Structural characterization of butadiene/acrylonitrile copolymers by fast atom bombardment mass spectrometric analysis of the partial ozonolysis products

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The partial ozonolysis of three random butadiene/acrylonitrile copolymers I–III, with butadiene contents of 78, 67 and 55 mol%, respectively, has been performed in order to form low-molecular-weight products by cleavage of double bonds along the main chain. The fragments thus obtained have been directly analysed by both positive and negative fast atom bombardment mass spectrometry (f.a.b.-m.s.). According to a random distribution of butadiene (Bt) and acrylonitrile (AN) subunits in the copolymer chains, peaks due to fragments with different Bt/AN ratio in the molecule have been detected in the mass spectra. The relative abundances of the species having the same total number of AN and Bt subunits, detected in the mass spectra of ozonolysed copolymers I–III, have been compared with those calculated according to a theoretical combination of AN and Bt units. Good agreement has been found between the two sets of data. A graphical procedure for rapid determination of Bt/AN copolymer composition by f.a.b.-m.s. data has been also developed.

(Keywords: characterization; copolymer; butadiene; acrylonitrile; fast atom bombardment; ozonolysed products; mass spectrometry)

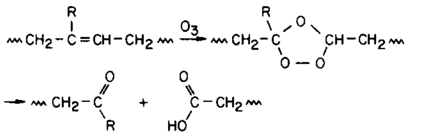
INTRODUCTION

There is great interest in the structural characterization of polymeric materials and in the determination of the monomer unit sequences along the copolymer chains.

Several reports concerned with the structural investigation of condensation copolymers by the fast atom bombardment mass spectrometry (f.a.b.-m.s.) technique have appeared in the literature[1–7].

Since macromolecules have molecular weights too high to be directly detected by a conventional mass spectrometer[1,8] (the difficulty in part is removed by use of new electrospray[9–11] and laser desorption[12] technologies), the procedure adopted has been that of producing low-molecular-weight products by partial chemical degradation of the polymer chains. Partial hydrolysis[3], ammonolysis[6] and photolysis[3] have been used to produce fragments that retained, at the same time, the original sequence of the copolymer. Successive f.a.b.-m.s. identification of these products allowed the characterization of the polymeric material.

Recently, we have demonstrated that a similar procedure can be used for addition polymers and copolymers having diene units in the main chain[13,14]. It has been established that ozonolysis is a suitable reaction to produce, in a controlled way, low-molecular-weight fragments from polymer materials. In the cases of polybutadiene, polyisoprene, polychloroprene and some butadiene/styrene copolymers, it has been shown that the cleavage of the double bonds, by ozone attack, produces compounds having aldehyde, ketone or acyl chloride and/or carboxyl end-groups, according to equation (1):



(1)

in which R corresponds to hydrogen, methyl or chlorine. The results obtained allowed the characterization of the different analysed samples[13,14].

In the present work, the structural characterization of the following commercial butadiene/acrylonitrile (Bt/AN) copolymers I–III (with *n* and *m* in mol%) by partial ozonolysis and successive f.a.b.-m.s. identification of the

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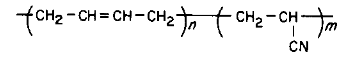
formed fragments, is reported:



$$-\!\!\left(CH_2-CH=CH-CH_2\right)_{n}\!\!-\!\!\left(CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}\right)_{m}\!\!-$$

I: $n = 0.78$, $m = 0.22$
II: $n = 0.67$, $m = 0.33$
III: $n = 0.55$, $m = 0.45$

EXPERIMENTAL

Materials

Basic materials were commercial products appropriately purified before use.

Polybutadiene (PBt) containing 98% *cis*-1,4 units was obtained from Janssen; three poly(butadiene-*co*-acrylonitrile) samples containing 78, 67 and 55 mol% of butadiene were provided by Polysciences Inc. All the polymer samples were purified by reprecipitation and the comonomer abundance in each sample was determined by ^1H n.m.r. analysis.

Ozonolysis procedure

The ozone was generated by passing dry oxygen (flow rate $3.6\,l\,h^{-1}$) through an ozone generator (model 500 from Fisher) at room temperature. The ozone/oxygen mixture contained about 2% of ozone.

Each polymer sample, approximately 200 mg, was dissolved in 100 ml of toluene or chloroform 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 CH_3COOH.

