



PYROLYSIS MASS SPECTROMETRIC ANALYSIS OF STYRENE–BUTADIENE BLOCK AND RANDOM COPOLYMERS

JALE HACALOGLU,*¹ TANER ERSEN,¹ NERGIS ERTUGRUL,¹
MUHAMMED M. FARES¹ and SEFIK SUZER²

¹Middle East Technical University, Chemistry Department, 06531 Ankara, Turkey

²Bilkent University, Chemistry Department, 06533 Ankara, Turkey

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Abstract—Direct pyrolysis mass spectrometric analysis of a styrene–butadiene–styrene block copolymer indicated that thermal decomposition of each block shows a resemblance to the related homopolymer, giving a possibility of differentiation of blocks. However, the random analog, the styrene butadiene rubber, degraded in a manner that is somewhat in between in nature of the thermal characteristics of both homopolymers. This technique shows promise to differentiate thermal behaviors of each sequence in block polymers if any exist. Indirect pyrolysis mass spectrometric analysis gave no clear evidence for differentiation of the nature and the composition of the copolymers. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Thermal decomposition of polystyrene and polybutadiene have received considerable attention [1–15]. It is established that in vacuum and oxygen free atmosphere thermal degradation of polystyrene (PS) at elevated temperatures (below 300°C) is initiated by random scissions of the main chain without evolution of the low molecular weight volatile products to give primary and secondary macroradicals which depolymerize by unzipping reactions and mainly produce the monomer [1–7]. Furthermore, the effect of polymerization technique, initiator used, and irregularities on thermal behavior are also well established [8, 9]. Considerable work on thermal decomposition of polybutadiene (PB) has also appeared in the literature [10–15]. It is proposed that thermal degradation of PB occurs readily at the sites b to the double bonds, as the presence of a double bond introduces a weakness in bonds which are b position to it. The free radicals produced unzip to yield the monomer. Bond scissions may also be accompanied by H-transfers resulting in the formation of saturated and unsaturated ends. Thermal degradation of BP samples having different initial contents of *cis*-1,4, *trans*-1,4 and 1,2 units were also investigated. However, only limited information is available on thermal behavior of butadiene–styrene copolymers [4, 16].

Recently, we applied direct and indirect pyrolysis mass spectrometric techniques in thermal analysis of styrene–isoprene–styrene copolymer [17]. Now, we report the results of direct and indirect pyrolysis mass spectrometric analysis of styrene–butadiene–styrene

(SBS) (block copolymer) and styrene–butadiene rubber (random copolymer).

EXPERIMENTAL

Direct and indirect pyrolysis mass spectrometric systems were described previously [7, 17, 18]. Direct pyrolysis MS equipment consists of a direct insertion probe, a stainless steel tube Ag-soldered to a copper sample holder assembly, its control unit, a Balzers QMG 311 quadrupole mass spectrometer and a personal computer for control of the instrument, data acquisition and processing. In the case of indirect pyrolysis (evolved gas analysis) by MS the same system with a pyrolysis chamber instead of the probe is used. The pyrolysis chamber is made from a Pyrex reactor and an oven is used for heating.

Styrene–butadiene–styrene, SBS (Kraton D 1101, styrene:butadiene ratio 31:69), and styrene–butadiene rubber, SBR (SBR-1502, styrene:butadiene ratio 25:75), were obtained from Shell Co. (Istanbul), *cis*-polybutadiene, PB, was obtained from PETKIM (Turkish Petrochemical Industries) and polystyrene, PS, was supplied by Aldrich. For direct pyrolysis experiments samples cast in the form of thin films from 20 mL 0.1% m/v polymer–benzene solutions on to copper sample holders were subjected to thermal degradation under high vacuum (10^{-7} mbar) by increasing the temperature rapidly to 100°C and then by heating at a rate of 5°C/min. For indirect pyrolysis experiments, 1.0 mg fine powder samples were heated at a rate of typically 10°C/min. Duplicate experiments indicated that pyrolysis products and temperature ranges of decomposition were reproducible.

