Microstructures of Butadiene Copolymers Determined by Ozonolysis/MALDI Mass Spectrometry

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ABSTRACT: Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry of ozonolysis degradation products was used to determine the microstructures of several butadiene copolymers. A random styrene−butadiene copolymer containing 45 wt % styrene was distinguished from a block (ABA) styrene−butadiene copolymer containing 38 wt % styrene. In addition, several acrylonitrile−butadiene copolymers with acrylonitrile contents ranging from 21 to 51 wt % were analyzed. The microstructures for the acrylonitrile−butadiene copolymers were confirmed to be fairly random. Quantitatively, the acrylonitrile compositions determined by ozonolysis/MALDI-MS were close to the reported values for these copolymers (typically within 5 wt %). The discrepancy between the reported and experimentally obtained compositions may be attributed, in part, to a composition bias arising from the ozonolysis process. A simple model for ozonolysis of a random copolymer was developed to investigate the effects of ozone exposure time on the oligomer distributions observed in the MALDI mass spectra.

Introduction

Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry is becoming a useful tool for the characterization of synthetic polymers. Determination of molecular weight distributions and identification of end groups has been performed for homopolymers such as poly(ethylene glycol), poly(methyl methacrylate), and polystyrene. Several recent studies[1−3] have shown that MALDI-MS may also be used to determine copolymer compositions. The mass signals for different composition polymer chains must be resolved in order to determine the copolymer compositions accurately. Currently, this mass resolution limit restricts the determination of monomer compositions to samples having $M_w < 10\ 000$. Even with the appropriate mass resolution, the molecular weight of a copolymer does not provide information about the sequence of the monomers within the copolymer chain. To obtain sequence information by mass spectrometry, the copolymer must be fragmented into shorter oligomers. For copolymers that produce intact molecular ions by MALDI, these fragments may be generated in the mass spectrometer using techniques such as collision-induced dissociation.[4,5] However, these techniques are not appropriate for high molecular weight copolymers that do not produce molecular ions by MALDI. For these types of copolymers, thermal or chemical methods may be used to degrade the original polymer chain into a representative set of oligomers that are amenable to MALDI analysis.

Thermal degradation methods typically involve pyrolyzing a small amount of solid copolymer (0.01−1 mg) with a heated probe inserted directly into the source region of the mass spectrometer. Thermal mass spectrometry is generally limited to qualitative analyses of synthetic copolymers such as identification of monomer types and distinguishing random from block microstructures. Quantitative analyses such as determination of monomer compositions and number-average sequence lengths are difficult to do by thermal degradation methods for several reasons. First, interpretation of the mass spectra is generally difficult because thermal degradation of synthetic polymers produces a wide array of pyrolysates. Interpretation of the pyrolysis mass spectra for polymers can be made easier by the use of ionization techniques such as low-voltage electron ionization,[6,7] field ionization,[8] and vacuum-ultraviolet photoionization.[9,10] These "soft" ionization techniques minimize fragmentation due to the ionization process and produce primarily molecular ions. However, the primary limitation for thermal degradation methods is that many copolymers do not produce pyrolysates that contain sequence information. For example, oligomers of styrene or methyl methacrylate units depolymerize to produce primarily monomer.[6,11−14] Even when pyrolysates containing sequence information are produced, thermal degradation usually only produces short oligomers (<5 monomer units) which places a limitation on the block lengths capable of being studied. Recent work[15] has shown that for certain copolymers this limitation can be resolved by using a partial pyrolysis-MALDI-MS technique.

Many of the copolymers that cannot be analyzed intact by MALDI-MS or by thermal methods can be chemically degraded into a representative set of oligomers using methods such as ozonolysis, hydrolysis, or ammonolysis. Montaudo and co-workers[16−21] have shown that structural information for a variety of synthetic copolymers may be obtained by combining chemical degradation methods with fast-atom bombardment (FAB) mass spectrometry. Once the peaks in the mass spectra have been assigned to a specific oligomer sequence, the oligomer distributions may be interpreted by fitting to statistical models in order to obtain monomer compositions and number-average sequence lengths. The main disadvantage of this method is that FAB-MS requires fairly polar compounds with molecular weights below 2000 Da.

In this work, acrylonitrile−butadiene and styrene−butadiene copolymers were analyzed by ozonolysis/

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Table 1. Polymers Studied by Ozonolysis/MALDI-MS

sample	polymer type	M_w[a]	source[b]
A	polybutadiene	5 500	1
B	polybutadiene	420 000	1
C	styrene−butadiene (block microstructure; 38 wt % styrene)	NA[c]	2
D	styrene−butadiene (random microstructure; 45 wt % styrene)	NA[c]	2
E	acrylonitrile−butadiene (19−22 wt % acrylonitrile)	>100 000	1
F	acrylonitrile−butadiene (30−32 wt % acrylonitrile)	>100 000	1
G	acrylonitrile−butadiene (37−39 wt % acrylonitrile)	>100 000	1
H	acrylonitrile−butadiene (51 wt % acrylonitrile)	>100 000	2

[a] Data provided by supplier. [b] (1) Aldrich; (2) Scientific Polymer Products, Inc. [c] NA = data not available.

