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Structural Characterization of Butadiene/Styrene Copolymers by Fast Atom Bombardment Mass Spectrometry Analysis of the Partial Ozonolysis Products

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ABSTRACT: The partial ozonolysis of some butadiene/styrene (Bt/St) copolymers has been performed in order to generate low molecular weight fragments by the cleavage of double bonds along the main chain. The mixtures obtained from ozonolysis were directly analyzed by fast atom bombardment mass spectrometry (FABMS). Compounds having aldehyde or carboxyl end groups have been detected, from which it has been possible to characterize the structure of the different copolymers investigated. The presence of compounds having aldehyde/aldehyde end groups and containing one ozonide unit in the molecule has been confirmed among the ozonolysis products of a Bt/St copolymer, by HPLC separation followed by FABMS analysis of the collected fractions. The ozonolysis kinetics has also been examined in order to value the extent of the ozonolysis reaction.

Introduction

There is today a great interest in the characterization of polymeric materials having complex structures, containing repeat units of high molecular weight, and in the determination of the sequences of repeating units in copolymers.

Mass spectrometry is able to look at the mass of individual molecules in a mixture, and it is therefore an interesting alternative to NMR for molecular characterization of copolymers.[1-6]

The fast atom bombardment mass spectrometry (FABMS) technique, introduced recently,[7] has already become widely used for the analysis of polar, labile organic molecules, including biomolecules of relatively high molecular weight.[8-11] There is therefore considerable interest in exploring the potential of FABMS analysis to other polymeric materials.

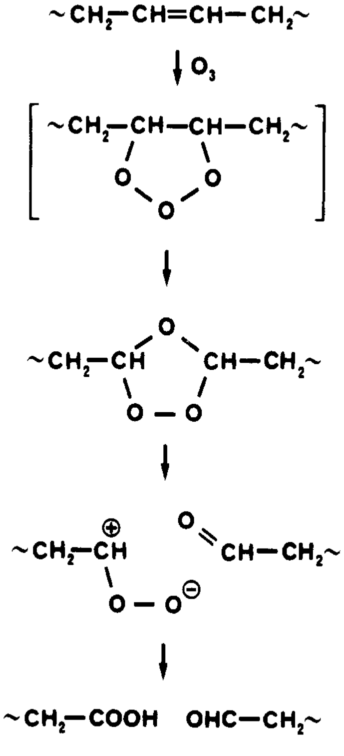
FABMS technique initially was not used correctly in the case of synthetic polymeric materials. Early researchers believed in the fact that the bombardment of fast atoms was sufficient to induce the cleavage of chemical bonds in the polymeric chains and that the ions detected were originating from the fragmentation of the macromolecules.[12,13]

Later studies demonstrated that the ions detected do originate from oligomeric species already present in the polymers and that the fast atom bombardment does not produce the cleavage of macromolecules.[14]

Since polymers have molecular weights too high to fit in the mass range of conventional mass spectrometer instruments, a partial degradation of the macromolecules is necessary to produce low molecular weight products, which retain, at the same time, the structural sequence of the original copolymer.

Recently, we have used FABMS to identify the compounds formed in the partial chemical degradation of several condensation copolymers. Namely, partial hydrolysis,[4] methanolysis,[15] ammonolysis,[5,6] photolysis,[4] and pyrolysis[16] have been used to degrade some copolyamides, copolyesters, and copolycarbonates.

Chart I



The results yielded detailed information about the structure and the sequence of the copolymers investigated and have established the basis for a new and straightforward method of sequencing condensation copolymers.

However, the controlled chemical degradation methods developed up to now are suitable for condensation copolymers, whereas addition copolymers cannot be treated.

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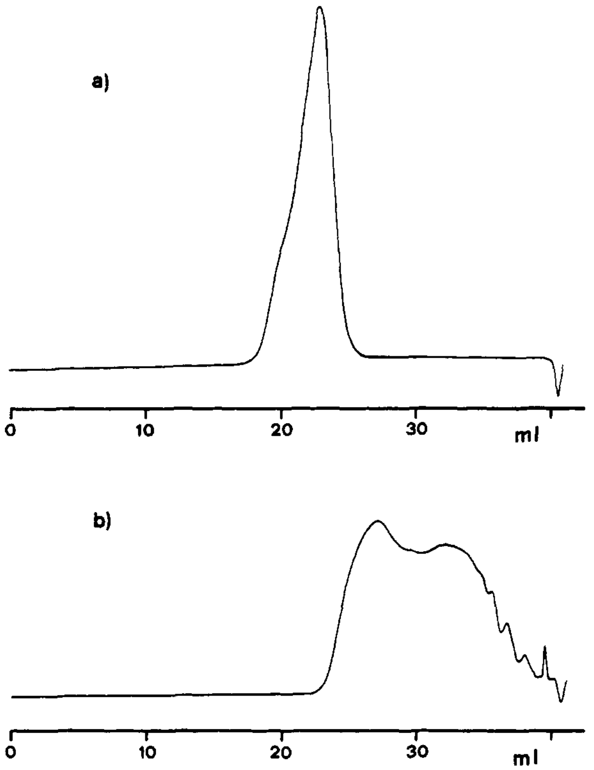
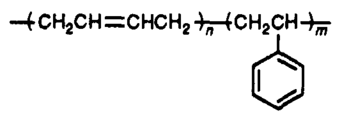