RESULTS AND DISCUSSION

Direct pyrolysis

Thermal decomposition of styrene–butadiene–styrene copolymer, SBS, and styrene–butadiene rubber, SBR, were studied by recording mass spectra as a function of temperature. The temperature values

*To whom all correspondence should be addressed.

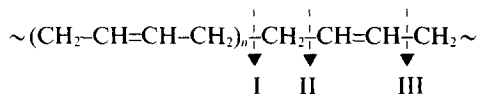
corresponding to maximum thermal degradation yields from both samples were quite similar at 213°C and 217°C for SBS and SBR, respectively. Furthermore, similar peaks were detected in the pyrolysis mass spectra of both polymers. The more intense and/or characteristic peaks observed in the spectra are collected in Table 1 with assigned chemical formulae. The summary of pyrolysis mass spectra of related homopolymers, polystyrene (PS) and polybutadiene (PB) at temperatures corresponding to their maximum decomposition yields (230°C for PS and 225°C for PB) are also included for comparison.

Note that mass spectra of the copolymers can be classified into two main groups:

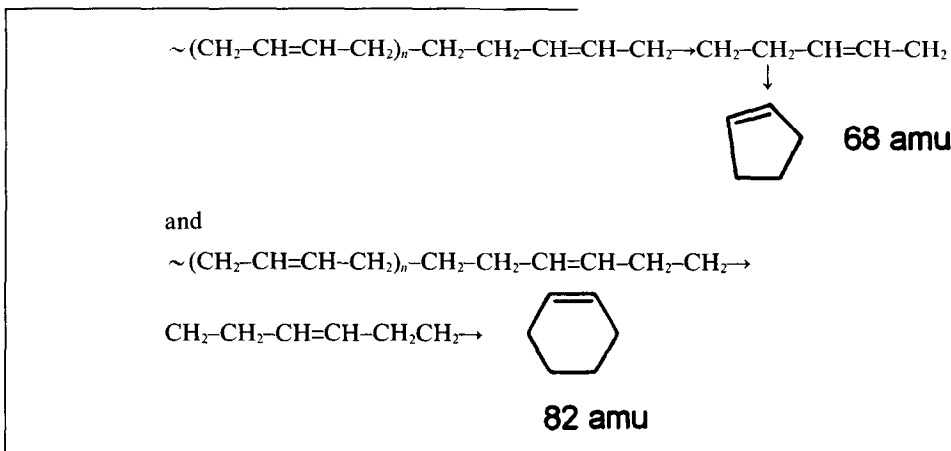
(a) Ions mainly due to butadiene block such as $C_4H_6^+$ at 54 amu (butadiene monomer), $C_5H_7^+$ at 67 amu, $C_6H_8^+$ at 81 amu, $C_8H_{12}^+$ at 108 amu (butadiene dimer), $C_{12}H_{18}^+$ at 162 amu (butadiene trimer), $C_{16}H_{24}^+$ at 216 amu (butadiene tetramer) and $C_{20}H_{30}^+$ at 270 amu (butadiene pentamer).

(b) Ions mainly due to styrene block such as $C_5H_5^+$ at 65 amu, $C_6H_5^+$ at 77 amu, $C_7H_7^+$ at 91 amu, $C_8H_8^+$ at 104 amu (styrene monomer) and $C_{16}H_{16}^+$ at 208 amu (styrene dimer). These ions were also detected, in very small yields, during the pyrolysis of PB. However, they are not regarded as diagnostic for PB.

(Table 1), it can be concluded that degradation proceeded by random bond scissions at points I, II and III.



