\rho(A)$$

$$I_{A_2B_2} = \rho(A)\rho(B)\rho(B)\rho(A)$$

$$I_{AB_3} = 0$$

$$I_{B_4} = 0 \tag{36}$$

In the case of Markovian distributions, from eqs 6, 7, 35, and 34 it follows

$$I_{A_2} = R^{\infty}_A P_{AA}$$

$$I_{AB} = 0$$

$$I_{B_2} = 0$$

$$I_{A_3} = R^{\infty}_A P_{AA} P_{AA}$$

$$I_{A_2B} = R^{\infty}_A P_{AB} P_{BA}$$

$$I_{AB_2} = 0$$

$$I_{B_3} = 0 \tag{37}$$

In the case of a sequential chain, from eqs 9, 35, and 34 it follows

$$I_{A_2} = N_{AA}/L$$

$$I_{AB} = 0$$

$$I_{B_2} = 0$$

$$I_{A_3} = N_{AAA}/L$$

$$I_{A_2B} = N_{ABA}/L$$

$$I_{AB_2} = 0$$

$$I_{B_3} = 0 \tag{38}$$

Equations 36–38 constitute a complete group of equations which can be used to compute the theoretical mass spectrum of a copolymer that follows a Bernoullian, Markovian, or sequential distribution in the case of totally selective cleavage processes. It is immediately apparent that the predicted intensities of MS peaks obtained using eqs 36–38 are different from those valid for nonselective cleavages (eqs 13–15). In fact, since only A units are cleaved, eqs 36–38 predict the appearance of oligomers containing at least two A units. The above equations also predict the systematic absence of peaks associated with oligomers B_n and AB_n ($n = 1, 2, 3, ...$), and this implies that the maximum number of peaks expected in the mass spectra in the case of totally-selective cleavage processes is $(n-1)$ (Table I). Furthermore, for an exactly alternating chain $(AB)_n$, eq 38 predicts that peaks associated with even oligomers (dimers, tetramers, hexamers, octamers, decamers, etc.) cannot appear in the mass spectrum.[28]

Another notable difference between selective and nonselective cleavages concerns the composition estimates. For nonselective cleavages, composition estimates c_x^A for the oligomer groups are predicted to be equal, as can be demonstrated by substituting the intensities of the MS peaks obtained using one of the equations (13), (14), and (15) into eq 32. The result is

$$c_1^A = c_2^A = c_3^A = c_4^A = c_5^A = c_6^A = c_7^A = c_8^A \tag{39}$$

Experimental evidence of these predictions is found in Table V and in Figure 5c,d. An analogous calculation for the totally-selective cleavage can be performed by substituting the intensities of the MS peaks generated by eqs 36, 37, and 38 into eq 32. The result is

Table V
Composition Estimates[a] for Various Copolymers

x-mers	$c^{HB\,b}$	$c^{HB\,c}$	$c^{HB\,d}$	$c^{HB\,e}$	$c^{OB\,f}$	$c^{OB\,g}$	$c^{BU\,h}$	$c^{ST\,i}$	$c^{ST\,j}$	$c^{BA\,k}$	$c^{TP\,l}$	$c^{TP\,m}$	$c^{RE\,n}$	$c^{TX\,o}$	$c^{Bu\,p}$
2	91.5	83.0	76.5	71.5	33.3			58.8			100	100	43.1	50.5	
3	92.0	86.0	79.3	74.0	29.3	35.1	62.4	56.4			93.3	83.2	44.0	51.0	100
4	93.0	84.8	77.8	72.3	24.4	40.0	63.6	55.9			90.6	75.5	42.6	49.2	83.3
5	92.9	84.2	80.0	73.6	33.3	41.2	61.1	53.8	52.2	27.7	86.2	70.4	42.8	49.8	79.3
6	92.6	85.5	79.5	72.8			63.2	52.3	51.6	27.3	81.4	66.6	43.5	49.7	74.2
7							62.5	51.5	49.9	27.8			42.0		76.0
8							62.5	49.8	50.4	26.1					73.5
9							60.5	49.6	49.7	27.0					68.5
10							62.6	50.8	49.6	28.1					70.4
11							64.1	49.0	50.3	26.0					76.4
12							62.7	49.7	50.4						78.6
13							60.5		50.0						
14							66.7		49.5						
15									50.5						
16									50.1						
av[q]	92.3	84.6	78.4	72.9			62.7	52.5	50.7	27.5			43.1	50.1	