Figure 1. GPC traces (THF as eluant) of (a) untreated and (b) partially ozonolyzed (30 min of ozonolysis) poly(butadiene).

A survey of chemical degradation methods, which may attack addition copolymers in a controlled way, brought into evidence the ozonolysis reaction as a suitable method of producing low molecular weight compounds from diene copolymers.[17-20]

Accordingly, we have attempted the structural characterization of butadiene/styrene (Bt/St) copolymers (I) by FABMS analysis of the partial ozonolysis products.



$$-\!\!\left(CH_2CH{=}CHCH_2\right)_n\!\!\left(CH_2CH(C_6H_5)\right)_m\!\!-$$

I

Two random copolymer samples ($n = 15/m = 85$ and $n = 55/m = 45$, Bt/St) were analyzed, together with a *cis*-1,4-poly(butadiene) (PBt) homopolymer and a styrene/butadiene/styrene (St/Bt/St) triblock copolymer.

The ozonolysis reaction, schematized in Chart I,[20] allows the fragmentation of the macromolecules by the cleavage of the double bonds and produces compounds of low molecular weight suitable for the FABMS analysis.

Several investigations concerned with various aspects of ozone degradation of polymeric materials have appeared in the literature.[17-20] However, these studies have never attempted the detailed structural analysis of the products obtained by ozonolysis.

Even more so, there has been no attempt to sequence diene copolymers.

Our results have allowed the structural identification of partial ozonolysis products with aldehyde/aldehyde or carboxyl/carboxyl end groups, from which it has been possible to characterize the different copolymers investigated.

Experimental Section

Materials. Basic materials were commercial products appropriately purified before use.

Poly(butadiene) containing 98% cis-1,4 units (PBt) was obtained from Janssen; two poly(butadiene-*co*-styrene) (Bt/St) samples containing 85% and 45% (w/w) of styrene, respectively, were provided by Polysciences, Inc.; styrene/butadiene/styrene (St/Bt/St) block copolymer, containing 28% (w/w) of styrene, was purchased from Scientific Polymer Products, Inc.

All the polymer samples were purified by reprecipitation. The abundance of the comonomers in each sample was determined by ^1H NMR analysis.

Ozonolysis Procedure. The ozone was generated by passing dry oxygen (flow rate 3.6 L/h) through an ozone generator (Model 500 from Fisher) at room temperature. The ozone/oxygen mixture contained about 2% of ozone.

Each polymer sample, approximately 500 mg, was dissolved in 100 mL of *n*-hexane in a glass reactor equipped with a magnetic stirrer and a tube for the oxygen/ozone inlet; the ozone residue was destroyed by passing the exhausted gas mixture through a solution of KI in diluted acetic acid.

The reactor containing the solution was maintained in an ice bath for the whole ozonolysis time.

Seven samples (each one of about 10 mL) of this solution were withdrawn after 1, 5, 10, 30, 60, 120, and 180 min of ozonolysis, and each sample, after distillation of the solvent, was tested, without other treatments, by GPC, HPLC, and FABMS analysis.

GPC Analysis. A Waters 6000A apparatus, equipped with four μ-Styragel columns (in the order 1000-, 500-, 10 000-, and 100-Å pore size), was used. The analyses were performed at room temperature by using THF as eluant at a flow rate of 1 mL/min.

HPLC Separation. The separation of the ozonolysis products was performed by HPLC, using a Varian Vista 5500 HPLC system, equipped with a Varian 2050 UV detector and a μBondapak C18 Waters column of 3.9 mm × 30 cm.