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

Three samples (each one of about 20 ml) of this solution were withdrawn after 5, 10 and 30 min of ozonolysis; each sample, after distillation of the solvent and without other treatments, was tested by g.p.c., h.p.l.c. and f.a.b.-m.s. analysis.

^1H n.m.r. analysis

^1H n.m.r. spectra were recorded in $CDCl_3$ solution with tetramethylsilane (TMS) as internal standard on a Brüker 250 A-CF spectrometer.

G.p.c. analysis

A Waters 6000 A 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 $CHCl_3$ as eluant at a flow rate of $1\,ml\,min^{-1}$.

H.p.l.c. separation

The separation of the ozonolysis products was performed by h.p.l.c., using a Varian Vista 5500 h.p.l.c. system, equipped with a Varian 2050 u.v. detector and a μ-Bondapak C-18 Waters column of 3.9 mm × 30 cm.

A total of 50 μl of the acetonitrile solution of the ozonolysed sample was injected and an elution gradient, starting with 100% H_2O maintained for 5 min and ending with 100% acetonitrile in 50 min, was used for the separation, at a flow rate of $1\,ml\,min^{-1}$. The separation compounds were revealed by u.v. detection at 205 nm.

F.a.b. mass spectrometry

F.a.b. analyses were performed on a double-focusing Kratos MS 50 S mass spectrometer, equipped with the standard f.a.b. source. Mass spectra were recorded by means of a u.v. 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 or 3-nitrobenzyl alcohol as matrix. Both negative and positive f.a.b. mass spectra of the investigated samples were examined.

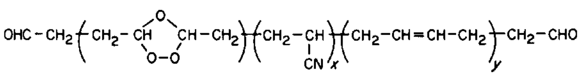
RESULTS AND DISCUSSION

Our previous experience in the structural characterization of diene polymers and copolymers[13,14] suggests that the analysis of the partial ozonolysed fragments by negative f.a.b. mass spectra provides very informative data.

It has been shown that materials containing butadiene units undergo controlled degradation by ozone attack on double bonds, producing low-molecular-weight species having aldehyde end-groups and one ozonide unit in the molecule (*Figure 1a* and *Table 1*: peaks at $m/z = 188 + n54$, as M^- ions) or carboxyl end-groups (peaks at $m/z = 117 + n54$, as $(m-1)^-$ ions), according to equation (1).

In the present work we have also recorded the positive f.a.b. mass spectra of the ozonolysed polybutadiene and, in *Figure 1b*, the spectrum of the products formed after 5 min of ozonolysis is reported. Comparing this spectrum with that detected in the negative f.a.b. mode, it can be observed that the two above-mentioned series of peaks present in *Figure 1a* are absent in the positive f.a.b. mass spectrum (*Figure 1b*), which is essentially constituted by the series of peaks at $m/z = 207 + n54$, with $n = 0$–15 (see *Table 2*). These peaks, also present with low intensity in the negative f.a.b. mass spectrum (at $m/z = 205 + n54$), correspond to molecular ions detected as $(M+1)^+$ of compounds with one ozonide unit and having aldehyde/aldehyde end-groups, which have bound one molecule of water, as shown in *Table 2*. However, the structure of these compounds remains undefined.

The negative f.a.b. mass spectra of the partial ozonolysis products, formed after 5 min of ozone reaction, of the three random butadiene/acrylonitrile (Bt/AN) copolymers I–III containing 78, 67 and 55 mol% of Bt units are shown in *Figures 2a*, *2b* and *2c*, respectively. The assignments of the compounds identified are reported in *Table 1*. The mass spectra are constituted essentially by a family of peaks corresponding to molecular ions of products having the following structure IV:



IV

indicated as (AN_xBt_y) in the text, in which the ozonide unit is in an unknown position in the molecule.

The positive f.a.b. mass spectra of the ozonolysed copolymers I–III have also been made and, in *Figures 3a*, *3b* and *3c*, those obtained after 5 min of reaction are reported. The spectra are constituted by peaks corresponding to molecular ions, identified as $(M+1)^+$ in *Table 2*, of compounds having the structure IV, which have bound, as in the PBt case, one molecule of H_2O.

