Sequence distribution of styrene–butadiene copolymers by ozonolysis, high-performance liquid chromatographic and gas chromatographic–mass spectrometric techniques

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Abstract

The sequence distribution of styrene units in various styrene–butadiene copolymers (SBR) was investigated by liquid chromatographic (LC) and gas chromatographic–mass spectrometric (GC–MS) measurements on their ozonolysis products. Ozonolysis was performed in methylene chloride followed by reductive degradation with lithium aluminium hydride. LC was found to be a very effective technique for the characterization and quantitative evaluation of the sequence distribution of random and tapered block copolymers because of its high detection efficiency of short and long sequences. LiChrospher C_{18} reversed-phase columns, a ternary gradient system and an evaporative light-scattering detector were used. Peaks corresponding to various low-molecular-mass species were identified by GC–MS and assigned to $1,4Bde-(Sty)_m-1,4Bde$ or $1,4Bde-(Sty)_m-(1,2Bde)_n-1,4Bde$ sequences of the original copolymers (Bde = butadiene, Sty = styrene).

1. Introduction

The sequence distribution of styrene units has been recognized as a dominant factor governing the mechanical and viscoelastic properties of styrene–isoprene and styrene–butadiene elastomers. There have been several reports concerning the structural investigation of random and tapered forms of these copolymers. Ozone degradation has been used to provide quantitative information about the distribution of styrene units in these copolymers [1–4]; a combination was proposed of ozonolysis and high-resolution gel-permeation chromatographic (GPC) measurements, followed by NMR analysis for molecular characterization of the collected fractions.

Montaudo and co-workers [5–9] demonstrated that mass spectrometry (MS) is a powerful and rapid method suitable for the detection of a series of oligomers formed in the partial ozonolysis. Their results yielded detailed information on the distribution of monomers for several condensation and addition copolymers.

In this paper, we propose a method for the quantitative evaluation of the distribution of styrene units in various styrene–butadiene rubbers by HPLC of the ozonolysis products. HPLC has been shown to be a very effective technique suitable for the detection of a series of oligomers because of its high detection efficiency for either short [3] or long sequences. GC–MS chemical ionization (CI) and desorption chemical ionization (DCI) were successfully used to identify the separated products.

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2. Experimental

2.1. Materials and ozonolysis

The chemical used were commercial and experimental products and were appropriately purified before use. The compositions of the samples are given in Table 1. All samples were ozonolysed following a procedure described by Tanaka and co-workers [1–4].

2.2. HPLC

The separation of the ozonolysis products was performed by HPLC using a Gilson (Biolabo, Milan, Italy) liquid chromatograph with a double-pumping system (Models 305 and 306). The LC measurements were conducted by using a LiChrospher C_{18} 5 μm analytical column (Bracco, Milan, Italy). The solvent flow-rate was 1 ml/min. Samples were injected via a 10-μl loop injector. Rainin Dynamax UV1 UV (Biolabo) and CONOW DDL21 light-scattering (Eurosep, Cergy, France) detectors were used. A linear mobile phase gradient from methanol–water to tetrahydrofuran (HPLC grade; Carlo Erba, Milan, Italy) was used. Preparative separations were performed with a high-resolution column (Rainin Microsorb C_{18} 5 μm; Biolabo). The solvent flow-rate was 10 ml/min. A total of 500 μl of the THF sample solution was injected. The LC effluent peaks were trapped in glass vials, dried and analysed by MS.

2.3. GC–MS

GC–MS analyses were performed with a Hewlett-Packard Model 5890 gas chromatograph combined with a Hewlett-Packard Model 5971A quadrupole mass spectrometer equipped with a CI ion source.

GC separations were accomplished on an HP1 silica capillary column (Hewlett-Packard). The transfer line was held at 280°C. The oven temperature programme was initial temperature 60°C, increased at 20°C/min to 320°C. Helium was used as the carrier gas. The mass spectrometer was scanned from m/z 10 to 650. Isobutane was used as the CI reagent gas.

