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Recent Advances in the Analysis of Polymers and Copolymers by Mass Spectrometry

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INTRODUCTION

Matrix Assisted Laser Desorption Ionization Mass Spectrometry (MALDI MS) is a soft ionization technique that allows desorption and ionization of very large molecules even in complex mixtures. For polymer analysis, the great promise of MALDI is to enable the direct identification of mass-resolved polymer chains, including intact oligomers within a molecular weights distribution (MWD), measurement of both MW averages and of MWD, and also the simultaneous determination of structure and end groups in polymer samples.

The ionization process in MALDI-TOF proceeds through the capture of a proton or a metal ion (usually Lithium, Sodium, Potassium), which forms a charged adduct with the molecular species. For the analysis of mass spectra of polymers, especially for quantitative applications, it has to be assumed that the number of charged adducts reflects the number of polymeric chains. In particular, the ionization yield of the various oligomer species present in polymers must not undergo any discrimination with respect to their mass values. Also, the MALDI-TOF detector should show a constant response to ions over a wide range of mass numbers.

Until recently, the MW characterization of synthetic polymers by MALDI MS has not been completely satisfactory. It has been found (1) that although molecular weight estimates from by MALDI MS data agree with the values obtained by conventional techniques for the case of samples with narrow MWD with polydisperse polymers MALDI MS fails to yield reliable MW values. We report here some progress in this area.

EXPERIMENTAL

MW averages and MWD of polydisperse polymer samples were obtained by off-line coupling of size exclusion chromatography (SEC) apparatus with the MALDI mass spectrometer (2-5). We recorded the SEC trace of polydisperse polymeric samples, namely polymethyl methacrylates, siloxanes and a number of aliphatic homo- and co-polyesters, collecting about

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40-100 fractions per run. Selected SEC fractions were analyzed by MALDI-TOF, and the average molecular weight of each fraction was determined from the mass spectrum. This permits calibration of the SEC curve against absolute molecular weights and enables us to compute the MW averages from the GPC curve. The procedure yields correct MW and MWD estimates.

RESULTS AND DISCUSSION

Our results open the way up to a new development of the technique, where the MALDI MS is used as the detector in the SEC fractionation of polydisperse polymer samples. The use of SEC standards for the universal calibration curve becomes unnecessary. One can calibrate specifically the SEC curve against absolute molecular weights for its own polymeric material, also computing the MW and MWD for the unfractionated sample.

In the case of siloxanes (3,4), we fractionated two samples, one made of linear chains and another made of cyclics. The theory predicts that cyclics in solution form random coils that are more tightly coiled with respect to linears of the same mass. The prediction is that a cyclic and a linear chain that occupy the same volume (V) have different masses, the cyclic being 1.25 times heavier than the linear. At masses in the range 100-500 Kg/mole, the ratio increases from 1.25 to 1.28. We compared our experimental results with the prediction. We measured the ratio (mass of cyclic)/ (mass of linear) as a function of the elution volume. We found (3,4) that below 100 Kg/mole, the ratio is between 1.2 and 1.3 and that for higher masses the ratio shows a slight increase.

We applied our SEC-MALDI method also to the study of size exclusion chromatography of copolymers. Traditional detectors often suffer because of their response depends not only from the mass of the copolymer but also on other parameters. For copolymers, light scattering (LS) is difficult to apply. If one prepares two solutions of two polymers having the same molar mass and one records the scattered light, one observes different apparent molar masses for the polymers, since the differential refractive indices are different. In a similar manner, if one prepares two solutions of two copolymers having the same molar mass but different composition and one records the scattered light, one finds different apparent molar masses for the polymers, since the scattered light is composition-dependent.

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

In an interesting article (6), the assumption was made that the size of an AB copolymer molecule is the sum of the sizes of the two portions of the molecule as though each were a homopolymer. Accordingly, the molar mass of a copolymer molecule was assumed as given by:

$$\log(MC) = wA \log(MA) + (1-wA) \log(MB) \qquad (1)$$

where MC, MA and MB are, respectively, the molar masses of the copolymer and of the two homopolymers measured at the same elution volume (Ve), and where wA is the weight fraction of A units in the copolymer. We fractioned (5) a series of totally aliphatic homo- and co-polyesters, collecting about 50-80 fractions per run and we analysed the fractions by MALDI. We found (5) significant deviations from the law given in eq. 1. In some cases, the calibration curve for the copolymer did not even lie in the region between by the calibration curves of the two homopolymers. Therefore, MALDI overcomes the problem of finding a detector in which the response depends exclusively on the molar mass.