MALDI mass spectrometry. Ozone was used to cleave the copolymer chain at sites containing butadiene monomers. The ozonolysis reaction was controlled for specific ozone exposure times, and reagents were used to produce oligomers with specific end groups.[22] MALDI-MS was used for mass analysis because of its extended mass range and ability to analyze both polar and nonpolar polymers. Oligomer distributions identified in the MALDI mass spectra were used to determine the microstructure (random vs block) and composition of monomers within the copolymer chain.

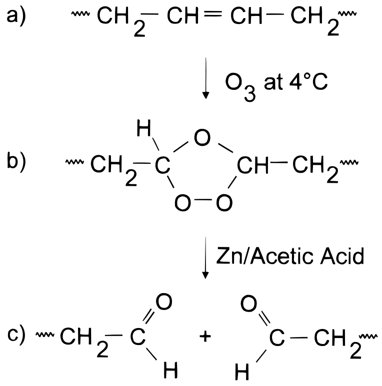
Experimental Section

Table 1 lists the polymers used in this work. Two polybutadienes (M_w = 5500 and 420 000) and three acrylonitrile−butadiene copolymers with reported acrylonitrile contents of 19−22, 30−32, and 37−39 wt % were obtained from Aldrich (Milwaukee, WI). An acrylonitrile−butadiene copolymer with a reported acrylonitrile content of 51 wt % was obtained from Scientific Polymer Products, Inc. (Ontario, NY). All of the acrylonitrile−butadiene copolymers had M_w > 100K and were synthesized using an emulsion polymerization. A random styrene−butadiene copolymer and a block (ABA) styrene−butadiene copolymer with reported styrene contents of 45 and 38 wt %, respectively, were also obtained from Scientific Polymer Products, Inc.

For insoluble copolymers, 0.5 g of polymer was sliced with a metal blade into approximately 2 mm pieces. The polymer samples were then extracted with methylene chloride for 30 min at 40 °C to remove additives. The solid polymer was then filtered and placed in a 50 mL round-bottom flask which was kept in an ice bath (∼4 °C). An ozone generator (Prozone International, Inc., Huntsville, AL) was used to produce a 1% mixture of ozone in air. For solid ozonolysis, the ozone/air mixture was flowed at 100 mL/min through a glass pipet located 1 cm above the sample. For the soluble polymers, 0.25 g of polymer was dissolved in 25 mL of toluene in a round-bottom flask which was placed in an ice bath. The ozone/air mixture flowed at 100 mL/min through a glass pipet into the toluene/polymer solution. To reduce oligomers to two aldehyde end groups, 25 mL of toluene (for solid ozonolysis only), 1.2 g of zinc granules, and 0.2 mL of acetic acid were added to the polymer solution and stirred with a magnetic bar. The temperature was allowed to gradually rise to 40 °C over 30 min.

All of the MALDI samples were prepared using dithranol (matrix) and silver trifluoroacetate (cationizing agent) obtained from Aldrich (Milwaukee, WI). A 15 μL aliquot of the ozonolysis products in toluene (after removal of any solid residue) was combined with 15 μL of dithranol (50 mM in toluene) and 5 μL of AgTFA (25 mM in toluene). A 0.5 μL aliquot of this solution was deposited on the sample probe and allowed to quickly dry in a vented hood. The sample probe was then immediately loaded into a 2.7 m reflecting time-of-flight mass spectrometer (Biflex III, Bruker Daltonics Inc., Billerica, MA). A 337 nm nitrogen laser was used to irradiate the sample. The mass spectrometer was operated in reflector mode with an accelerating voltage of 19 kV and a delayed extraction of 250 ns. Mass spectra were averaged over 50 individual laser shots. Peak areas were obtained using the Integ module of the XTOF software (Bruker Daltonics, Billerica, MA). The initial mass calibration was performed with poly(ethylene glycol) 1000. This calibration was used to identify ozonolysis products from the M_w 420 000 polybutadiene sample (polymer B). Once identified, the exact masses of these products were used to calibrate subsequent spectra with a three point calibration between 500 and 2000 *m*/*z*. The model for simulating the ozonolysis of a random copolymer was written using the Matlab programming language (The Mathworks Inc., Natick, MA).

Scheme 1. General Mechanism for Ozonolysis of a Polymer Chain Containing a Butadiene Monomer[a]



[a] A reduction of the ozonolysis products is performed to produce oligomers with aldehyde end group functionalities.