2.4. DCI

Experiments were performed using a Finnigan TSQ 700 triple-stage quadrupole mass spectrometer. The ion source was kept at 60°C. A rhenium wire (standard from Finnigan) was used. The wire heating current was programmed from 0 to 1 A at 40–80 mA/s (about 40–80°C/s, up to about 1000°C). The CI reagent gas mainly used was isobutane at a pressure of 0.5 mbar. The resolution was unitary.

3. Results and discussion

It is known that the double bonds of 1,4- and 1,2-units in styrene–butadiene copolymers (SBR) were completely decomposed under the ozonolysis conditions used here [1–4]. The resulting products are represented by the following general formula:
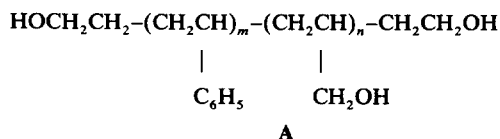
$$HOCH_2CH_2-(CH_2CH)_m-(CH_2CH)_n-CH_2CH_2OH$$
$$\begin{array}{cc} | & | \\ C_6H_5 & CH_2OH \end{array}$$

A

Table 1
Compositions of SBR samples

Sample	Styrene (mol %)	1,2-Butadiene (mol %)	1,4-Butadiene (mol %)
(a) Experimental SBR	17.4	16.5	66.1
(b) SBR 1721	17.3	8.5	74.2
(c) Solprene 1205	11.4	9.1	79.5

The sequence distribution of styrene units can be determined by HPLC measurements of A.

3.1. Random SBR by anionic polymerization

A model SBR prepared with potassium *tert.*-amylate (KTA) as a modifier was analysed by the ozonolysis–HPLC method, as shown in Fig. 1.

By MS measurements of the collected fractions, the peaks were assigned to the products derived from the $1,4Bde-(Sty)_m-1,4Bde$ ($n = 0$ and $m = 1,2,3$, etc., in formula A) and $1,4Bde-(1,2Bde)_n-(Sty)_m-1,4Bde$ ($n = 1$ and $m = 1,2,3$, etc., in formula A) sequences respectively (Sty = styrene; Bde = butadiene), which are represented by Sm and SmV (Table 2). As shown in Fig. 1, LC analysis was able to separate the two sequences and the relative diastereomers for lower oligomers, as confirmed by NMR analysis [3].

This kind of efficiency was decreased in the long sequences ($n > 4$), where the two families were co-eluted. Good resolution was found for styrene sequences of up to 21 monomeric units.

In order to carry out a quantitative analysis of the styrene sequence distribution, both the UV and evaporative light-scattering detection (ELSD) traces were analysed. A UV detection system has been used previously in GPC, where the molar absorptivity per styrene unit at 254 nm

Fig. 2. Sequence distribution of styrene units in sample (a) (Table 1) with UV and ELS detection.

was independent of the sequence length [2]. During ternary gradient elution in HPLC, a considerable drift of the baseline was observed owing to the continuous change in solvent composition; this could be a problem for the accurate quantitative evaluation of the separated oligomers. The choice of ELSD, with a response virtually independent of the gradient, was useful in order to test the UV detection efficiency when the gradient was applied. Further, ELSD was used to control the extent of the ozonolysis reaction in order to exclude the presence of possible dienic sequences not or partially
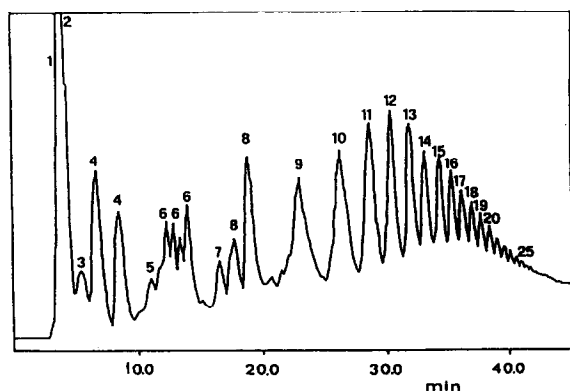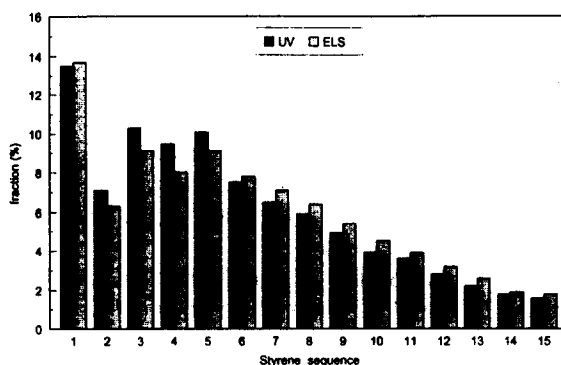