For copolymers (7), mass spectrometry allows also to calculate both the composition of the copolymer and the sequence distribution (8-22). The latter can obviously be deduced from NMR measurements (7), but the MS method presents distinct advantages in some cases. It provides information on higher oligomer sequences, such as pentamers, decamers, thirtymers, etc. It can sequence multicomponent copolymers; it can detect if a sample is composed of a single copolymer or a mixture of copolymers; it can analyze condensation copolymers having large aliphatic comonomer units. Therefore, the analysis of copolymer sequence by MS is a useful complement to the NMR technique, which until recently was the only method available for this measurement. Block copolymers can be also analyzed, since MALDI-TOF spectrometers are capable of yielding mass resolved oligomer peaks beyond 10,000 Da.

The problem of decoding the intensity of peaks appearing in the mass spectra of copolymers and of relating them to the comonomers sequence has been approached, providing a method for deducing the sequence distributions and composition of comonomers in copolymers. (8,9,14) Therefore, the determination of sequence and composition in copolymers having large comonomer subunits can be achieved by Mass Spectrometry (MS) (8-22), as it is able to look at the mass of individual molecules in a mixture of homologs, and thereby complements NMR that has until recently been the only method able to perform this kind of analysis. (7) Chain statistics (Bernoullian, first or second order Markoffian) allow one to generate any arrangement of comonomer units along the chain. Starting from any sequential arrangement of sub-units, a theoretical mass spectrum can be generated, based (8-22) on the assignment of each spectroscopic peak to a specific sequence.

In the MS of a copolymer, the relative abundance of all the co-oligomers of a defined chain length reflects the composition and sequence present in the copolymer. (8,9) This means that one has the possibility to build a theoretical mass spectrum for any given co-oligomer set, that may be compared with the experimental mass spectrum corresponding to the copolymer sample being investigated. Therefore, each series of oligomers (dimers, trimers, etc.) allows the calculation of the copolymer composition and sequence distribution, and since the mass spectra often provide information up to decamers, beyond. The MS method provides an excellent way to evaluate these two quantities with good precision. (8-22)

Copolymers with two components contain co-oligomers of the type A_mB_n, respectively, where m,n are the number of the sub-units in the macromolecule. The theoretical number of peaks that can appear in the mass spectra of these copolymers can be calculated a priori, and it increases in a linear manner with the length of the copolymer chain. (9) In addition to the determination of copolymer composition, other quantities can be determined from the mass spectral intensities , namely average length of long blocks of like monomers, degree of randomness, reactivity ratios, and the compositional heterogeneity index (which indicates if the composition changes as the length of the chain length grows). (8-22)

We present in the following our "recipe" for analysing an unknown copolymer. We apply first order Markoffian statistics. If the minimization yields an agreement factor higher than 20%, we explore the possibility that the sample is compositionally heterogeneous. We group the peaks due to dimers, trimers, tetramers, pentamers, etc., and compute the "composition estimates" (9, 12) for each group and then we plot the estimates as a function of the degree of polymerization. In this way, we characterize the sample and its heterogeneity.It must be noted that it has been shown (9) that first order Markoffian statistics yields "composition estimates" that are leveled on a single value and are therefore incompatible with compositionally heterogeneous samples. If the minimization yields an agreement factor lower than 20%, we look at the probability matrix. If the sum, R, of the two elements belonging to the first diagonal of the P matrix is close to 1 (as in the case of a poly(hydroxybutyrate-co-hydroxy valerate) sample (8)), then the copolymer is degenerate in the sense that it follows Bernoulli law. If R is close to 2 (as for the case of a poly(ethylene adipate-co-ethylene terephthalate) sample (12)), then the copolymer possesses long AAAA and BBBB blocks. If R is close to 0 (as is the case for a poly(resorcinecarbonate-co-bisphenol-A-carbonate) sample (9)) then the copolymer has a strong tendency to alternate.