Comparing the negative f.a.b. mass spectra of the ozonolysed products of copolymers I–III (*Figure 2*) with

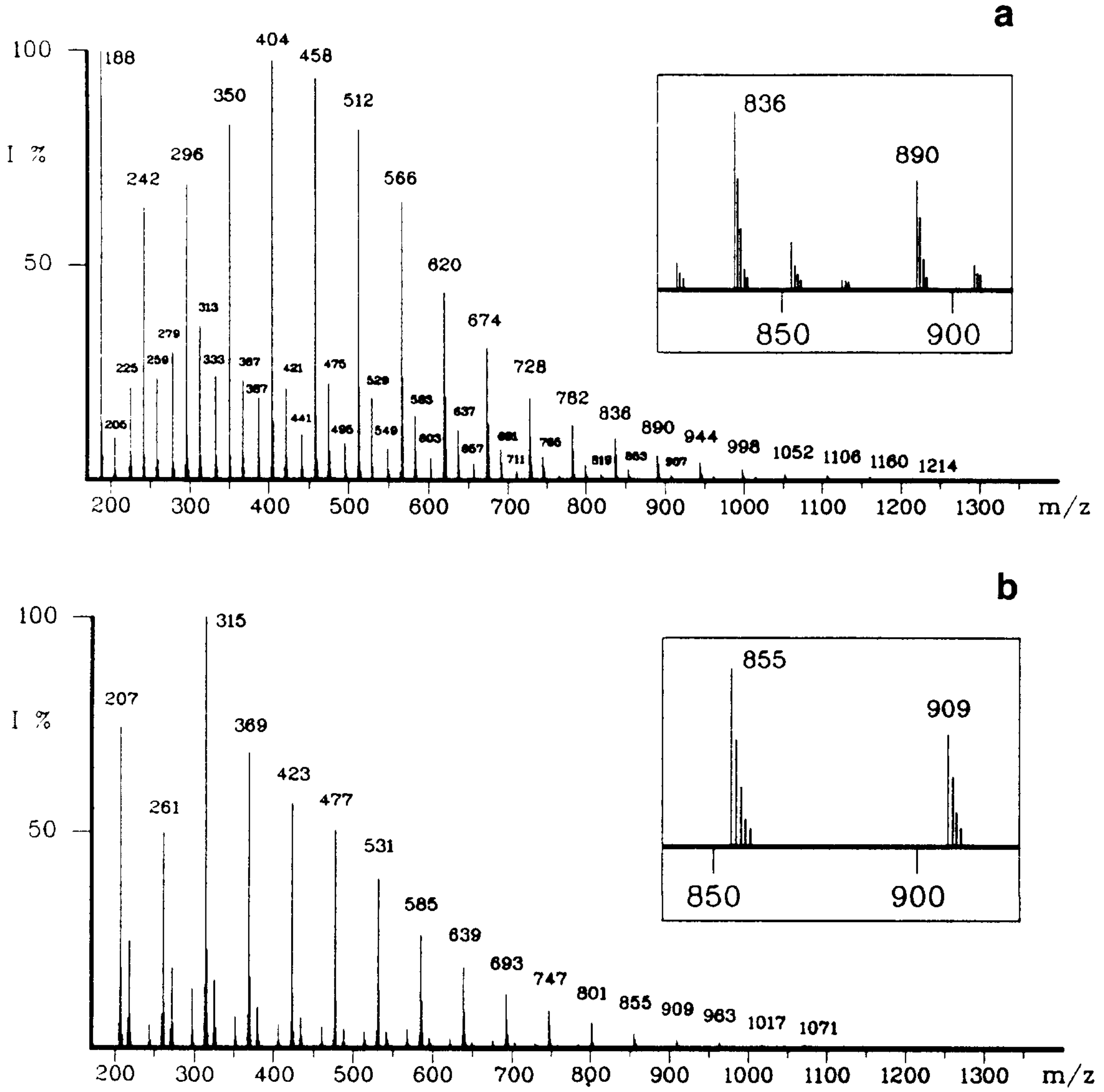


Figure 1 (a) Negative and (b) positive f.a.b. mass spectra, detected using DEA/TMU mixture as matrix, of polybutadiene sample ozonolysed for 5 min

that of polybutadiene (*Figure 1a*), it can be observed that to each peak in *Figure 1a* corresponds a complex cluster of peaks in the spectra of the copolymers. This difference is more evident by observing the 'windows' in *Figures 1a* and *2*, corresponding to an enlargement of the spectra between $m/z = 800$ and 950 values. Furthermore it can be noted that, in each cluster of *Figures 2a*, *2b* and *2c*, the peaks correspond to molecular ions of compounds (AN_xBt_y, structure IV) having the same total number $(x+y)$ of monomeric subunits, and the peak of maximum relative abundance is shifted to lower m/z values on going from the spectrum of copolymer I (*Figure 2a*, 78% Bt) to that of copolymer III (*Figure 2c*, 55% Bt). This is also observed in each f.a.b. mass spectrum (*Figure 2*) on going towards clusters of peaks at higher m/z values. Analogous behaviour can be observed in positive f.a.b. mass spectra.