Results and Discussion

Polybutadiene. The expected ozonolysis mechanism for polybutadiene is shown in Scheme 1.[18−21] An ozone molecule adds across the double bond of a butadiene monomer (Scheme 1a). The product then rearranges to form a more stable ozonide intermediate (Scheme 1b). The ozonide may then split to form a variety of different end groups including aldehyde, carboxylic acid, or hydroxyl groups. By performing a reduction with zinc and acetic acid, oligomers with aldehyde end groups (Scheme 1c) may be selectively produced.[22] Alternative pathways to Scheme 1 are discussed later.

The ozonolysis process in Scheme 1 was verified using both low and high molecular weight polybutadiene (polymers A and B in Table 1). The low molecular weight sample (polymer A) could be detected intact by MALDI-MS, providing the opportunity to monitor both reactant and product oligomers during ozonolysis. A solution of low molecular weight polybutadiene was dissolved in toluene and exposed to ozone for 5 min. The MALDI mass spectrum of the polymer after exposure to ozone contained many peaks below 2000 *m*/*z* that were not detected in the original sample. The most intense low *m*/*z* peaks corresponded to butadiene oligomers with two aldehyde end groups. In addition, the intensities of “high” *m*/*z* peaks from the original polymer (5000−6000 *m*/*z* range) were greatly reduced after 5 min of exposure to ozone. These results confirm that the ozonolysis is capable of degrading polybutadiene into products that are amenable to MALDI analysis.

Next, the ozonolysis/MALDI technique was applied to a higher molecular weight polybutadiene sample (polymer B). Currently, it is not possible to analyze this polymer intact using MALDI-MS. Polymer B was dis-

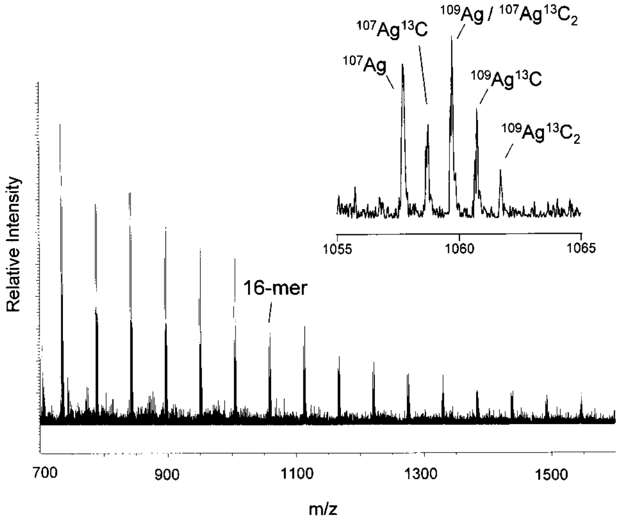


Figure 1. MALDI mass spectrum of the ozonolysis products for a high molecular weight polybutadiene sample (polymer B). The expanded mass region shows peaks assigned to the different isotopes of the product having 16 intact butadiene monomers plus two terminal aldehyde groups that existed as additional butadiene monomers in the original polymer strand.

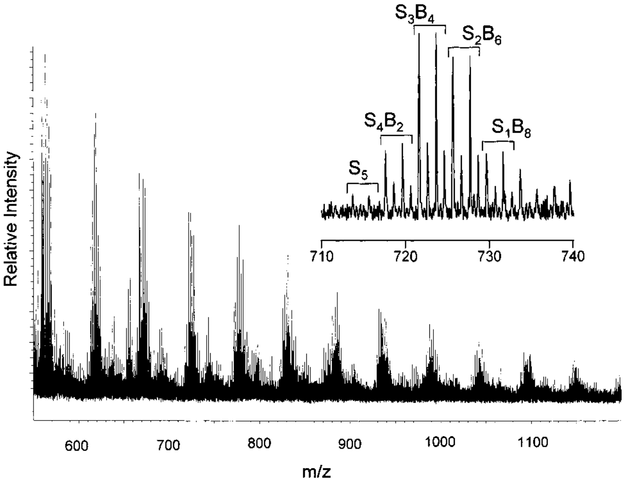


Figure 2. MALDI mass spectrum of the ozonolysis products for a random styrene–butadiene copolymer with a styrene content of 45 wt % (polymer D). The expanded mass region shows the groups of peaks assigned to different composition oligomers. These groups do not include the ^{109}Ag^{13}C$_2$ isotopic peak which overlaps the ^{107}Ag isotopic peak of the oligomer containing two additional butadiene units and one less styrene unit.

solved in toluene and exposed to ozone for 20 min. As shown in Figure 1, the MALDI mass spectrum after 20 min of ozonolysis contains an intense series of peaks corresponding to oligomers with two aldehyde end groups. The expanded mass spectrum for the 16-mer (i.e., 16 intact butadiene monomers plus two terminal aldehyde groups that existed as additional butadiene monomers in the original polymer strand) shows that each oligomer consists of five mass peaks due to the ^{12}C/^{13}C and ^{107}Ag/^{109}Ag isotopes.