[a] Computed using eq 32. [b] Molar fraction for comonomer HB estimated using spectral intensities taken from Table V (sample 2) in ref 11. [c] Molar fraction for comonomer HB estimated using spectral intensities taken from Table V (sample 3) in ref 11. [d] Molar fraction for comonomer HB estimated using spectral intensities taken from Table V (sample 4) in ref 11. [e] Molar fraction for comonomer HB estimated using spectral intensities taken from Table V (sample 5) in ref 11. [f] Molar fraction for comonomer OB estimated using spectral intensities taken from Figure 3 in ref 21. [g] Molar fraction for comonomer OB estimated using spectral intensities taken from Figure 4 in ref 21. [h] Molar fraction for comonomer BU estimated using spectral intensities taken from Figure 2 in ref 16. [i] Molar fraction for comonomer ST estimated using spectral intensities taken from Figure 3c in ref 16. [j] Molar fraction for comonomer ST estimated using spectral intensities taken from Figure 4 in ref 16. [k] Molar fraction for comonomer BA estimated using spectral intensities taken from Figure 2c in ref 8. [l] Molar fraction for comonomer TP estimated using spectral intensities taken from Table II, column 2, in ref 17. [m] Molar fraction for comonomer TP estimated using spectral intensities taken from Table II, column 3, in ref 17. [n] Molar fraction for comonomer RE estimated using spectral intensities taken from Table I in ref 18. [o] molar fraction for comonomer TX estimated using spectral intensities taken from Table III, column 6, in ref 19. [p] Molar fraction for comonomer BU estimated using spectral intensities taken from Figure 6a in ref 20. [q] Average composition computed using eq 33.

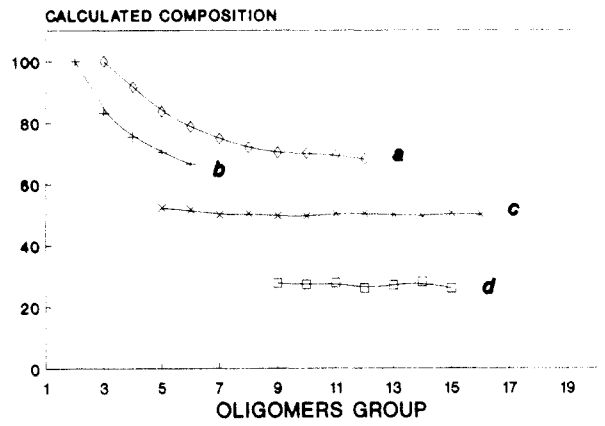


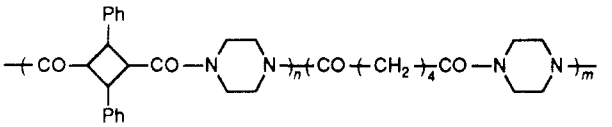
Figure 5. Composition estimates (c_x^A) versus oligomer group (x) for various copolymer samples computed using eq 32: (a) molar fraction of BU units;[20] (b) molar fraction of TP units;[17] (c) molar fraction of BU units;[16] (d) molar fraction of BA units.[8]

$$c_2^A = 1.00 \tag{40}$$

$$c_2^A > c_3^A > c_4^A > c_5^A > c_6^A > c_7^A > c_8^A > c_9^A$$

We used eqs 32 and 36 to compute composition estimates c_n^A for a Bernoullian copolymer and we plotted c_n^A versus n for different values of the composition $\rho(A)$. The resulting diagram (Figure 1S) shows that the difference $c_\infty^A - \rho(A)$ is never negligibly small (c_∞^A is the asymptotic value). Experimental evidence of these predictions is found in Table V and in Figure 5a,b.