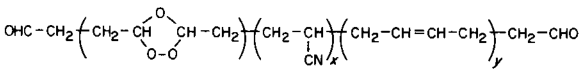
According to a random distribution of the Bt and AN subunits along the copolymer chains, fragments of different relative abundance of the AN and Bt units are expected by cleavage of the macromolecules. Besides this, the peaks due to molecular ions of compounds having the same number $(x+y)$ of monomeric subunits but different relative abundance of AN and Bt units, because the molecular weights of acrylonitrile (53) and butadiene (54) only differ by one mass unit, must appear very near in the spectra, so forming the complex clusters observed in *Figures 2* and *3*.

Although it is usually maintained that the mass spectrometric response should not be considered quantitative, in our particular case the relative abundance of the peaks corresponding to species having the same total number of subunits $(x+y)$ in each cluster may be representative of the original copolymer composition. This semiquantitative approach is possible because we compare, in each cluster, the abundance of compounds having similar structure and molecular weight, for which a similar behaviour under f.a.b. conditions may be supposed[6,15].

The best results in the evaluation of copolymer composition have been obtained for short ozonolysis times, when only few per cent of the butadiene is degraded. In fact, at higher reaction times, almost all the Bt units were destroyed by ozone attack[9], and compounds containing only AN units are formed, inducing an underestimation of the butadiene content in the copolymer.

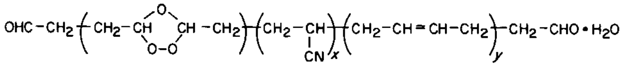
The relative abundances of compounds having the

Table 1 Compounds present in ozonolysed samples of polybutadiene or Bt/AN copolymers I–III detected in the negative f.a.b. mass spectra

Structure[a]		Molecular ions (m/z) for																			
		$y=0$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	14	16	17	18	19
	$x=0$	188	242	296	350	404	458	512	566	620	674	728	782	836	890	944	998	1052	1106	1160	1214
	1	241	295	349	403	457	511	565	619	673	727	781	835	889	943	997	1051				
	2	294	348	402	456	510	564	618	672	726	780	834	888	942	996	1050	1104				
	3	347	401	455	509	563	617	671	725	779	833	887	941	995	1049	1103					
	4		454	508	562	616	670	724	778	832	886	940	994	1048	1102	1156					
	5				615	669	723	777	831	885	939	993	1047	1101	1155	1209					
	6						776	830	884	938	992	1046	1100	1154	1208						
	7						829	883	937	991	1045	1099	1153	1207							
	8						882	936	990	1044	1098	1152									
	9								1043	1097	1151										
$HOOC-CH_2(CH_2-CH=CH-CH_2)_y CH_2-COOH$		117	171	225	279	333	387	441	495	549	603	657	711	765	819						

[a] The molecular ions of the compounds with the first structure appear in the negative f.a.b. mass spectra as M^-. The ozonide unit is in an unknown position in the molecule. The molecular ions of the compounds with the second structure appear as $(M-1)^-$ only in the negative f.a.b. mass spectra of ozonolysed PBt

Table 2 Compounds present in ozonolysed samples of polybutadiene or Bt/AN copolymers I–III detected in the positive f.a.b. mass spectra

Structure[a]		Molecular ions (m/z) for															
		$y=0$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	$x=0$	207	261	315	369	423	477	531	585	639	693	747	801	855	909	963	1017
	1		314	368	422	476	530	584	638	692	746	800	854	908	962		
	2			421	475	529	583	637	691	745	799	853	907	961	1015	1069	
	3			474	528	582	636	690	744	798	852	906	960	1014	1068	1122	1176
	4				581	635	689	743	797	851	905	959	1013	1067	1121	1175	1229
	5					688	742	796	850	904	958	1012	1066	1120	1174	1228	
	6						795	849	903	957	1011	1065	1119	1173	1227	1281	
	7								956	1010	1064	1118	1172	1226	1280		
	8									1063	1117	1171	1225				