MALDI analysis of the ozonolysis products prior to end group reduction showed that oligomers with a variety of different end groups may be produced. By heating the solution to 40 °C after ozonolysis, an increase in the intensities of the product ion signals was observed. This increase in signal intensity was attributed to a significant amount of stable intermediates that remained in solution and were split upon heating to 40 °C. However, an increase in the variety of end groups, particularly oligomers with one or two acid groups, was also observed which made interpretation of the mass spectrum more difficult. In contrast, reduction with zinc and acetic acid greatly improved the spectra by selectively producing aldehyde end groups and significantly increasing the intensities of product oligomer ions.

Although alternate reaction pathways for ozonolysis leading to the formation of epoxides or peroxides are possible, there is no spectroscopic evidence for these products when the zinc/acetic acid reduction step is used. The spectrum in Figure 1 is dominated by butadiene product oligomers having two terminal aldehyde groups. If, for example, one or more butadiene monomers within a product oligomer were converted to epoxides, additional ions would be observed at +16 Da intervals corresponding to the incorporation of one or more oxygen atoms. However, no such ions are observed above the “chemical” noise in this or other spectra taken after ozonolysis and reduction.

Styrene–Butadiene Copolymers. Random and block styrene–butadiene copolymers (polymers C and D in Table 1) are readily distinguished using the ozonolysis/MALDI-MS method. The block copolymer, polymer C, was exposed to ozone for 30 min. The MALDI mass spectrum for this polymer closely resembled the ozonolysis/MALDI mass spectrum for polybutadiene in Figure 1. Since the reaction rate constant for ozonolysis of polybutadiene is approximately 6 orders of magnitude greater than for ozonolysis of polystyrene,[23,24] the absence of signals in the mass spectra due to styrene oligomers is not surprising. After 2 h of ozonolysis, the mass signals due to butadiene oligomers decreased substantially, and no styrene oligomers were detected. For this experiment, the styrene block lengths may have been too high in mass or too low in concentration to be detected efficiently.

A random styrene–butadiene copolymer with a styrene content of 45 wt % (polymer D) was analyzed by solid ozonolysis for 30 min. Figure 2 shows the MALDI mass spectrum of the ozonolysis products from this copolymer. Groups of peaks whose mean *m*/*z* values are separated by approximately 54 *m*/*z* were detected up to 1500 *m*/*z*. These peaks correspond to oligomers with a combination of styrene and butadiene monomeric units and two aldehyde end groups. At 16 *m*/*z* units higher from each of these peak groups, a second, less intense group of peaks is observed. These peaks are due either to incomplete reduction of acid end groups or to the formation of an epoxide on an internal butadiene monomer. The expanded mass spectrum in Figure 2 shows that the mass signal for each oligomer contains several peaks due to ^{12}C/^{13}C and ^{107}Ag/^{109}Ag isotopes. In addition, several series of peaks are contained within each group separated by 4 *m*/*z*. These peaks are due to substitution of a styrene monomer (104 Da) for two butadiene monomers (108 Da). For example, the 7-mer (^{12}C/^{107}Ag) containing three intact styrene monomers, four butadiene monomers, and two terminal aldehydes that existed as additional butadiene monomers in the original polymer strand appears at 721 *m*/*z*, and the 8-mer (^{12}C/^{107}Ag) containing two intact styrene monomers, six intact butadiene monomers, and two terminal aldehyde groups appears at 725 *m*/*z*. The MALDI mass spectrum clearly identifies this compound as a random copolymer since mass signals due to oligmers with a combination of butadiene and styrene monomers have much greater intensities than mass signals due to pure butadiene and pure styrene oligomers.

The oligomer distributions produced from polymer D were used to calculate the monomer compositions. All possible combinations of styrene and butadiene monomers for a given oligomer length appear over a fairly wide mass range. For example, an 8-mer of butadiene ($^{12}C/^{107}Ag$) appears at 625 *m/z* while a 8-mer containing eight styrene and two butadiene monomers ($^{12}C/^{107}Ag$) appears at 1025 *m/z*. The compositions for the oligomer distributions containing 8–10 intact monomers were calculated using eq 1:

$$\text{wt \% styrene for } n\text{-oligomer} = \frac{\displaystyle\sum_{x=0}^{n}(S_xB_{(n-x)})\left(\frac{MW_S(x)}{MW_S(x)+MW_B(n-x+2)}\right)}{\displaystyle\sum_{x=0}^{n}S_xB_{(n-x)}} \tag{1}$$