Fig. 1. HPLC separation of the ozonolysis products from sample (a) (Table 1). Structural identification of the collected fractions is reported in Table 2.
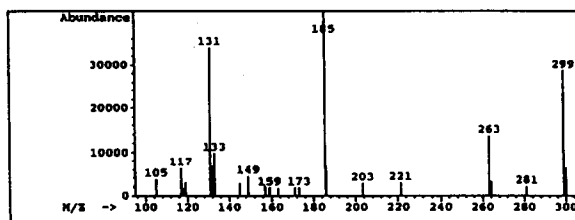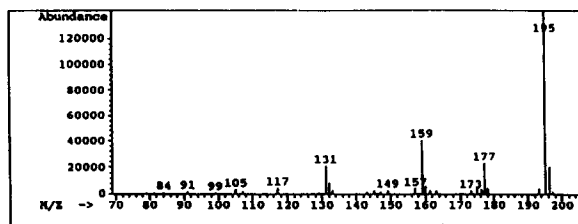

Fig. 3. GC–MS (CI) mass spectra of fractions S1 and S2.

ozonolysed. Fig. 2 shows the good agreement between the sequence distribution of styrene units obtained from the UV and ELSD traces.

In Fig. 3 the GC–MS spectra of the early separated HPLC peaks are reported. The molecular ion $[MH]^+$ and fragment ion $[MH - 18]^+$ are observed, indicating that these are OH-terminated oligomers.

DCI mass spectra of the higher LC cuts are shown in Fig. 4. Only molecular ion regions are displayed, but fragment ions were essentially absent, even for the higher molecular mass oligomers.

3.2. Random SBR by emulsion polymerization

The LC trace of SBR 1721 is shown in Fig. 5. Here only the peaks denoted S1, S1V, S2, S2V, S3 were present. The sequence distribution was determined from the integrated intensity of the UV peaks. In Fig. 6 is reported the sequence distribution of styrene units and the theoretical
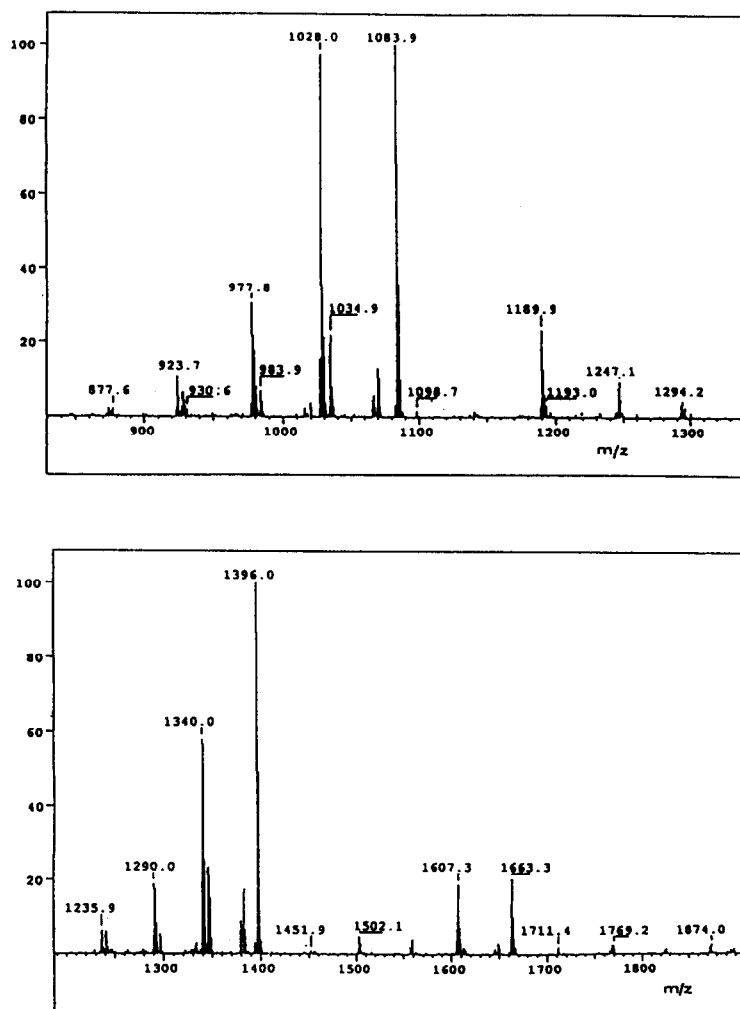