[a] The molecular ions of these compounds appear in the positive f.a.b. mass spectra as $(M+1)^+$. The ozonide unit is in an unknown position in the molecule

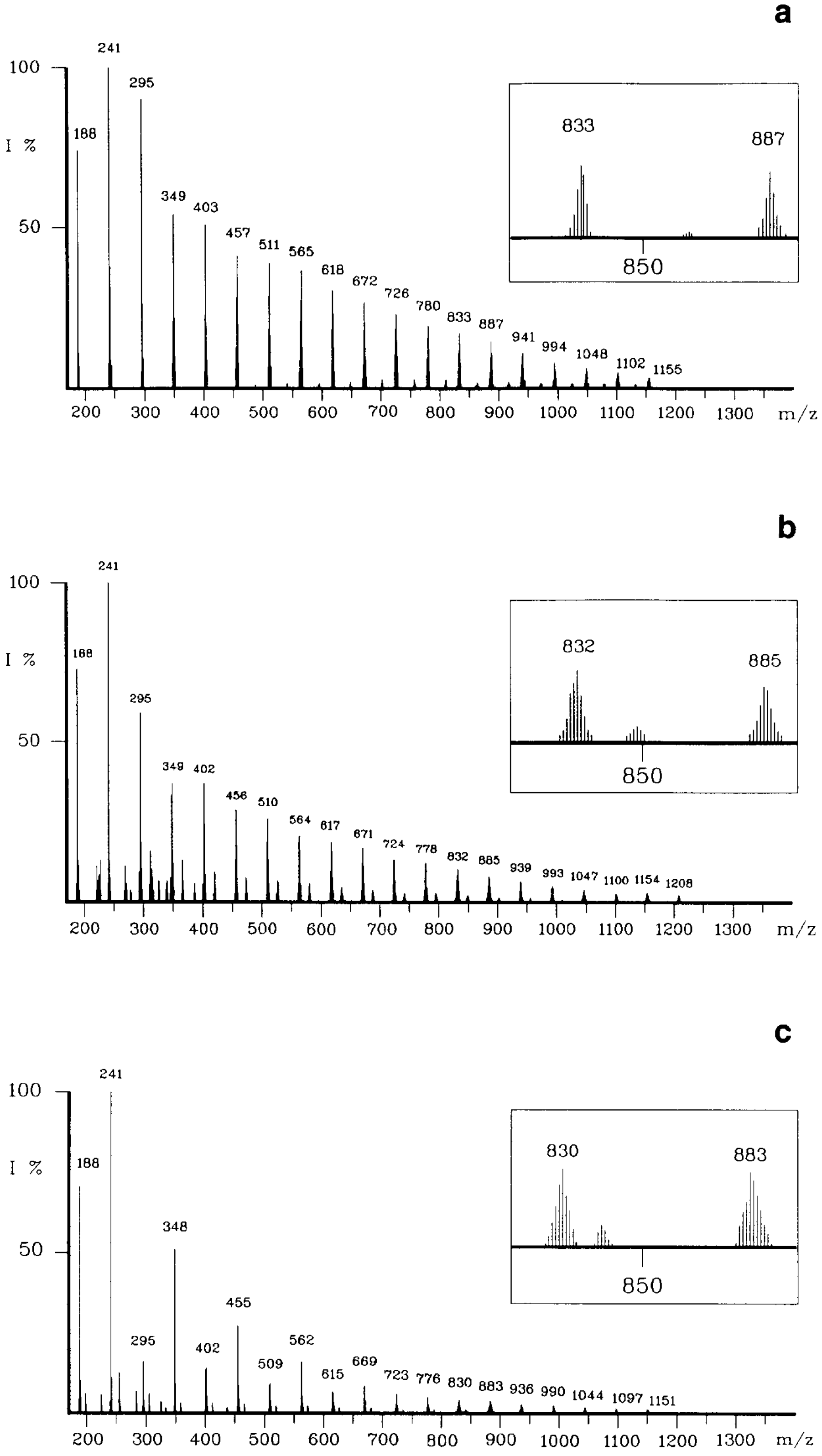


Figure 2 Negative f.a.b. mass spectra of 5 min ozonolysed butadiene/acrylonitrile random copolymer samples: (a) copolymer I (78% Bt); (b) copolymer II (67% Bt); (c) copolymer III (55% Bt). DEA/TMU mixture was used as matrix

same total number $(x+y)$ of subunits (from $Bt_{(x+y)}AN_0$ to $Bt_0AN_{(x+y)}$), calculated according to a theoretical combination of AN and Bt units, have been compared with those of the peaks detected in negative or positive f.a.b. mass spectra of 5 min ozonolysed copolymers I–III (the peak intensities have been corrected for isotopic contribution).