A total of 50 μL of the acetonitrile solution of the ozonolyzed sample was injected and an elution gradient, starting with 100% H_2O maintained for 5 min and ending with 100% acetonitrile in

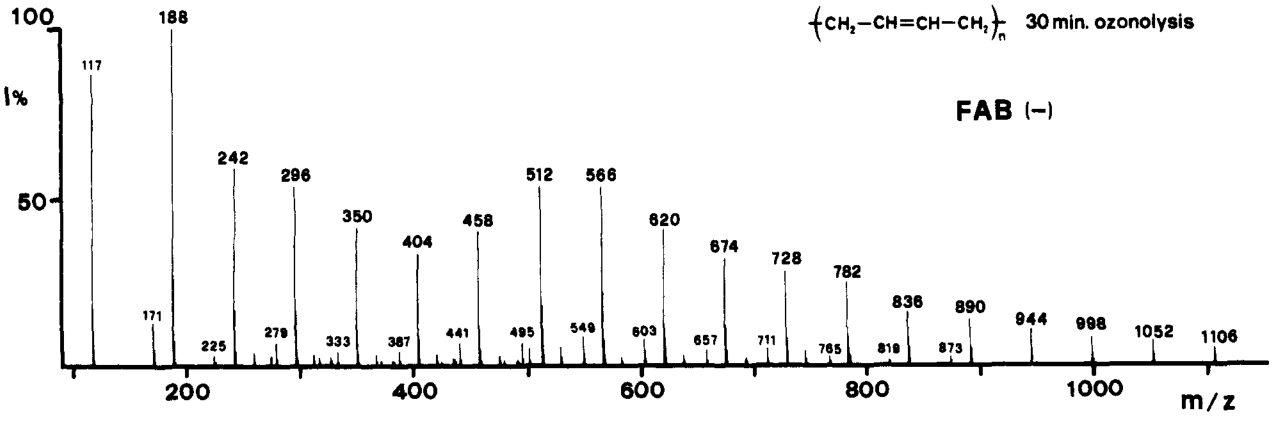
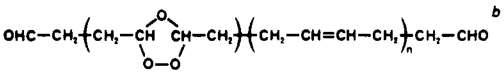


Figure 2. Negative FAB mass spectrum of a poly(butadiene) sample ozonolyzed 30 min.

Table I
Compounds Present in the 1,4-Poly(butadiene) Sample Ozonolyzed 30 min, Detected in the Negative FAB Mass Spectrum

	molecular ions (m/z) at n =																	
structure	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
$\mathrm{HOOC{-}CH_2{-}(CH_2{-}CH{=}CH{-}CH_2)_n{-}CH_2{-}COOH}$ [a]	117	171	225	279	333	387	441	495	549	603	657	711	765	819	873			
 $\mathrm{OHC{-}CH_2{-}(CH_2{-}CH\overset{O}{\underset{O-O}{\frown}}CH{-}CH_2)(CH_2{-}CH{=}CH{-}CH_2)_n{-}CH_2{-}CHO}$ [b]	188	242	296	350	404	458	512	566	620	674	728	782	836	890	944	998	1052	1106

[a] The molecular ions of these compounds appear in the negative FAB mass spectra as $(M-1)^-$. [b] The moleculr ions of these compounds appear in the negative FAB mass spectra as $(M)^-$. The ozonide unit is in an unknown position in the chain.