We proceed now to illustrate some examples of totally-selective processes. A random copolyamide containing adipoylpiperazine units (AP) and truxilloylpiperazine units (TP) (structure III) was subjected to a partial photolysis process that resulted in the cleavage of the photolabile TP units contained in the copolymer main chain.[17] Such cleavages are totally selective; in fact, oligomers produced in the degradation process were identified by FAB-MS[17] and were all found to contain cinnamoyl end groups (Figure 2b). Experimental data are available[17] for two copolyamide samples having different AP/TP ratios: 20/80 for sample 1 (Table 4S) and 50/50 for sample 2 (Table VI). To proceed to the microstructure determination, the observed[17] MS peak intensities (Table 4S and Table VI) corresponding to oligomers ranging from dimers up to heptamers were given as input to MACO 4. Both samples turned out to follow a pure Bernoullian distribution: Sample 1 has a best-fit composition $\rho(AP) = 0.20$, $\rho(TP) = 0.80$ (AF = 7.3%, Table 4S) and sample 2 has a best-fit composition $\rho(AP) = 0.50$, $\rho(TP) = 0.50$ (AF = 6.2%, Table VI). Figure 1a reports the FAB mass spectrum[17] of the partial photolysis residue of sample 1, and Figure 1b displays the mass spectrum calculated by statistical modeling (Table 4S). We may notice that monomer peaks do not appear in the experimental spectrum, in agreement with the selective character of the cleavage process. Also the reduced number of MS peaks appearing in Figure 1 is due to the selective cleavage of the copolyamide chain.



III

If the experimental MS peak intensities of sample 1 are inserted in eq 32, we can obtain the estimated molar fraction of comonomer TP for the various groups of oligomers (c_x^{TP}) and may see how well these values fit the theoretical predictions (eq 40). The results, reported in Figure 6, confirm the predictions and show that c_x^{TP} decreases steadily when the oligomer size increases.

Another totally-selective cleavage process is the ozonolysis of a butadiene/styrene (BU/ST) copolymer, synthesized by a free-radical process.[20] The ozonolysis split the butadiene units into two parts (Figure 2c), and the partial ozonolysis residue was analyzed by FAB-MS.[20] To proceed to the microstructure determination, the observed[20] MS peak intensities of the 41 mass peaks cor-

Table VI
Experimental[a] and Calculated[b-d] Relative Amounts of the Partial Photolysis Products of an AP-TP Copolyamide (AP = Adipoylpiperazine, TP = Truxilloylpiperazine)[17]

oligomer	m/z	obsd[a] FAB-MS	calc[b]	calc[c]	calc[d]
$(TP)_2$	347	21.3	21.3	21.3	21.3
$(AP)_2(TP)$	393	0	0	0	0
$(AP)_4$	439	0	0	0	0
$(AP)(TP)_2$	543	20.1	24.0	20.0	16.0
$(AP)_3(TP)$	589	0	0	0	0
$(AP)_5$	635	0	0	0	0
$(TP)_3$	693	19.8	16.0	20.0	24.0
$(AP)_2(TP)_2$	739	6.5	9.9	6.9	2.0
$(AP)_4(TP)$	785	0	0	0	0
$(AP)_6$	831	0	0	0	0
$(AP)(TP)_3$	889	14.1	13.2	13.8	13.2
$(AP)_3(TP)_2$	935	0	2.1	1.2	0.6
$(AP)_5(TP)$	981	0	0	0	0
$(TP)_4$	1039	7.0	4.4	6.9	9.9
$(AP)_2(TP)_3$	1085	4.6	4.1	3.6	2.7
$(AP)_4(TP)_2$	1131	0	0.2	0.1	0.1
$(AP)(TP)_4$	1235	4.9	2.7	3.6	4.1
$(AP)_3(TP)_3$	1281	0	0.6	0.5	0.4
$(TP)_5$	1385	0	0.3	0.3	1.0
$(AP)_2(TP)_4$	1431	1.5	0.6	1.0	1.0
AF[e]			0.193	0.062	0.190

[a]Relative intensities of the $(MH)^+$ ions in the FAB mass spectrum taken from Table II column 3 in ref 17. [b]Computed using formula 36 with $\rho(AP) = 0.4$ and $\rho(TP) = 0.6$. [c]Computed using formula 36 with $\rho(AP) = 0.5$ and $\rho(TP) = 0.5$. [d]Computed using formula 36 with $\rho(AP) = 0.6$ and $\rho(TP) = 0.4$. [e]Agreement factor computed using formula 1.