Good agreement has been obtained between the two sets of data. In *Table 3* the abundances expected and found for the peaks corresponding to the tetradecamers $(x+y=14)$ (peaks coincident with the windows in *Figures 2a*, *2b* and *2c*, negative case, and *Figures 3a*, *3b* and *3c*, positive case) are compared as a representative example. It can be observed that each experimental distribution

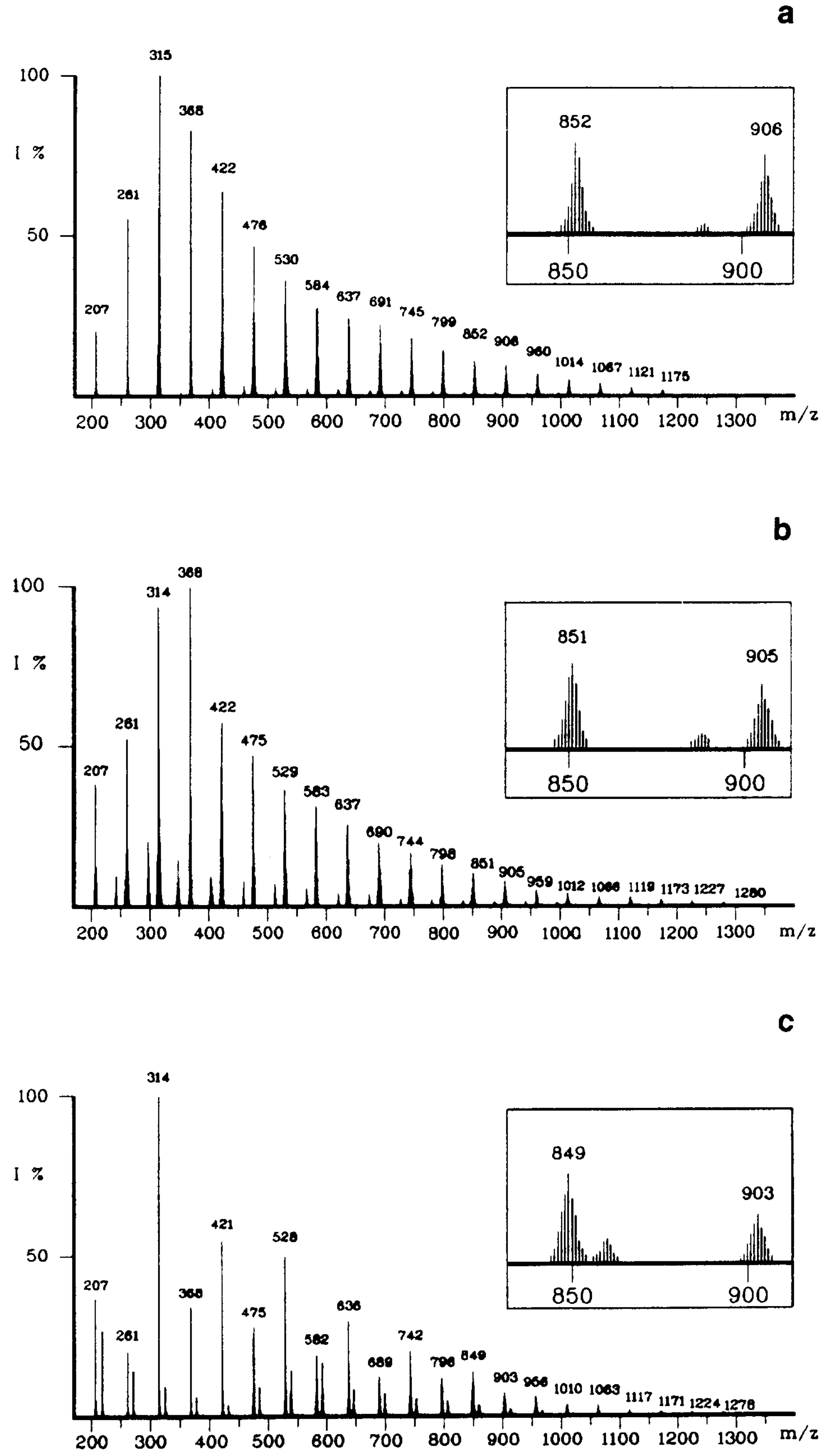


Figure 3 Positive f.a.b. mass spectra of 5 min ozonolysed butadiene/acrylonitrile random copolymer samples: (a) copolymer I (78% Bt); (b) copolymer II (67% Bt); (c) copolymer III (55% Bt). DEA/TMU mixture was used as matrix

of the intensities, in *Table 3*, couples only with one set of theoretical data.