Fig. 4. Positive-ion DCI mass spectra of fractions S9 and S12.

Table 2
Identification of the ozonolysis products from sample (a) (Table 1) by HPLC and MS analysis

HPLC peak No.	Nominal mass[a]	$HOCH_2CH_2(Sty)_m–(1,2Bde)_n–CH_2CH_2OH$		
		m	n	Designation
1	252	1	1	S1V
2	194	1		S1
3	352	2	1	S2V
4	298	2		S2
4	298	2		S2
5	460	3	1	S3V
6	402	3		S3
6	402	3		S3
6	402	3		S3
7	564	4	1	S4V
8	506	4		S4
8	506	4		S4
9	610	5		S5
10	714	6		S6
11	818	7		S7
12	922	8		S8
13	1026	9		S9
14	1130	10		S10
15	1234	11		S11
16	1338	12		S12
17	1442	13		S13
18	1546	14		S14
19	1650	15		S15
20	1754	16		S16
21	1858	17		S17
22	1962	18		S18
23	2066	19		S19
24	2170	20		S20
25	2274	21		S21

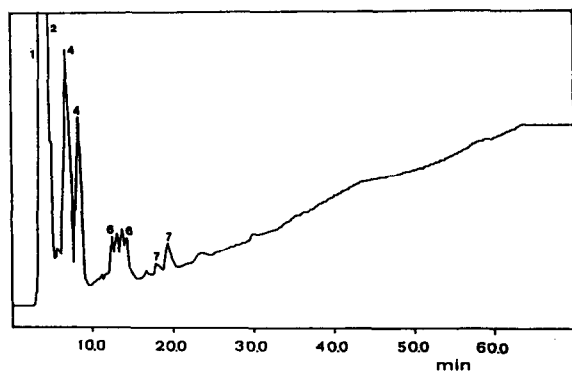[a] Nominal mass spectrometric molecular weight ($C = 12$; $H = 1$; $O = 16$).

Fig. 5. HPLC separation of the ozonolysis products from sample (b) (Table 1). For peak numbers, see Table 2.
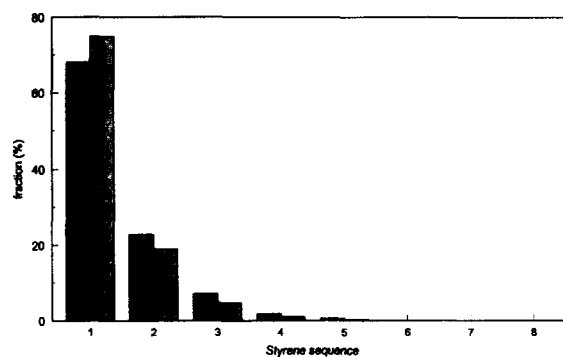