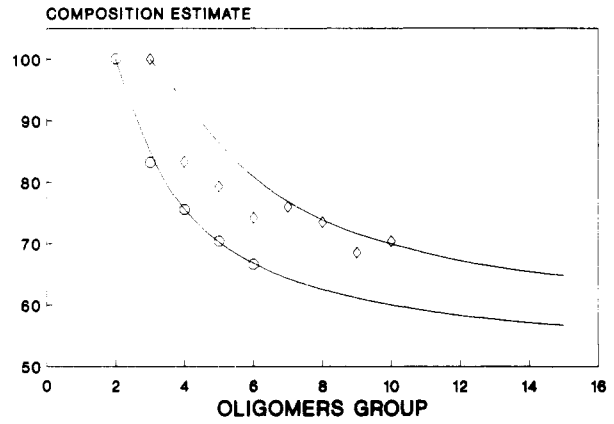


Figure 6. (○) Molar fraction of TP units in copolyamide III, estimated using MS peak intensities[17] reproduced in Table VI, column 3. The overlying curve (continuous line) represents the theoretical composition estimates c_x^{TP}, computed using eq 32. (◇) Molar fraction of BU units in BU/ST copolymer, estimated using MS peak intensities[20] reproduced in Table 5S, column 3. The overlying curve (continuous line) represents the theoretical composition estimates c_x^{BU}, computed using eqs 32 and 36.

responding to oligomers ranging from trimers up to 12-mers (Table 5S) were given as input to MACO 4 employing eqs 36 and 37. Three different chain models Z1, Z2, and Z3, were considered: Model Z1 is a pure Bernoullian distribution defined by $\rho(BU) = 0.65$, $\rho(ST) = 0.35$, which gave the best agreement factor among pure Bernoullian distributions in the minimization process. Model Z2 is a pure Markovian distribution having **P** matrix elements $P_{BU,BU} = 0.69$, $P_{BU,ST} = 0.31$, $P_{ST,BU} = 0.39$, and $P_{ST,ST} = 0.61$ with an associated composition $\rho(BU) = 0.53$, $\rho(ST) = 0.47$ and $\langle n_{BU} \rangle = 3.22$, $\langle n_{ST} \rangle = 1.64$, which gave the best agreement factor among pure Markovian distributions in the minimization process. Model Z3 is a pure Markovian distribution having **P** matrix elements $P_{BU,BU} = 0.22$, $P_{BU,ST} = 0.78$, $P_{ST,BU} = 0.90$, and $P_{ST,ST} = 0.10$ with an associated

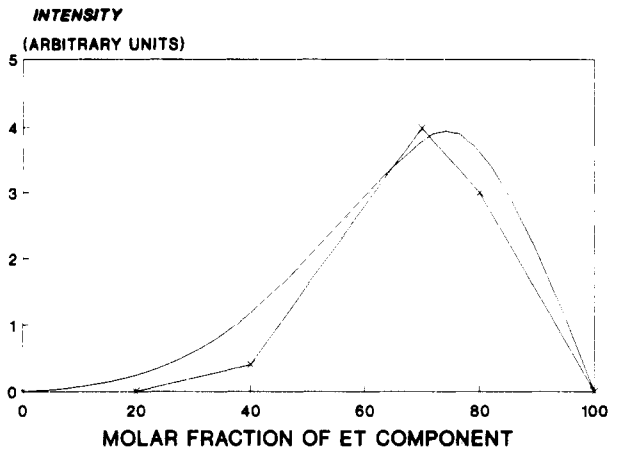
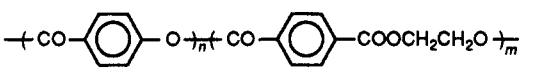


Figure 7. Comparison between experimental peak intensities (×) and the theoretical probability curve of the pentamer $(ET)_4(OB)$, generated by applying eq 36 to four samples of copolyester IV of different compositions.

composition $\rho(BU) = 0.52$, $\rho(ST) = 0.48$ and $\langle n_{BU} \rangle = 1.28$, $\langle n_{ST} \rangle = 1.11$. This model is an almost alternating distribution (number-average lengths almost equal to unity), having the same monomer ratio as model Z2.

The theoretical mass spectra (Table 5S) reported for these three models show that the copolymer chain is best described by a Markovian distribution (model Z2, AF = 6.2%), as could be expected from free-radical copolymerization theory.[15] The molar ratio of comonomers associated with model Z2 (BU/ST = 53/47) is in good agreement with the 55/45 molar ratio found by ^1H NMR.[20] Analogous to the previous example (see data in Figure 6), we can compare the composition estimates predicted by eq 40 with the estimates obtained inserting the experimental MS peak intensities from Table 5S in eq 32. The results reported in Figure 6 do not fit as well as in the previous example, and only the general trend predicted by eq 40 is confirmed in this case.