where *n* refers to the number of intact monomers, $S_xB_{(n-x)}$ is the sum of the peak areas for the four mass signals due to $^{12}C/^{13}C$ and $^{107}Ag/^{109}Ag$ isotopes as indicated in Figure 2, and the molecular weights for styrene and butadiene, denoted MW_S and MW_B, respectively, are multiplied by the number of monomers of each in the original polymer strand. The factor of 2 included in the number of butadiene monomers takes into account the two terminal aldehyde groups that existed as additional butadiene monomers in the original polymer strand. On the basis of the oligomer distributions for the 8-mer through the 10-mer for three replicates, an average styrene composition of 41 ± 2 wt % was obtained for the random copolymer with a reported composition of 45 wt %.

Several factors may contribute to the discrepancy between the reported compositions and the compositions obtained by ozonolysis/MALDI-MS. The compositions obtained from MALDI analysis may be biased due to differences in the molecular weights, cation attachment, and solubility of the oligomers. The molecular weight distributions for polymers with wide polydispersities determined by MALDI have been shown to favor detection of lower molecular weight polymer chains.[25−28] For styrene–butadiene oligomers, the molecular weight of a styrene unit (104 Da) is almost twice the molecular weight of a butadiene unit (54 Da). For a given oligomer length, oligomers with higher butadiene contents have lower molecular weights and therefore a bias toward higher butadiene compositions may result. The efficiency of ionization in the MALDI process may also depend on the choice of cation.[29−32] In this experiment, silver cations, which have been shown to be effective cationizing agents for both polystyrene and polybutadiene,[33−36] were added to the sample for MALDI analysis. However, a cation preference for a particular styrene–butadiene oligomer cannot be dismissed due to the very different molecular structures of styrene and butadiene. A bias due to solubility differences is not likely because both styrene and butadiene oligomers are highly soluble in toluene. A compositional bias may also result from the ozonolysis process. The polymer chain must undergo multiple ozonolysis reactions before a large number of oligomers are produced in a mass range detectable by MALDI-MS. Since ozone preferentially attacks the butadiene monomers, segments of the polymer chain containing higher amounts of butadiene are more quickly degraded.

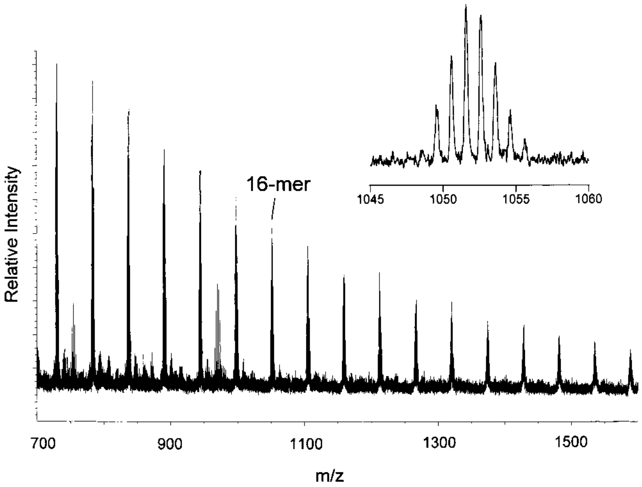


Figure 3. MALDI mass spectrum of the ozonolysis products for a random acrylonitrile–butadiene copolymer with an acrylonitrile content of 38 wt % (polymer G). The expanded mass region shows the distribution of peaks for products having 16 intact monomeric units plus two terminal aldehyde groups that existed as additional butadiene monomers in the original polymer strand.

Finally, eq 1 does not fully take into account the ^{13}C isotopic substitution. The four mass signals used to calculate $S_xB_{(n-x)}$ do not include the mass signal from the $^{109}Ag^{13}C_2$ isotopic peak. This peak, which accounts for approximately 2% of the total ion current from the oligomer, is isobaric with the ^{107}Ag isotopic peak from an oligomer containing one less styrene and two additional butadiene monomers. Deconvolution approaches were investigated to extract the relative contributions of each oligomer to the total signal intensities at the isobaric mass-to-charge ratios. Unfortunately, the inherently low signal-to-noise ratios of the spectra added considerable uncertainty to the deconvolution calculation, and no improvement in the precision or accuracy of the composition measurement was obtained. Despite these limitations, the compositions determined by MALDI-MS for the random styrene–butadiene copolymer were within 4 wt % of the reported value determined by FT-IR analysis.