When we know how the copolymer has been synthetized, we can compare the experimental sequence distribution with the sequence predicted by the theory. Various models of copolymerization have been reported in the literature. Each model predicts the sequence distribution of the resulting copolymer. The ultimate model is ideally suited to describe condensation copolymerization. It predicts that the sequence distribution of the copolymers is Bernoullian. (23) The terminal model was developed initially for free-radical copolymerization. It predicts that the sequence distribution of the copolymers follow first order Markoff statistics. (23) The penultimate model was developed for those cases when and the rate of growth of the chain depends not only on the terminal unit of the growing radical but also on the penultimate unit. It predicts that the sequence distribution of the copolymers follows second order Markoff statistics. (23) The complex participation model was developed for those cases when the monomers form complexes. It predicts that the sequence distribution of the copolymers follows a very particular law with a large number (six) of degrees of freedom. In some free-radical copolymerizations, the propagation of the growing radical is opposed by depropagation. This happens for instance, when α-methyl styrene is polymerized with methyl methacrylate, acrylonitrile or styrene. The model for these copolymer systems predicts that the sequence distribution of the copolymers follows a complex law (23) that differs from those mentioned above. The production of a copolymer can be achieved starting with a homopolymer by "polymer analog" reactions. Using this synthetic route, one can produce, for instance, copolymers containing units of styrene and of styrene sulfonic acid or copolymers containing units of vinylacetate and of vinyl alcohol. The model for "polymer analog" reactions has been developed for a long time. It predicts that the sequence distribution is not overly different from a Bernoullian (especially at the initial stages of the reaction). Block copolymers can be produced using an anionic initiator. At first, a single monomer (A) is polymerized, thereafter a second monomer (B) is added. This process of block copolymerization has been modelled. It predicts that the sequence distribution of the resulting copolymer follows a "double Poisson" law, i.e. a Poisson law for monomer A times a Poisson law for monomer B. This implies that it predicts that the copolymer formed will display a particular sequence distribution. In fact, the probability of finding sequences containing two or more AB linkages (e.g. BAABBAAB or BAABBBAAAB) is exactly zero. The production of a copolymer can be also achieved by reactive blending of two homopolymers. The model developed to describe this process is quite simple and it predicts that the sequence distribution of the resulting copolymer follows first order Markoff statistics. When free radical copolymerization is conducted in batch at high conversion, one monomer is often incorporated at a higher rate than the other in the chain. The model for this process predicts that the sequence distribution of the resulting copolymer follows a "perturbed Markoffian" which consists of a Markoff of the first order modified by a pertubation parameter. (24) Copolymers can also be prepared in emulsion. The process has been modelled by extending the classical Smith-Ewart "0-1" model. It predicts that the sequence distribution of the resulting copolymer follows a "saturation" law, which shows a first order Markoff statistics as an asymptote. (25) Low molecular weight copolymers may be formed by subjecting a copolymer to partial degradation such as pyrolysis, hydrolysis, methanolysis, photolysis or aminolysis. The model for this process predicts that the sequence distribution of the resulting copolymer is identical to that of the native polymer. When one repeat unit is preferentially degraded, partial selective cleavage occurs. The model for this process predicts the sequence distribution of the resulting copolymer follows a particular law, characterized (9) by a "partially selective index". Copolymer fractions can be obtained by subjecting a copolymer to chromatographic fractionation and collecting the fractions. The model for this process predicts that no "chromatographic skewing" occurs and thus the sequence distribution of the resulting copolymer is identical to that of the unfractionated copolymer. (8,21) Copolymers of styrene and methacrylic acid have been obtained using carbon tetrachloride and dioxane as solvents. Furthermore, styrene has been copolymerized with methacrylic acid and methacrylonitrile in benzene and dimethyl formamide. The model for this process predicts that the sequence distribution of the resulting copolymer follows a law (26), which resembles closely a Markoff of the first order modified by a Flory-Huggins temperature dependent interaction term (the sequence is controlled by thermodynamics).

It can be seen that sequence distribution predicted by the various models of copolymerization is quite complex. As a consequence, the comparison with the experimental sequence distribution is difficult.

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