The last example considered concerns four copolymer samples (structure IV) containing different amounts of ethylene terephthalate units (ET) and *p*-oxybenzoate units (PO).[21] The copolymers were examined by direct-pyrol-



IV

ysis MS, which results in thermally degrading the copolymer directly in the spectrometer.[21] EI mass spectra were recorded at temperatures below 480 °C. At these values, the chain cleavage process is totally selective, since PO units are stable and chain cleavage occurs exclusively at ET units[21] (Figure 2a). Mass spectra of these copolyesters are quite complex[21] since they display many mass series corresponding to PET units and to different copolymer fragments. Each mass series contains only a small number of peaks, and furthermore the EI peak intensities may not reflect the actual oligomer abundances. We attempted to perform our simulation by using only one mass series (Tables VII and VIII). Despite this, significant statistical analysis could be performed, because the selective character of the pyrolysis greatly reduces the number of oligomers produced in the partial degradation process. To proceed to the microstructure determination, the observed MS peak intensities corresponding to oligomers generated in the partial pyrolysis of two samples of copolyester IV (molar ratio OB/ET = 30/70 and 60/40, respectively[21]) were given as input to MACO 4 using eqs 36

Table VII
Experimental[a] and Calculated[b-d] Relative Amounts of the Partial Pyrolysis Products from an OB-ET Copolymer (ET = Ethylene Terephthalate, OB = p-Oxybenzoate)[21]

oligomer	m/z	obsd[a] FAB-MS	calcd[b]	calcd[c]	calcd[d]
$(ET)_2(OB)$	312	30.8	30.8	30.8	30.8
$(ET)_2(OB)_2$	432	9.9	6.3	9.6	14.2
$(ET)_3(OB)$	504	46.9	50.5	47.2	42.6
$(ET)_2(OB)_3$	552	0	0.1	0.4	0.9
$(ET)_3(OB)_2$	624	2.5	2.2	3.1	4.1
$(ET)_4(OB)$	696	8.6	8.7	7.6	6.1
$(ET)_3(OB)_3$	744	0	0.1	0.3	0.4
$(ET)_4(OB)_2$	816	1.2	1.0	1.0	0.9
AF[e]			0.088	0.026	0.119

[a] Relative intensities of the ions from electron impact mass spectrum taken from Figure 3 in ref 21. [b] Computed using eq 36 with $\rho(OB) = 0.2$ and $\rho(ET) = 0.8$. [b] Computed using eq 36 with $\rho(OB) = 0.3$ and $\rho(ET) = 0.7$. [d] Computed using eq 36 with $\rho(OB) = 0.4$ and $\rho(ET) = 0.6$. [e] Agreement factor computed using formula 1.

Table VIII
Experimental[a] and Calculated[b-d] Relative Amounts of the Partial Pyrolysis Products from an OB-ET Copolymer (ET = Ethylene Terephthalate, OB = p-Oxybenzoate)[21]

oligomer	m/z	obsd[a] FAB-MS	calcd[b]	calcd[c]	calcd[d]
$(ET)_2(OB)_2$	432	27.0	22.1	28.4	35.7
$(ET)_2(OB)$	504	39.3	44.2	37.9	30.6
$(ET)_2(OB)_3$	552	4.1	2.6	4.2	6.3
$(ET)_3(OB)_2$	624	9.8	7.7	8.3	8.2
$(ET)_4(OB)$	696	4.1	7.7	5.5	3.5
$(ET)_3(OB)_3$	744	7.4	6.2	7.7	9.5
$(ET)_4(OB)_2$	816	8.2	9.3	7.8	6.1
AF[e]			0.167	0.058	0.778

[a] Relative intensities of the ions from the electron impact mass spectrum taken from Figure 4 in ref 21. [b] Computed using eq 36 with $\rho(OB) = 0.5$ and $\rho(ET) = 0.5$. [c] Computed using eq 36 with $\rho(OB) = 0.6$ and $\rho(ET) = 0.4$. [d] Computed using eq 36 with $\rho(OB) = 0.7$ and $\rho(ET) = 0.3$. [e] Agreement factor computed using formula 1.

and 37, valid for totally-selective processes. Both samples turned out to follow Bernoullian distributions, with best-fit values $\rho(OB) = 0.30$ and $\rho(OB) = 0.60$, respectively (Tables VII and VIII). The good agreement between the known[21] and the computed composition confirms the validity of our statistical modeling.