Acrylonitrile–Butadiene Copolymers. Several different composition acrylonitrile–butadiene copolymers (polymers E–H in Table 1) were analyzed by solid ozonolysis/MALDI-MS. The study of acrylonitrile–butadiene copolymers by mass spectrometry is advantageous because the monomers are very close in molecular weight. The mass of a butadiene unit is 54 Da, which is 1 Da greater than the mass of an acrylonitrile unit (53 Da). Therefore, all possible combinations of monomers for a given oligomer length appear over a narrow mass range. For example, an 8-mer of butadiene (eight intact butadiene monomers plus two terminal aldehyde groups that existed as additional butadiene monomers in the original polymer strand) appears at 625 *m/z* ($^{12}C/^{107}Ag$) whereas an 8-mer of acrylonitrile (eight intact acrylonitrile monomers plus two terminal aldehyde groups that existed as additional butadiene monomers in the original polymer) appears at 617 *m/z* ($^{12}C/^{107}Ag$). Figure 3 shows the MALDI mass spectrum for the ozonolysis products of an acrylonitrile–butadiene copolymer con-

Table 2. Acrylonitrile Contents (wt %) for Different Composition Acrylonitrile−Butadiene Copolymers Determined by Different Methods

FT-IR analysis	pyrolysis−photoionization MS	solid ozonolysis/MALDI MS
19−22 wt % A	21 ± 1	24.5 ± 1.1
30−32 wt % A	32 ± 1	35.4 ± 0.8
37−39 wt % A	38 ± 1	38.9 ± 0.7
51 wt % A	50 ± 1	43.7 ± 0.8

taining 38 wt % acrylonitrile (polymer G). Mass signals separated by 53−54 Da are detected up to 2000 *m*/*z*. The expanded mass spectrum for one of these mass signals reveals a series of peaks separated by 1 *m*/*z* with a fairly Gaussian distribution. Since the different oligomers are so close in molecular weight, mass peaks for different isotopes of a given oligomer composition overlap other mass peaks from different composition oligomers. Therefore, a comparison of means was used to determine the average composition at each oligomer length. The mean *m*/*z* (MP_n) for an oligomer distribution of a given oligomer length is calculated using eq 2

$$\mathrm{MP}_n = \frac{\sum_{m=53n+193}^{54n+197} (m)(\mathrm{area}_m)}{\sum_{m=53n+193}^{54n+197} \mathrm{area}_m} \qquad (2)$$

where m is the *m*/*z* of a peak in the series and area_m is the peak area at that *m*/*z*. The summations take into account the masses of terminal aldehyde groups, the silver cation, and isotopic substitutions. The average number of acrylonitrile units (A) for the *n*-oligomer series was then calculated from the difference between the mean *m*/*z* values for a pure butadiene oligomer (MP B_n) and the acrylonitrile−butadiene copolymer (MP AB_n) using eq 3:

$$\bar{A} \text{ for } n\text{-oligomer} = \frac{\mathrm{MP\ B}_n - \mathrm{MP\ AB}_n}{\mathrm{MW_B} - \mathrm{MW_A}} \qquad (3)$$

where $\mathrm{MW_B}$ and $\mathrm{MW_A}$ are the exact masses for butadiene and acrylonitrile, respectively. For each value of n, the average number of acrylonitrile units determined by eq 3 is divided by $(n + 2)$ where the factor of 2 takes into account the two terminal aldehyde groups that existed as additional butadiene monomers in the original polymer strand. The results from eq 3 for several values of n are averaged and converted to a weight percentage of acrylonitrile.

The compositional data in Table 2 show a discrepancy between the acrylonitrile compositions obtained by ozonolysis/MALDI-MS compared with other techniques. The acrylonitrile−butadiene copolymers with low acrylonitrile contents (polymers E, F, and G; 21, 32, and 38 wt %, respectively) gave slightly higher acrylonitrile compositions while the acrylonitrile−butadiene copolymer with 51 wt % acrylonitrile (polymer H) gave a lower acrylonitrile composition by ozonolysis/MALDI-MS.

Why might the ozonolysis/MALDI-MS results differ from the other methods? Any mass discrimination effect due to the MALDI process should be very minimal for these copolymers since all possible combinations of monomers for a given oligomer length appear over a narrow mass range. To explore the effect of solubility, the ozonolysis products for the acrylonitrile−butadiene copolymer containing 51% acrylonitrile (polymer H) were dissolved in acetonitrile rather than toluene. Dissolution of the ozonolysis products in acetonitrile should favor oligomer with higher acylonitrile contents. However, changing the solvent did not significantly change either the mass spectrum obtained or the acyrlonitrile composition determined for this copolymer. The distributions produced from a random copolymer contain oligomers with fairly similar compositions with an average difference of only a couple of monomer units. Because of this structural similarity, a cation attachment preference was not believed to be the major factor contributing to the discrepancy in compositions observed. The remaining possibility, a bias in composition due to the ozonolysis process, was investigated with the aid of a random ozonolysis model.