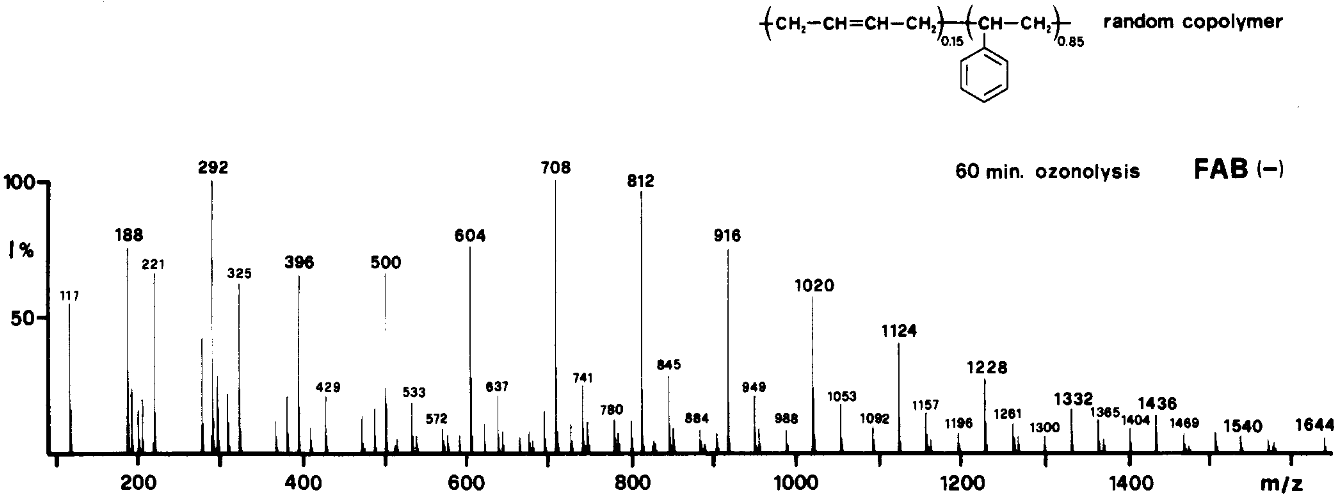
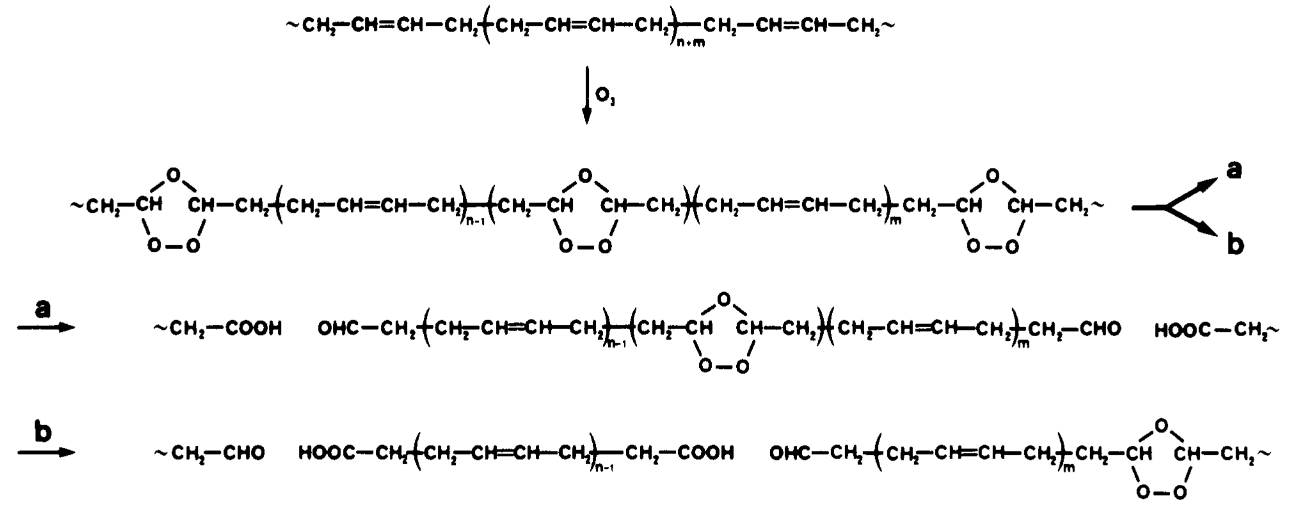


Figure 3. Negative FAB mass spectrum of a random butadiene/styrene (15/85) copolymer ozonolyzed 60 min.

Chart II



50 min, was used for the separation, at a flow rate of 1 mL/min. The separated compounds were revealed by UV detection at 205 nm.

FAB Mass Spectrometry. FAB analyses were performed on a double-focusing Kratos MS50S mass spectrometer, equipped with the standard FAB source. Mass spectra were recorded by means of a UV recorder. Xenon was used as bombarding gas, with an energy of 8 kV. Mass resolution was approximately 2000. Spectra were obtained by using a diethanolamine/tetramethylurea (DEA/TMU) mixture as matrix. Both negative and positive FAB mass spectra of the investigated samples were examined. However, the negative FAB mass spectra appear more informative, so only these are discussed in this paper.

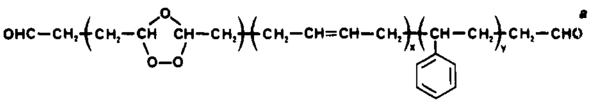
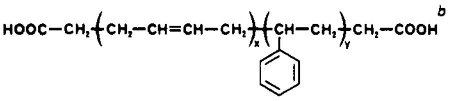
Results and Discussion

Identification of Ozonolysis Products from *cis*-1,4-Poly(butadiene). In Figure 1 the GPC traces of an untreated poly(butadiene) (PBt) (curve a) and of partially ozonolyzed sample (curve b) are reported; comparing the two curves, a marked lowering of the molecular weight can be observed.

In the Figure 2 the negative FAB mass spectrum of the products formed after 30 min of ozonolysis from PBt is shown.

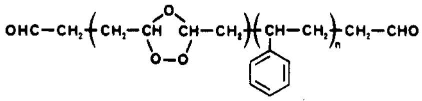
Although apolar molecules such as hydrocarbons do not yield intense molecular ions in FAB mode, the ozonolysis of PBt produces hydrocarbon compounds with polar (aldehyde or carboxyl) end groups (Chart I), which can instead be detected in the negative FAB mode. The best spectra have been obtained by using a basic matrix (DEA/TMU) in order to enhance the acidity of the end groups of the ozonolysis products.