Groups of ions produced due to cleavages at position I were in general more abundant. It is known that cleavage occurs more readily at the sites β to the double bonds, as the presence of double bonds weakens the adjacent C-C bonds. In spite of this general trend the 67 amu peak was the base peak from SBS and PB and the peak at 81 amu was among the most abundant. It may be assumed that cyclopentene and cyclohexene were produced during thermal decomposition due to cleavages at α positions followed by cyclization reactions. The ions at 67 and 81 amu may be generated from these molecules during electron impact ionization in the ion source of the mass spectrometer by H losses. Thus it may be concluded that degradation of butadiene block proceeds mainly through α and β chain scissions, yielding fragments that can be stabilized by cyclization reactions:



The relative intensities of peaks observed from SBS were noticeably similar to those observed from PB. However, there existed considerable differences in the relative intensities of peaks observed from SBS and SBR. The base peak was at 67 amu ($C_6H_7^+$) in the pyrolysis mass spectra of SBS and at 91 amu ($C_7H_7^+$) in the case of SBR. Furthermore, the relative intensities of all the peaks, arising mainly from butadiene sequence, were more pronounced when they were produced during the thermal decomposition of SBS. This trend may be directly related to styrene/butadiene ratios in these samples being 25/75 in SBR and 31/59 in SBS. Yet in both spectra, the relative intensity of the peak at 108 amu due to 4-vinylcyclohexene, the butadiene dimer, was quite similar. This indicates that the decomposition paths in the block and random samples are certainly different.

Considering the products related to butadiene sequences in all three polymers, SBS, SBR and PB

The relative intensities of styrene sequence related peaks from the copolymers were somewhat different from the PS homopolymer. The peak at 104 amu due to the styrene monomer was the most intense from polystyrene, indicating that degradation was initiated by random scissions of the main chain to yield primary and secondary macroradicals which depolymerize to the monomer in accordance with the literature findings [1-7]. Yet, in the case of the copolymer, the peak at 91 amu, most probably due to tropylium ion, was more abundant. Nevertheless, one should take into account the production of the same peak from the butadiene units (see the pyrolysis mass data of PB in Table 1). Thus, a similar degradation mechanism for the styrene blocks in the copolymer can be assigned as in the case of the homopolymer.

Another point that should be pointed out is that the present results indicated a lower stability for PB compared to PS. This behavior was contrary to previous relative stability results. The T_h value (the

Table 1. Relative intensities and assigned chemical formulae of some characteristic and/or intense peaks observed during the direct pyrolysis of SBS at 213 and 231 °C, SBR at 219 °C, PB at 225 °C and PS at 230 °C

m/z	SBS T (°C)	SBS 231	SBR 219	PB 225	PS 230	Assignment
54	450	119	257	556	7	Butadiene monomer ion
67	1000	374	583	1000	31	C ₅ H ₇ ⁺
77	300	463	396	298	369	C ₆ H ₅ ⁺
81	808	415	585	700	5	C ₆ H ₆ ⁺
82	337	203	289	366	3	C ₆ H ₅ ⁺
91	583	1000	1000	530	967	C ₇ H ₇ ⁺ tropylium ion
95	343	263	341	398	5	C ₇ H ₁₁ ⁺
96	194	157	155	182	3	C ₇ H ₁₂ ⁺
104	196	753	507	135	1000	Styrene monomer ion
108	236	125	223	282	1	Butadiene dimer ion
121	221	117	234	285	1	C ₈ H ₁₃ ⁺
136	122	98	110	147	—	C ₁₀ H ₁₆ ⁺
162	103	122	84	121	—	Butadiene trimer ion
208	99	65	60	20	25	Styrene dimer ion
216	12	8	24	37	—	Butadiene tetramer ion
270	4	3	10	14	—	Butadiene pentamer ion

temperature corresponding to 50% loss of weight of the polymer) of polybutadiene is considerably higher than that of polystyrene [19] (407°C for PB and 364°C for PS). Thermogravimetric (TG) and differential thermogravimetric (DTG) studies [12] showed that decomposition of polybutadiene under nitrogen atmosphere occurs in two stages. Decomposition temperatures fall in the range 370–385°C for the first stage and between 460–475°C for the second one. Differential scanning calorimetric (DSC) results indicated that the first decomposition was an exothermic process, probably due to extensive cyclization reactions. The weight loss in the first degradation step was less than 15%. However, in our dynamic high vacuum conditions weight loss should be more pronounced, even at low temperatures.