Fig. 6. Sequence distribution of styrene units in sample (b) (Table 1): experimental and theoretical. Solid bars = UV detection; dotted bars = statistical.
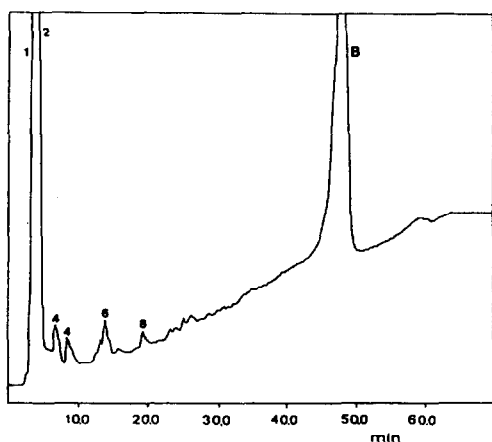
Fig. 7. HPLC separation of the ozonolysis products from sample (c) (Table 1). For peak numbers, see Table 2; B = long styrene sequences.

distribution that follows an exponential function, assuming a statistical copolymerization.

3.3. Partially blocked SBR by anionic polymerization

Fig. 7 shows the ozonolysis–HPLC trace of sample (c) (tapered copolymer), Solprene 1205. The peaks were assigned by using the relationship shown in Table 2. The broad peak observed at 40–45 min in Fig. 7 was assigned to the long styrene sequences; the average sequence length was estimated by GPC to be 90–100. The relative intensity of the block sequence peak was found to be 20% according to the GPC measurements [2]. Fig. 8 reports the sequence distribution of styrene units obtained from the relative intensity of the LC peaks.
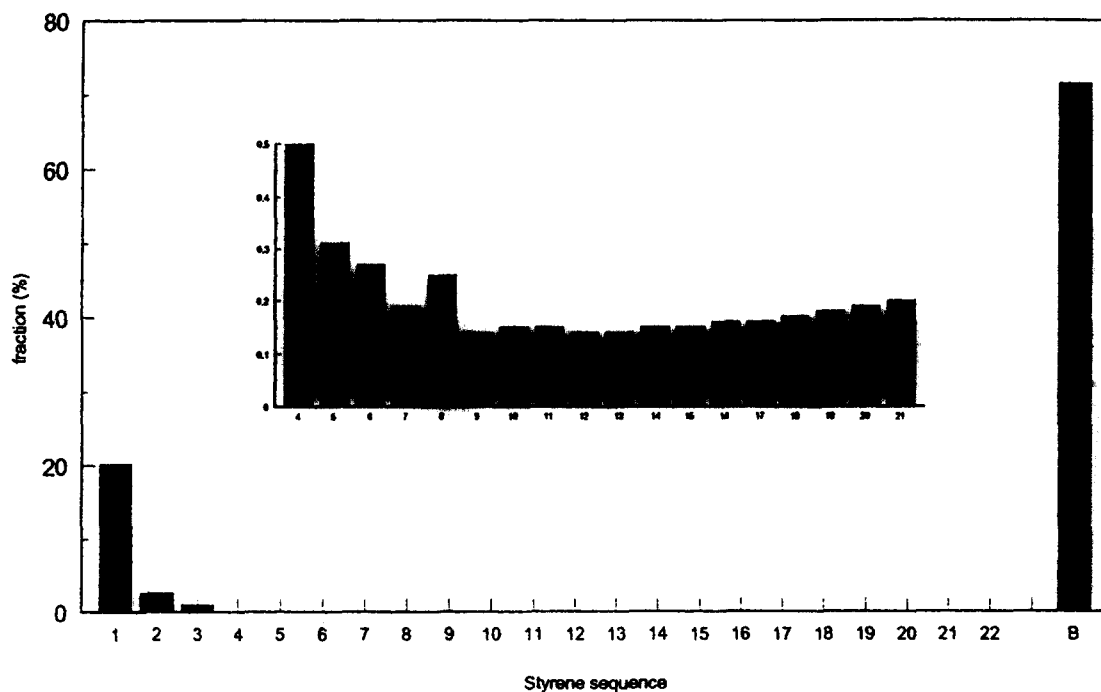

Fig. 8. Sequence distribution of styrene units in sample (c) (Table 1).

4. References

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