Table II
Compounds Present in the Styrene/Butadiene Random Copolymer Samples after Ozonolysis, Detected in the Negative FAB Mass Spectra

structure	x	molecular ions (m/z) for y =														
		0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
 [a]	0	188	292	396	500	604	708	812	916	1020	1124	1228	1332	1436	1540	1644
	1	242	346	450	554	658	762	866								
	2	296	400	504	608	712	816	920								
	3	350	454	558	662	766	870									
	4	404	508	612	716	820	924									
	5	458	562	666	770											
	6	512	616	720	824											
	7		670	774												
 [b]	0	117	221	325	429	533	637	741	845	949	1053	1157	1261	1365	1469	
	1	171	275	379	483	587	691									
	2	221	329	433	537	641										
	3	279	383	487	591	695										
	4	333	437	541	645											
	5		491	595	699											

[a] The molecular ions of these compounds appear in the negative FAB mass spectra as $(M)^-$. The ozonide unit is in an unknown position in the chain. [b] The molecular ions of these compounds appear in the negative FAB mass spectra as $(M-1)^-$.

Table III
Identification of the Ozonolysis Products from a Random Styrene (85%)/Butadiene (15%) Copolymer by HPLC and Negative FAB Mass Spectrometric Analysis



HPLC peak no.	MW[a] (n)
1	396 (1)
2	500 (2)
3	nd
4	604 (3)
5	nd
6	812 (5)
7	916 (6)
8	1020 (7)
9	1124 (8)
10	1228 (9)
11	1332 (10)

[a] The molecular ions of these compounds appear in the negative FAB mass spectra as $(M)^-$.

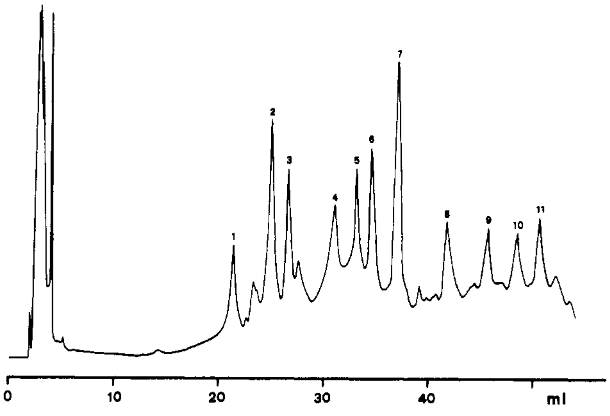


Figure 4. HPLC separation of the ozonolysis products from the random butadiene/styrene (15/85) copolymer. Structural identification of the collected fractions is reported in Table III.

Two families of peaks appear in the spectrum of Figure 2. The most abundant series is constituted by the molecular ions of compounds having m/z 188 + n54, with n = 0–17. The other series appears at m/z 117 + n54, with n = 0–14. These two families correspond to compounds having aldehyde/aldehyde or carboxyl/carboxyl end groups, as shown in Table I.

As can be seen in Table I, the ozonolysis reaction yields products that are more complex with respect to the process indicated in Chart I. Actually, the degradation reaction can be schematized as in Chart II.

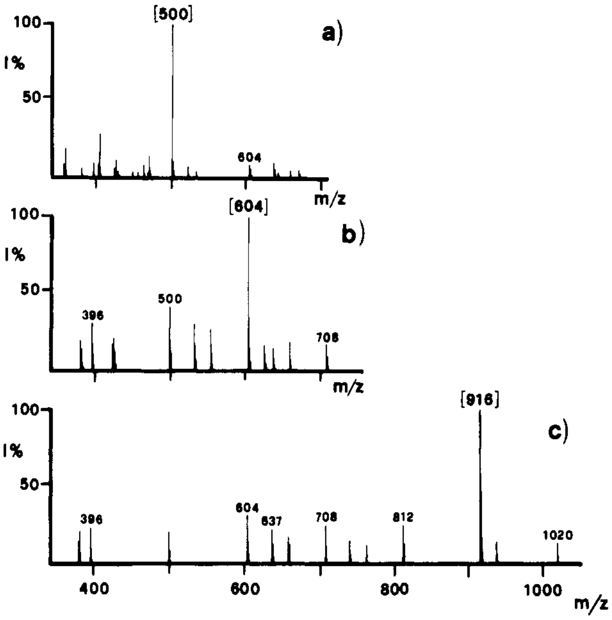


Figure 5. Negative FAB mass spectra of the fractions 2 (a), 4 (b), and 7 (c) collected in the HPLC separation of an ozonolyzed butadiene/styrene (15/85) copolymer sample (Figure 4). For the structural assignments, see Table III.