Random Ozonolysis Model. Mass signals in the 9-mer to 18-mer range were used for compositional calculations shown in Table 2. Below the 9-mer, mass signals from the matrix and cation clusters interfered with mass signals from the ozonolysis products. Oligomer signal intensities decrease fairly rapidly above the 9-mer such that for oligomers longer than the 18-mer the entire oligomer distributions are not easily identifiable. Since oligomers are observed in a specific size range, the average composition of the oligomers should change as a function of ozone exposure time.

A model was developed to simulate the ozonolysis of a random copolymer and determine how the composition of oligomers in the 8-mer to 18-mer range changes with increasing ozone exposure time. A random sequence of monomers is generated by the model for a specified polymer chain length and composition. The model then randomly selects a position in the polymer chain for a simulated ozone attack. If the monomer at the selected position is a butadiene, a break in the sequence is denoted. If the monomer at the selected position is an acrylonitrile unit or the site of a previous cleavage, the sequence remains intact. The simulation is halted after a specified number of simulated ozone attacks on the polymer chain. A new polymer sequence is then generated, and the simulation is repeated. After simulating the ozonolysis of a specified number of polymer sequences, the total number of oligomers at each oligomer length and composition are calculated. (To be consistent with the experimental results, these calculations treat the two terminal aldehyde groups as two additional butadiene monomers in the original polymer strand.) Finally, the average composition in the 8-mer to 18-mer range is determined.

Figure 4 shows the effect of the number of ozone attacks upon the acrylonitrile composition for ozonolysis products in the 8-mer to 18-mer range. The model data were generated for simulated ozonolysis of 1000 polymer chains each containing 1000 monomers. Initially, the ozonolysis products in the 8-mer to 18-mer range have a lower acrylonitrile content than the overall polymer due to the quicker degradation of high butadiene segments of the copolymer. As the number of ozone attacks on the polymer chain increases, the acrylonitrile content of the ozonolysis product also increases. These results suggest that the slightly higher acrylonitrile compositions obtained by ozonolysis/MALDI-MS may result from repetitive ozone attacks on the polymer chains.

As a test of the modeling results in Figure 4, an acrylonitrile−butadiene copolymer containing 21%

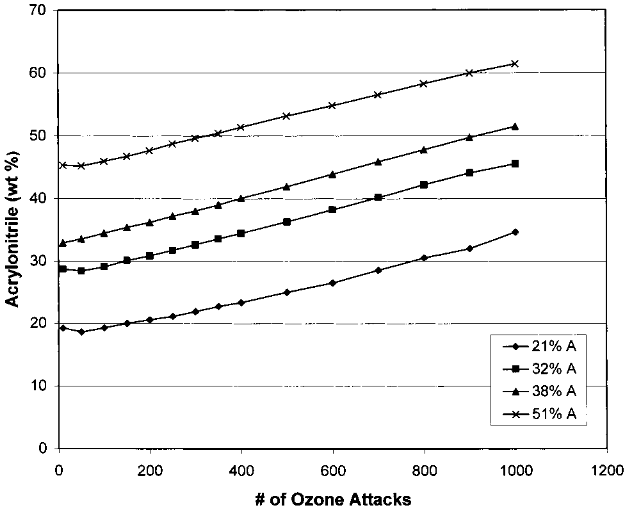


Figure 4. Theoretical change in the average acrylonitrile composition of oligomers in the 8-mer to 18-mer range as a function of the number of simulated ozone attacks for several different acrylonitrile−butadiene copolymers.

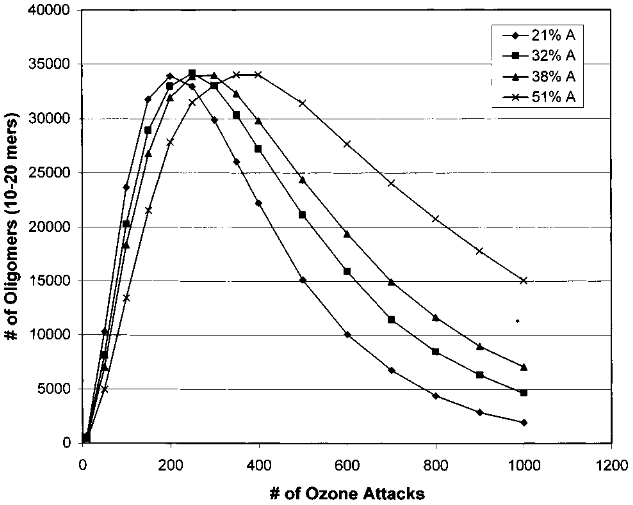


Figure 5. Theoretical change in the number of oligomers generated in the 8-mer to 18-mer range as a function of the number of simulated ozone attacks for several different acrylonitrile−butadiene copolymers.