In order to get a better insight, the ion-temperature plots, variation of intensities as a function of temperature, were studied. In Figs 1 and 2 the ion-temperature plots of peaks at 67 amu C₅H₇⁺, 77 amu C₆H₅⁺, 91 amu C₇H₇⁺, 104 amu C₈H₈⁺ and 108 amu C₈H₁₂⁺ observed from SBS and SBR are given. Notice that two maxima exist in the ion-temperature plots of SBS at 213°C and 231°C indicating a two stage decomposition, while only a single maximum at 217°C is present in ion-temperature plots in the case of SBR. It is clear that the peaks stemming mainly from the butadiene block gave a maximum at 213°C, whereas the peaks that were mainly related to the styrene block showed a maximum at 231°C. The normalized mass spectrum at 231°C is also included in Table 1. To our surprise

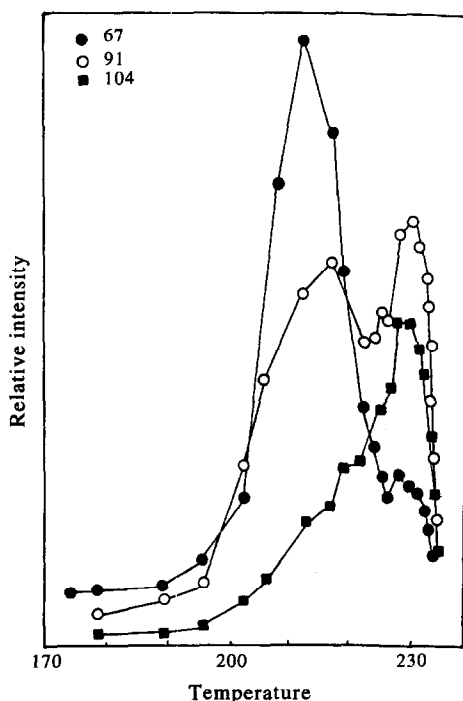


Fig. 1. Ion-temperature profiles of some characteristic fragments observed during the direct pyrolysis of SBS.

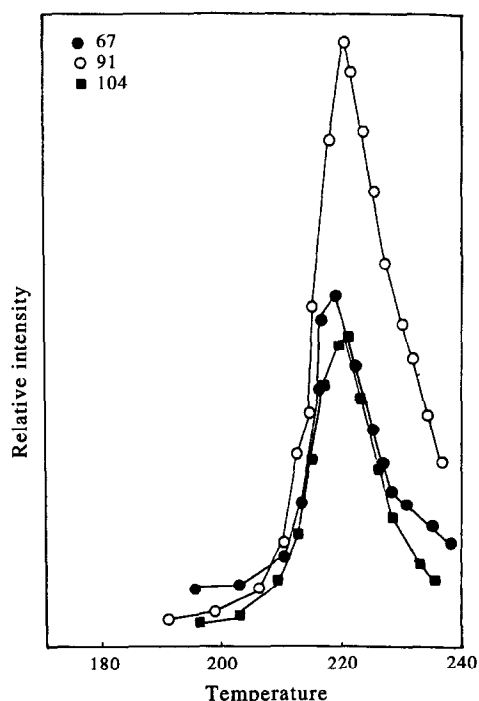


Fig. 2. Ion-temperature profiles of some characteristic fragments observed during the direct pyrolysis of SBR.

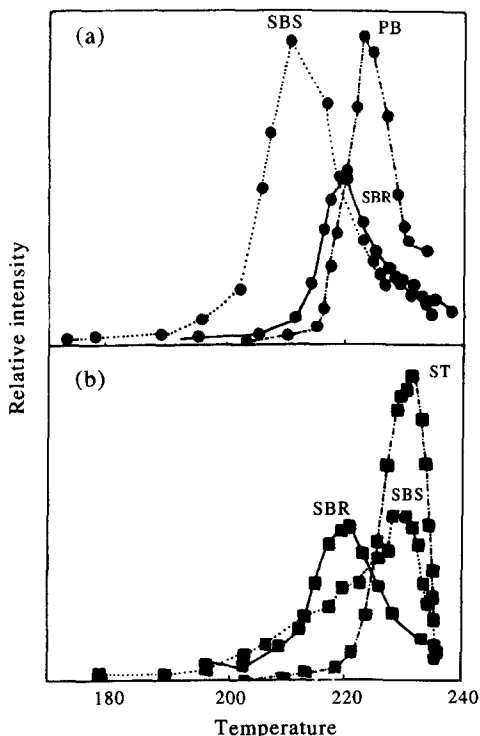


Fig. 3. Ion-temperature profiles of (a) $C_3H_7^+$ at 67 amu observed during the direct pyrolysis of SBS, SBR and PB, and (b) $C_6H_5^+$ at 104 amu (styrene) observed during the direct pyrolysis of SBS, SBR and PS.