In the case of ozonolysis compounds detected in the negative FAB mass spectrum (Figure 2) having aldehyde/aldehyde end groups, one ozonide group, in an unknown position along the chain, remains uncleaved in the molecule (Chart II).

It can be noted that compounds having aldehyde and carboxyl end groups are absent among the ozonolysis products. It is difficult to conceive a totally satisfactory explanation of this behavior, but ozonide units were detected only in degradation products having both aldehydic end groups. This can indicate that the presence of a carboxyl group in the molecule induces the cleavage of the ozonide unit to form another carboxyl end group.

Furthermore, it must be remarked that ozonolyzed samples analyzed after about 2 weeks showed a strong increase of the relative abundance of compounds having carboxylic end groups with respect to those having aldehydic end groups.

It can also be noted that the negative FAB mass spectrum in Figure 2 shows a series of molecular ions up

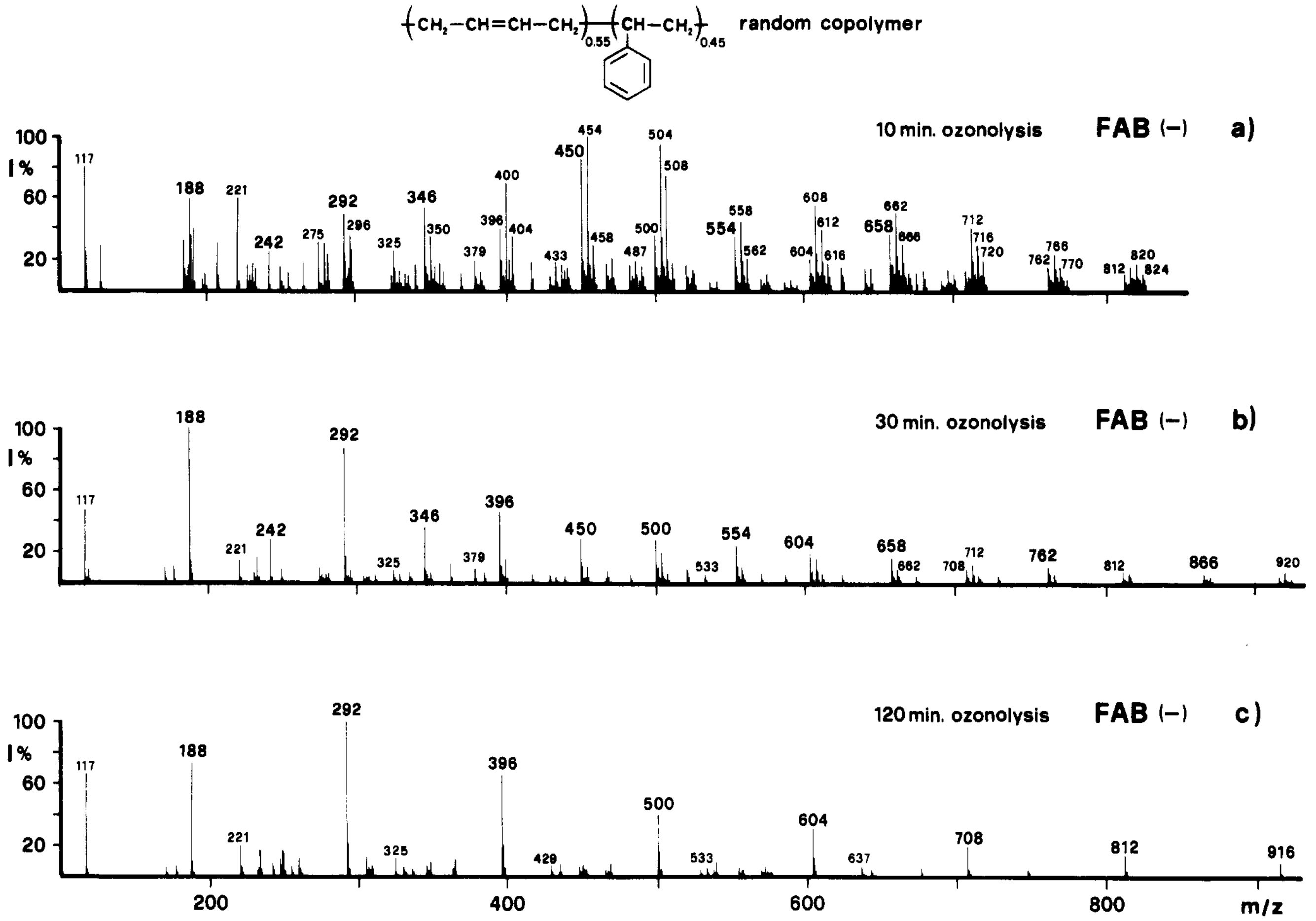


Figure 6. Negative FAB mass spectra of a partially ozonolyzed butadiene/styrene (55/45) random copolymer sample: (a) 10 min, (b) 30 min, and (c) 120 min of ozonolysis.