In the case of copolyester IV, the availability of MS data for four copolymer samples of different compositions[21] allows us to test the predictions of eq 36. Figure 7 reports the normalized intensities measured[21] for each copolymer for the peak at $m/z = 696$ (corresponding to the $(ET)_4(OB)$ pentamer) versus the molar fraction of the ET component in the copolymers. The experimental data[21] are compared in Figure 7 with the theoretical probability curve of the pentamer $(ET)_4(OB)$ applying eq 36 to the four copolymers, and it can be seen that the agreement between the two curves is acceptable.[29] Remarkably, the probability curves generated by eq 36 (valid for the totally-selective processes) have the same shape as those generated by eq 13 (valid for nonselective cleavages) and they differ only by a proportionality factor.

9. Oligomer Distributions Generated by Partially-Selective Chain Cleavage Processes

Equation 3 is an exact formula, but of very limited applicability because it describes the cleavage process making use of many variables, denoted generically as σ. An approximate solution of eq 3 can be derived on the assumption that the cleavage process can be described by a composition-independent variable, ϵ, which is an index of partial selectivity. The starting implicit equation is

$$I_{XXXX} = f(R^{\infty}_{XXXX}, \epsilon) \tag{41}$$

where f indicates a generic dependence. For a chain that follows Bernoullian statistics, three limiting cases have to be considered. In the case of totally-selective cleavages at the comonomer B, eq 41 must reduce to

$$I_{A_2} = 0$$

$$I_{AB} = 0$$

$$I_{B_2} = \rho(B)\rho(B)$$

$$I_{A_3} = 0$$

$$I_{A_2B} = 0$$

$$I_{AB_2} = \rho(B)\rho(A)\rho(B)$$

$$I_{B_3} = \rho(B)\rho(B)\rho(B) \tag{42}$$

In the case of totally-selective cleavages at comonomer A the explicit form of eq 41 is given by eq 36. Furthermore, eq 41 must reduce to eq 13 in the case of nonselective cleavages. We have found that these three constraints are sufficient to define a solution of eq 41, which is the following:

$$I_A = \epsilon\epsilon\rho(A)$$

$$I_B = (1-\epsilon)(1-\epsilon)\rho(B)$$

$$I_{A_2} = \epsilon\epsilon\rho(A)\rho(A)$$

$$I_{AB} = \epsilon(1-\epsilon)(\rho(A)\rho(B) + \rho(B)\rho(A))$$

$$I_{B_2} = (1-\epsilon)(1-\epsilon)\rho(B)\rho(B)$$

$$I_{A_3} = \epsilon\epsilon\rho(A)\rho(A)\rho(A)$$

$$I_{A_2B} = \epsilon(1-\epsilon)(\rho(A)\rho(A)\rho(B) + \rho(B)\rho(A)\rho(A)) + \epsilon\epsilon\rho(A)\rho(B)\rho(A)$$

$$I_{AB_2} = \epsilon(1-\epsilon)(\rho(A)\rho(B)\rho(B) + \rho(B)\rho(B)\rho(A)) + (1-\epsilon)(1-\epsilon)\rho(B)\rho(A)\rho(B)$$

$$I_{B_3} = (1-\epsilon)(1-\epsilon)\rho(B)\rho(B)\rho(B) \tag{43}$$

Analogously, if a chain follows Markovian statistics, one

obtains

$$I_A = \epsilon\epsilon R_A^\infty$$

$$I_B = (1-\epsilon)(1-\epsilon)R_B^\infty$$

$$I_{A_2} = \epsilon\epsilon R_A^\infty P_{AA}$$

$$I_{AB} = \epsilon(1-\epsilon)(R_A^\infty P_{AB} + R_B^\infty P_{BA})$$

$$I_{B_2} = (1-\epsilon)(1-\epsilon)R_B^\infty P_{BB}$$

$$I_{A_3} = \epsilon\epsilon R_A^\infty P_{AA} P_{AA}$$

$$I_{A_2B} = \epsilon(1-\epsilon)(R_A^\infty P_{AA} P_{AB} + R_B^\infty P_{BA} P_{AA}) + \epsilon\epsilon R_A^\infty P_{AB} P_{BA}$$

$$I_{AB_2} = \epsilon(1-\epsilon)(R_A^\infty P_{AB} P_{BB} + R_B^\infty P_{BB} P_{BA}) + (1-\epsilon)(1-\epsilon)R_B^\infty P_{BA} P_{AB}$$