this spectrum was much more identical to the pyrolysis mass spectrum of SBR at 217°C with the base peak at 91 amu ($C_3H_7^+$).

To make a better comparison between the copolymers under investigation and the related homopolymers, variations of intensities of peaks at 67 and 104 amu as a function of temperature during the thermal decomposition of SBS, SBR and PB and SBS, SBR and PS are plotted in Fig. 3 [(a) and (b), respectively]. As can be seen from Fig. 3, the peak started to appear in the pyrolysis mass spectra of SBS around 190°C. The temperatures at which degradation started in SBR and PB shifted to 210 and 215°C, respectively. Another point that can be noticed directly from the figure is that the decomposition temperature range gets narrower in the order SBS > SBR > PB [Fig. 3(a)]. The temperature at which maximum degradation yield was observed also shifted to higher values in the same order: 213, 219 and 225°C for SBS, SBR and PB, respectively. Note that the SBR decomposition range overlaps with that of SBS and the high temperature range of both of the copolymers overlaps with that of PB. The decomposition range yielding styrene is also narrower in polystyrene compared to those observed in the copolymers [Fig. 3(b)]. Furthermore, the temperature range in which styrene production was detected from SBS covers those of both SBR and PS. The maximum decomposition yield of 104 amu fragment produced from SBS at 231°C is very close to that observed from polystyrene (at 230°C). A shoulder around 219°C is also present in the ion-temperature profile of fragment 104 amu from

SBS. This temperature is the temperature at which maximum styrene production occurs from SBR.

These observations lead us to conclude that thermal stability and behavior of each block in the block copolymer resembles the corresponding homopolymer more than the random copolymer. Yet, each unit also influences every other to some extent in the block copolymer. In general, thermal stability is lower in these copolymers. However, this may also be directly related to the molecular weight of each repeating unit. It is known that an increase in molecular weight increases thermal stability. Therefore, it is not possible to make strict conclusions on the influence of each unit on the thermal stability of the other. Actually, the effect should be more pronounced in the random copolymer. Each block can be expected to behave independently in the block copolymer when the chain lengths are sufficiently long. The experimental observations are in accordance with this fact. The ion-temperature profiles of fragments from SBS showed two maxima, indicating that each unit in the copolymer decomposed independently, whereas the single maximum in the ion-temperature profiles of SBR pointed out that each unit affected every other considerably. Shoulders at high temperature ranges may be related to the presence of relatively long chain units along the random copolymer.

Indirect pyrolysis

Indirect pyrolysis analysis of both copolymers did not indicate any sign that can be used to differentiate block and random copolymers from each other. The peaks that may be related to styrene units, such as those at 51, 78, 91 and 104 amu, were more intense. This is an unexpected trend considering the compositions and the direct pyrolysis results of the copolymers. It is most likely that the products observed during the indirect pyrolysis mass spectrometric analysis are not the primary decomposition products but mainly secondary reaction products produced in the pyrolysis chamber. A similar behavior was observed in the pyrolysis mass spectrometric analysis of styrene-isoprene-styrene block copolymer [17].

CONCLUSION

The present work points out that direct pyrolysis MS technique can be used to differentiate block and random copolymers from each other. It is found that each block in a SBS copolymer behaved independently during thermal decomposition following the same degradation pathways of the related homopolymers. Similar products were also observed for the random copolymer, SBR. Yet, it was not possible to differentiate different blocks in this sample. Indirect pyrolysis analysis showed no clear evidence for determining the nature (random or block) and composition of the copolymers under investigation.

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