to the 20-mer (*m/z* 1106). This leads to expectation that the FAB spectra of the low molecular weight compounds generated in the ozonolysis of Bt/St copolymers may contain a sufficient number of comonomeric units to provide detailed sequential information.

Identification of Ozonolysis Products from Random Butadiene/Styrene Copolymers. In Figure 3 the negative FAB mass spectrum of the partial ozonolysis products from the Bt/St (15/85) copolymer is shown. The structures corresponding to the molecular ions in the spectrum are reported in Table II.

As in the case of PBt homopolymer, two families of compounds are present in the spectrum, and the most abundant series is constituted by the peaks at *m/z* 188 + *n*104, with $n = 0$–14, corresponding to molecular ions of compounds having both aldehyde end groups (compounds *a* in Table II, with $x = 0$).

The other series, which appears with low intensity at *m/z* 117 + *n*104, with $n = 0$–13, is constituted by the peaks of the compounds with two carboxylic end groups (compounds *b* in Table II, with $x = 0$).

Different from the PBt case, the presence of compounds containing butadiene units is not observed (Table III), since the butadiene amount in the copolymer is low (15%), and therefore the butadiene units are consumed by the ozone to form the aldehyde or carboxyl end groups of the ozonolysis products.

In order to confirm that the peaks appearing in the negative FAB mass spectrum in Figure 3 are molecular ions of ozonolysis compounds, a portion of the ozonolyzed copolymer sample was subjected to HPLC separation.

The HPLC trace of the partial ozonolysis products originating from the random Bt/St (15/85) copolymer is reported in Figure 4. The HPLC peaks are resolved well enough, allowing the collection of fractions corresponding to each peak in Figure 4. The fractions collected were lyophilized and analyzed by negative FABMS. In Figure 5 the FAB mass spectra of some separated HPLC peaks are reported. The molecular ions and the corresponding structures detected in the FABMS spectrum of each HPLC peak are reported in Table III.

It can be noted that the products corresponding to the HPLC peaks in Figure 4 have one ozonide group inner to the chain and two aldehyde end groups (Table III). The ozonolysis products having carboxyl end groups (Figure 3; Table II) are not separated by the HPLC column.

Ozonolysis Kinetics. The ozonolysis of a Bt/St (55/45) random copolymer afforded the opportunity of running a kinetic experiment, monitoring the disappearance of butadiene units as a function of the ozonolysis time.

In Figure 6 three negative FAB mass spectra recorded, respectively, after 10, 30, and 120 min of ozonolysis are shown. Structural assignments of the compounds identified are reported in Table II.

It can be noticed that in the spectrum in Figure 6a are present several peaks of comparable intensity, which belong to compounds containing both styrene and butadiene units.

The series of peaks at *m/z* 188 + *n*54 corresponds to compounds having only butadiene units (Table II). Other series of peaks are present at *m/z* 242 + *n*104, at *m/z* 296 + *n*104, etc. The latter possess different ratios of butadiene and styrene units (Table II). The series of peaks at

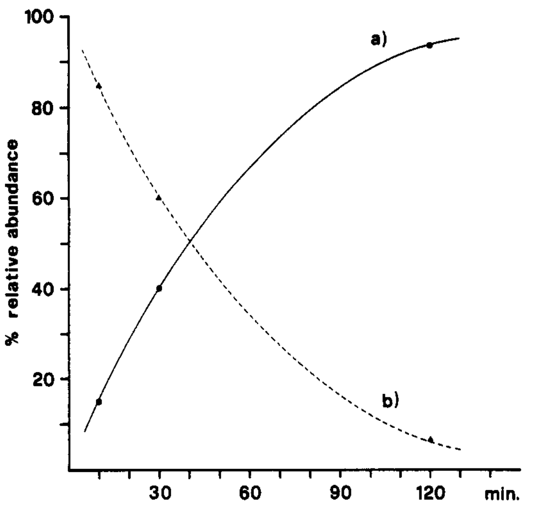


Figure 7. Relative abundance of the ozonolysis products as a function of the reaction time: (a) compounds having only styrene units in the molecule, (b) compounds containing also butadiene units (see ref 21).

m/z 188 + n104 corresponds to compounds containing only styrene units (except for the ozonide and the end groups).