Remarkably, we have found that the original copolymer composition can be rapidly determined from a graphical plot (*Figure 4*) in which the numbers of AN and Bt units (x and y in AN_xBt_y, formula IV) present in the molecular ion corresponding to the higher peak detected in each cluster of the ozonolysed (5 min) copolymers I–III f.a.b. mass spectra are reported.

In *Figure 4*, the points on the abscissa represent

Table 3 Calculated[a] and found[b] distributions of butadiene (Bt) and acrylonitrile (AN) subunits in tetradecamers[c] obtained from ozonolysed copolymers I–III f.a.b. mass spectrometric analysis

	Negative f.a.b.						Positive f.a.b.					
	I, 78% Bt		II, 67% Bt		III, 55% Bt		I, 78% Bt		II, 67% Bt		III, 55% Bt	
Ozonolysed[c] products	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Bt_4AN_{10}					15	14					15	11
Bt_5AN_9			6	3	36	22			6	4	36	26
Bt_6AN_8			18	7	67	54			18	14	67	51
Bt_7AN_7	6	5	41	26	93	84	6	5	41	30	93	73
Bt_8AN_6	19	14	73	65	100	100	19	13	73	55	100	100
Bt_9AN_5	44	33	99	83	81	72	44	27	99	81	81	68
$Bt_{10}AN_4$	77	67	100	100	50	47	77	56	100	100	50	48
$Bt_{11}AN_3$	100	100	74	64	22	16	100	100	74	75	22	14
$Bt_{12}AN_2$	88	80	37	28	7	7	88	66	37	38	7	7
$Bt_{13}AN$	48	39	12	8			48	32	12	13		
Bt_{14}	12	5					12	13				

[a] The theoretical abundances of tetradecamers Bt_yAN_x are calculated using the following relation:

$$P(Bt_yAN_x)=\binom{x+y}{y}(Bt_n)^y(AN_m)^x$$

in which Bt_n and AN_m are the molar fractions of the monomers in the copolymers. The obtained values are referred to the most abundant one (assumed as 100%)

[b] The reported values are corrected for the isotropic contribution and referred to the most intense peak in each cluster (assumed as 100%)

[c] The products are indicated according to formula IV in which the part of the molecule including the ozonide unit and the two end-groups has been assumed to correspond to Bt_2