acrylonitrile (polymer E) was exposed to ozone for times of 5, 10, 30, and 60 min to determine whether different exposure times had an effect on the compositions obtained by MALDI-MS. For 5 min of ozone exposure, the mass signals were very weak, and a compositional calculation was not possible. For 10 min of ozone exposure, the mass signals were not as intense as for 30 min of ozone exposure, but the acrylonitrile compositions were similar (24.2% for 10 min vs 24.5% for 30 min). After 60 min of ozone exposure, the mass signals were also less intense than for 30 min of ozone exposure, and the acrylonitrile composition obtained was slightly higher (26.5 wt %). Thus, the acrylonitrile compositions determined from 10 to 60 min of ozone exposure are consistently higher than the reported composition, and the compositions tend to increase with increasing exposure.

Figure 5 shows the number of oligomers generated in the 8-mer to 18-mer range from 1000 polymer chains each containing 1000 monomers as a function of the number of ozone attacks. The number of oligomers generated from these polymer chains is initially very low. As the number of ozone attacks increases, the number of oligomers reaches a maximum after 200−400 ozone attacks and then decreases steadily until almost all of the polymer is completely degraded to lengths below eight intact monomer units. For copolymers with low acrylonitrile content, the polymer is degraded more quickly due to the greater probability of an ozone molecule cleaving a butadiene unit. Figure 5 also shows that a significant amount of ozone degradation is required before a great number of oligomers in the 8-mer to 18-mer range are produced.

The random ozonolysis model explains, in part, the higher acrylonitrile compositions determined for the acrylonitrile−butadiene copolymers containing 21%, 32%, and 38% acrylonitrile. In this study, the acrylonitrile−butadiene copolymers were typically exposed to a 1% ozone mixture in air for 30 min. The model shows for high amounts of ozone exposure that the acrylonitrile compositions will increase within a specific oligomer range. In addition, the model shows that a significant number of chain cleavages is required in order to produce a large number of oligomers in the 8-mer to 18-mer range. The model for extensive ozonolysis also shows a steady decrease in the number of oligomers from the 8-mer to longer oligomer lengths similar to the decrease detected in the MALDI mass spectrum.

Extensive ozonolysis does not explain the lower acrylonitrile content obtained for the copolymer with a reported acrylonitrile content of 51 wt %. Number-average sequence lengths obtained by pyrolysis−photoionization mass spectrometry indicate this copolymer is not a completely random copolymer.[9] If this copolymer contains some longer acrylonitrile segments, these segments may not degrade into the 9- to 18-mer range detected by MALDI, and lower acrylonitrile compositions would be determined.

Finally, one needs to consider how best to include the terminal aldehyde groups in the composition calculations. It this work, both the experimentally determined compositions and the compositions determined by the random ozonolysis model counted the terminal aldehyde groups as butadiene monomers. For example, an 8-mer (i.e., an oligomer containing eight intact monomers) was treated in the calculations as a 10-monomer sequence in the original polymer having two terminal butadiene monomers. This approach was adopted because it gives the correct strand sequence that must have been present in the original polymer in order to produce that oligomer. Alternatively, one might argue that the two terminal aldehydes should be counted as only one butadiene monomer since each butadiene monomer degraded by ozone produces two aldehydes. Counting the terminal aldehydes as only one butadiene monomer would have the effect of raising the experimentally determined styrene and acrylonitrile compositions by a few percent. (The exact amount depends on the specific polymer considered.) While this approach would bring the experimentally determined compositions of some polymers (styrene−butadiene; 51% acrylonitrile−butadiene) closer to the reference values, it would push the experimentally determined compositions of other polymers (19−22%, 30−32%, 38−40% acrylonitrile−butadiene) further away. Figure 4 shows that a composition bias is inherent to the ozonolysis procedure when only one of the comonomers reacts efficiently. Treating the end groups as only a single butadiene monomer in the composition calculations will uniformly shift the points in Figure 4 to slightly higher acrylonitrile contents, but this treatment will not eliminate the time-dependent change in composition that is suggested by the model and observed experimentally.

Conclusion

The microstructures of high molecular weight and insoluble butadiene copolymers were determined using ozonolysis/MALDI mass spectrometry. Using this method, a block (ABA) styrene–butadiene copolymer was distinguished from a random styrene–butadiene copolymer. Several acrylonitrile–butadiene copolymers with different compositions were also analyzed using ozonolysis/MALDI-MS. The compositions obtained from the oligomer distributions detected by MALDI mass spectrometry were close to the reported compositions for these copolymers (typically within 5 wt %). The discrepancy in the values can be explained, in part, to a compositional bias resulting from the ozonolysis process. This bias arises when only one of the comonomers reacts efficiently with ozone.

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