With comparison of the spectra in Figure 6, it can be noted that the series of peaks with higher butadiene content decreases in intensity at longer ozonolysis times. After 120 min of ozonolysis, the spectrum (Figure 6c) shows only the series at m/z 188 + n104, which contains only styrene units (Table II), since the butadiene units have been destroyed by the ozone attack.

This behavior is visualized in Figure 7, where the intensities of the series of peaks containing only styrene units (curve a) and of those containing also butadiene units (curve b) (see ref 21) have been reported as a function of the ozonolysis time.

These results show that the extent of ozonolysis can be conveniently monitored through the negative FAB mass spectra and that the ozonolysis reaction proceeds smoothly up to completion; it can therefore be stopped at the degree of degradation that is judged most convenient for both analytical or preparative purposes (oligomer synthesis).

Comparing the results obtained for the two random copolymers, it can be noted that compounds containing up to 14 consecutive styrene units are detected in the spectrum of the Bt/St (15/85) copolymer (Figure 3; Table II), whereas compounds containing only seven consecutive styrene units are detected in the case of the 55/45 copolymer (Figure 6c; Table II). Provided that the peak intensities in Figures 3 and 6c do not represent relative abundances, due to different FAB sensitivity through the ozonolysis products, it can be observed as this fact reflects the statistical distribution of the comonomer units in the two copolymers.

Identification of Ozonolysis Products from SBS Triblock Copolymer. Besides the ozonolysis of the two random copolymers reported above, we have attempted the ozonolysis of an SBS triblock copolymer with a molecular weight of about 100 000, containing a molar ratio of St/Bt 17/83, as estimated by ^{1}H NMR.

In this case, the ozone attack produces compounds with butadiene sequences of various sizes and other compounds with long styrene sequences, because the lateral styrene blocks are constituted from about 135 styrene units (about 14 000 Da). The latter are not therefore visible in the FABMS since their molar weight exceeds the cutoff range of the mass spectrometer (about 2000 Da, in the present case).

As expected, the negative FAB mass spectrum of the partial ozonolysis products of the SBS block copolymer (omitted here for brevity) contains only peaks related to butadiene units, and it resembles very closely that of the pure polybutadiene shown in Figure 2.

It is therefore possible to distinguish a random from a block Bt/St copolymer by analyzing the negative FAB mass spectra of their partial ozonolysis products.

Conclusions

The analysis of products formed by partial ozonolysis of the investigated butadiene/styrene copolymers reveals that the random cleavage of double bonds of butadiene units along the main chain produces low molecular weight compounds having aldehyde or carboxyl end groups.

The identification of these products has been achieved by the FABMS technique, which appears to be a suitable and rapid method to analyze these complex mixtures.

Unambiguous confirmation of the presence, among the ozonolysis products, of compounds having aldehyde/aldehyde end groups and containing one ozonide unit in the molecule, is obtained from HPLC separation, followed by FABMS analysis of the collected fractions.

From the examination of the partial ozonolysis products can be distinguished the random or block sequential structure of a Bt/St copolymer. The amount and the distribution of the two monomers in the copolymer can also be nearly determined. In a random copolymer, in fact, an increment of the styrene content determines an extent of the consecutive styrene blocks in the ozonolysis products.

The ozonolysis kinetics has also been examined in order to value the extent of this reaction. In this way, the most convenient degree of degradation to obtain fragments of optimal size to be analyzed by FABMS and containing important structural information can also be determined.

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(21) The values of relative abundances reported in Figure 7 are calculated by the peak intensities in the negative FAB mass spectra of Figure 6 on the basis of the following formulas:

$$\frac{\sum_{y=1}^{n} \mathrm{St}_y}{\sum_{y=1}^{n} \mathrm{St}_y + \sum_{x=1,y=1}^{n} \mathrm{Bt}_x\mathrm{St}_y} \quad \text{(points ●)}$$

$$\frac{\sum_{x=1,y=1}^{n} \mathrm{Bt}_x\mathrm{St}_y}{\sum_{y=1}^{n} \mathrm{St}_y + \sum_{x=1,y=1}^{n} \mathrm{Bt}_x\mathrm{St}_y} \quad \text{(points ▲)}$$

where $\mathrm{Bt}_x\mathrm{St}_y$ indicates the ozonolysis products having butadiene and styrene units in the molecule whereas St_y indicates those compounds having only styrene units (a part of the two butadiene residue end groups and the ozonide unit in the chain) (see Table II).

Registry No. (Bt)(St) (copolymer), 9003-55-8; PBt (homopolymer), 9003-17-2; (St)(Bt) (block copolymer), 106107-54-4.