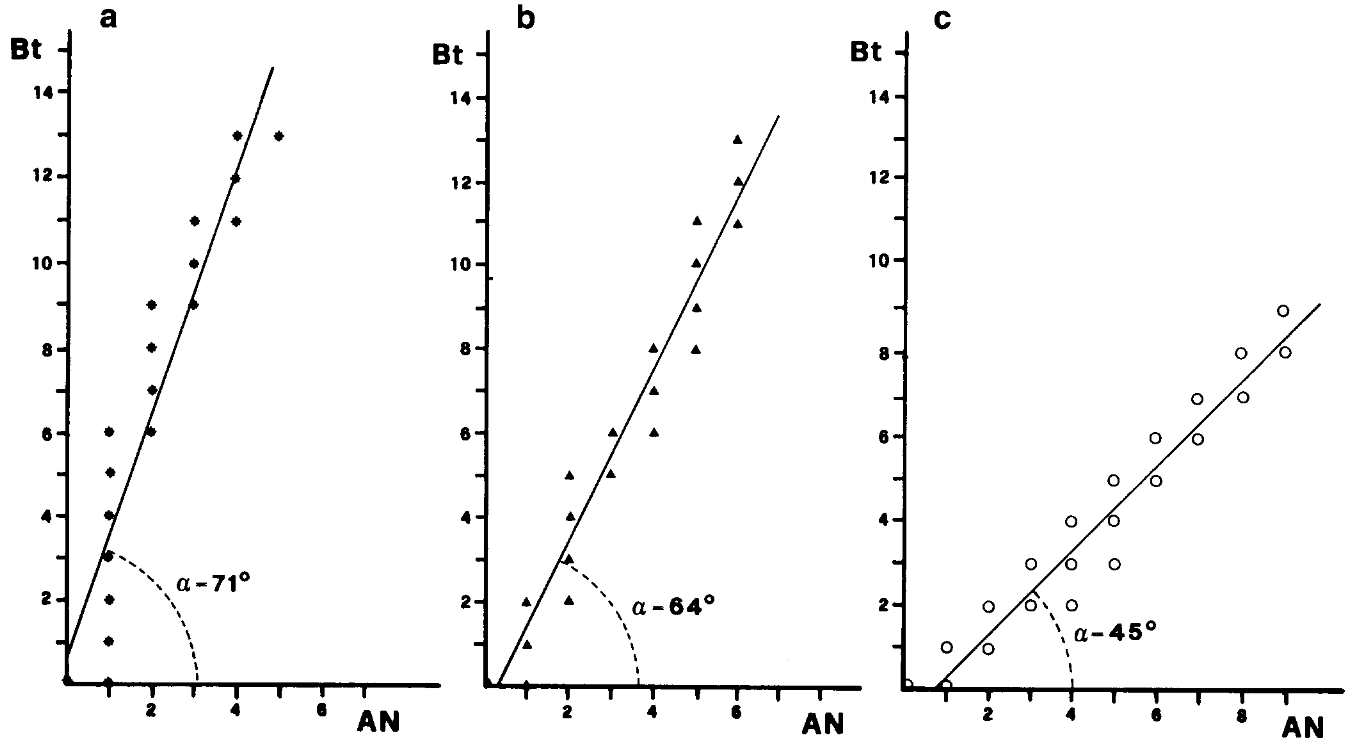


Figure 4 Plot of number of AN and Bt units (according to x and y in formula IV) present in the molecular ion corresponding to the most intense peak in each cluster of the ozonolysed (5 min) negative f.a.b. mass spectra of: (a) copolymer I (see *Figure 2a*); (b) copolymer II (see *Figure 2b*); (c) copolymer III (see *Figure 2c*)

compounds having only acrylonitrile units ($y=0$, formula IV) and those on the ordinate products containing only butadiene units ($x=0$, formula IV). Ozonolysis products containing both AN and Bt units are indicated with * (*Figure 4a*), ▲ (*Figure 4b*) or ○ (*Figure 4c*) for copolymers I–III, respectively. So, for example, the point at $x=5$ and $y=10$ in *Figure 4b* corresponds to the product having structure AN_xBt_y (formula IV) detected in the negative f.a.b. mass spectrum of the ozonolysed copolymer II (*Figure 2b*) at $m/z=188+5\times53+10\times54=993$.

The angle value ($\alpha=71°$ (copolymer I), $\alpha=64°$ (copolymer II) and $\alpha=45°$ (copolymer III) in *Figure 4*) of each best straight line obtained from each set of experimental points is related to the butadiene content (Bt%) present in the copolymer, considering the

Table 4 Butadiene content (Bt% values) in copolymers I–III determined by negative and positive f.a.b. mass spectra of ozonolysed (5 min) fragments[a] compared with those obtained by n.m.r.[b]

	Bt% in the sample		
Sample	(−) f.a.b.	(+) f.a.b.	n.m.r.
Copolymer I	79	78	78
Copolymer II	71	67	67
Copolymer III	50	52	55

[a] Values obtained from the angles reported in *Figure 4* (for the negative mass spectrometric data), considering the angle of 90° to correspond to 100% Bt. The same procedure was used to determine the Bt% content by positive f.a.b. mass spectrometric data

[b] Values obtained by ^{1}H n.m.r. spectra recorded in $CDCl_3$ solution

angle of 90° to correspond to a Bt content of 100% ($Bt\% = 100\alpha/90$). The compositions of copolymers I–III have also been estimated starting from the positive f.a.b. mass spectrometric data.

In *Table 4*, the Bt% content of the three copolymers investigated, determined by negative and positive f.a.b. mass data, are compared with those calculated by ^{1}H n.m.r. measurements. Good agreement can be observed among the three sets of data.

This procedure may therefore be used to estimate the unknown composition of a Bt/AN copolymer, and it establishes an interesting alternative to n.m.r. analysis because the f.a.b. mass spectrum of an ozonolysed sample also gives information about the copolymer microstructure.

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