$$I_{B_3} = (1-\epsilon)(1-\epsilon)R_B^\infty P_{BB} P_{BB} \qquad (44)$$

In the case of a sequential disrtibution we have

$$I_A = \epsilon\epsilon N_A/L$$

$$I_B = (1-\epsilon)(1-\epsilon)N_B/L$$

$$I_{A_2} = \epsilon\epsilon N_{AA}/L$$

$$I_{AB} = \epsilon(1-\epsilon)(N_{AB}/L + N_{BA}/L)$$

$$I_{B_2} = (1-\epsilon)(1-\epsilon)N_{BB}/L$$

$$I_{A_3} = \epsilon\epsilon N_{AAA}/L$$

$$I_{A_2B} = \epsilon(1-\epsilon)(N_{AAB}/L + N_{BAA}/L) + \epsilon\epsilon N_{ABA}/L$$

$$I_{AB_2} = \epsilon(1-\epsilon)(N_{ABB}/L + N_{BBA}/L) + (1-\epsilon)(1-\epsilon)N_{BAB}/L$$

$$I_{B_3} = (1-\epsilon)(1-\epsilon)N_{BBB}/L \qquad (45)$$

Equations 43–45 constitute a complete group of equations that can be used to obtain the intensities of the MS peaks of Bernoullian, Markovian, and sequential copolymers in the case of partially-selective processes. Although examples of partially-selective cleavage processes are not yet available, it is possible at least to check the correctness of eq 43. For this purpose, the observed[17] MS peak intensities for copolyamide III were given as input to MACO 4, using eq 43. The values of ρ(AP), ρ(TP), and ϵ which yielded a minimum for the AF were ρ(AP) = 0.20, ρ(TP) = 0.80, and $\epsilon = 1.0$. Figure 8 reports the agreement factors between the observed and calculated MS peak intensities for the AP/TP copolyamide as a function of the index of partial selectivity ϵ in the cleavage process. The plot, which displays the best AF for $\epsilon = 1.0$, was obtained keeping fixed the copolymer composition at values ρ(AP) = 0.20 and ρ(TP) = 0.80 in eq 43, and the result is the expected one, since the photolysis of copolyamide III is totally selective.

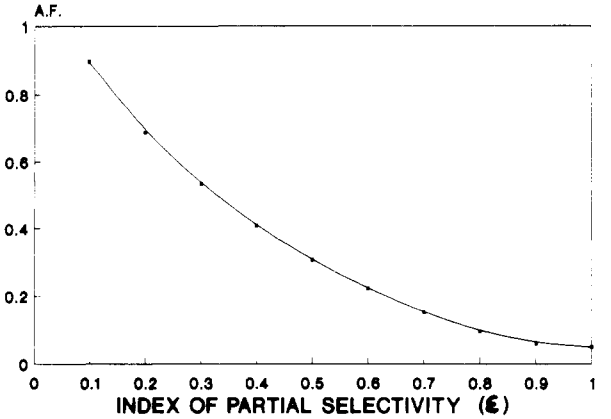


Figure 8. Agreement factor (AF) between experimental and computed MS peak intensities as a function of the index of partial selectivity (ϵ) in the case of copolyamide III (molar ratio AP/TP = 20/80).

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Supplementary Material Available: Experimental and calculated relative amounts of preformed MA–BA oligomers (Table 1S), of the partial aminolysis products from a RE–BP copolycarbonate (Table 2S), of the partial pyrolysis products from an AN–BU copolymer (Table 3S), of the partial photolysis products of an AP–TP copolyamide (Table 4S), and of the partial ozonolysis products from a BU–ST copolymer (Table 5S); Figure 1S showing a plot of composition estimate vs oligomer groups (7 pages). Ordering information is given on any current masthead page.

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(26) Sometimes the composition can be calculated simply from the ratio I_A/I_B when MS peak intensities corresponding to monomers A and B are reliable. Attempts to obtain approximate composition estimates have appeared in the most recent literature.[8,20,27]

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(28) The above discussion has been restricted to the totally-selective cleavage processes involving only the cleavage of A units (Figure 2). Therefore, the selection rules derived here for the oligomers formed in the partial degradation process are valid strictly for this case. On the other hand, if cleavage of an alternating AB copolymer occurs at A–B linkages and not at B–A linkages, then only even oligomers will appear. However, examples of the latter type are not yet available in the literature.

(29) The same order of agreement was found for the remaining oligomer groups (A_2B, A_2B_2, A_3B), whose normalized intensities are reported in Figure 6 of ref 21.