Pyrolysis mass spectrometric analysis of styrene–isoprene–styrene copolymer

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Abstract

Thermal analysis of styrene–isoprene–styrene block copolymer, using the direct pyrolysis mass spectrometry (MS) technique, indicated that each block showed very similar thermal behavior with the corresponding homopolymer. The isoprene block was found to be thermally less stable, decomposing by random scissions followed by cyclization reactions. The more stable styrene block degraded by a radical depolymerization mechanism. With an indirect pyrolysis MS technique, it was found that production of benzene, toluene, 1-methyl cyclopentene and 1-methyl cyclohexene was more effective when degradation was carried out in a closed reactor. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Pyrolysis mass spectrometry (MS) techniques can be regarded as one of the most powerful analytical methods for thermal analysis of polymers. Not only thermal stability, but also degradation products, can be analyzed with these techniques [1–10]. In general, the pyrolysis system used determines the limits of the method. A common disadvantage of the pyrolysis MS techniques is the analysis of the complicated data obtained. Recently, we applied direct and indirect pyrolysis MS methods simultaneously for a better understanding [5, 11].

In this communication, the thermal decomposition of styrene–isoprene–styrene (SIS), a block copolymer, is studied with the use of direct pyrolysis and indirect pyrolysis mass spectrometry techniques. Thermal behavior of the copolymer is also compared with those of the corresponding homopolymers. Although thermal stability and degradation of polystyrene have been extensively studied [4, 12–15] only a few works of literature exist on thermal behavior of styrene copolymers [16–19]. Our main aim is to investigate the limits of the two pyrolysis techniques in the thermal analysis of copolymers.

2. Experimental

Polymer samples were supplied by various producers. The styrene–isoprene–styrene copolymer, Kraton D 1107, (styrene/isoprene ratio 14/86) was obtained from Shell (Istanbul), polystyrene from Aldrich, Co. and polyisoprene from PETKIM (Turkish Petrochemical Industries).

The details of the pyrolysis MS systems used were given in our previous publications, see Refs [5, 11]. Direct pyrolysis MS equipment simply consists of a direct insertion pyrolysis probe and its control unit designed in our laboratories, a Balzers QMG 311 quadruple mass spectrometer and a personal computer

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for the control of the instrument and data acquisition and processing. The probe is a stainless steel tube Ag-soldered to a copper sample holder assembly. Temperature was increased to $100°C$ rapidly and then the heating rate was kept constant at $5°C/min$. Samples casted in the form of thin films, from 20 μL 0.1% (m/v) polymer–benzene solutions onto the flat-based copper sample holders, were subjected to thermal degradation under high vacuum (10^{-7} mbar).

In the case of indirect pyrolysis (evolved gas analysis by MS), the same system with a pyrolysis chamber instead of the pyrolysis probe was used. Samples (1.0 mg) of fine powder polymer were heated at a rate of typically $10°C/min$.

3. Results and discussions

3.1. Direct pyrolysis

Thermal decomposition products of poly(styrene–isoprene–styrene) copolymer, SIS, have been studied by recording mass spectra as a function of temperature. When the temperature was sufficiently high, the thermal cleavage generates volatile fragments which undergo electron impact fragmentation prior to analysis by the spectrometer. In order to identify the diagnostic peaks, the mass spectrum corresponding to maximum product yield was selected. In general, the peaks due to low mass fragments, below 50 amu, such as peaks related to $CH_3-C=CH^+$ and $CH_2=CH_2^+$ at 40 and 28 amu, respectively, were

more intense. However, it has to be remembered that the peaks observed in the mass spectra cannot be directly attributed to thermal degradation products of the sample as further fragmentation by electron impact ionization occurs in the ion formation room of the mass spectrometer. As high mass peaks are more diagnostic, only peaks above 50 amu will be discussed. The relative intensities of abundant and/or characteristic ions above 50 amu are collected in Table 1 with assigned chemical formulae.

Note that the ions detected can be classified into two groups:

1. Diagnostic fragments of the isoprene block, such as $C_5H_8^+$ (monomer) at 68 amu, $C_6H_9^+$ at 81 amu, $C_7H_{12}^+$ at 96 amu, $C_{10}H_{16}^+$ (dimer) at 136 amu, $C_{15}H_{24}^+$ (trimer) at 204 amu, and $C_{19}H_{30}^+$ at 258 amu.
2. Diagnostic fragments of the styrene block, such as $C_5H_5^+$ at 65 amu, $C_6H_7^+$ at 77 amu, $C_7H_7^+$ at 91 amu, and $C_8H_8^+$ (monomer) at 104 amu.

The yields of ions arising principally from the styrene sequences were considerably low. This may be directly related to the composition of the copolymer (styrene/isoprene ratio 14/86). Two types of scissions may be assumed for polyisoprene: (i) β scissions to double bonds, and (ii) scissions accompanied by a hydrogen transfer [19]. For high *trans*-polybutadienes, formation of cyclopentene and 1,3-cyclohexadiene was observed, although scission of a single bond at a site other than β to a double bond is energetically more difficult [20].
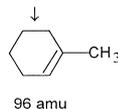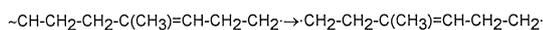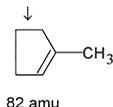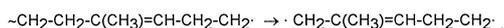
Table 1
The relative intensities (RI) of the characteristic peaks observed during the direct pyrolysis of SIS, and the related homopolymers, polyisoprene PIs and polystyrene, PSt, with the assigned chemical formulae

Relative intensities					
m/z	SIS	PIs	SIS	PSt	Chemical formulae
T($°C$)	213	219	227	230	
68	456	629	125	72	isoprene monomer $^+$
77	121	122	413	370	$C_6H_5^+$
78	117	129	550	584	$C_6H_6^+$
81	1000	1000	213	5	$C_5H_7-CH_2^+$
82	154	731	88	3	$C_5H_7-CH_3^+$
91	192	190	1000	890	$C_7H_7^+$
95	643	673	150	8	$C_6H_9-CH_2^+$
96	119	435	75	4	$C_6H_9-CH_3^+$
104	40	54	888	1000	styrene monomer $^+$
121	382	500	63	3	$CH_2=C(CH_3)-CH_2-CH_2-C(CH_3)=CH^+$
136	147	384	5	—	isoprene dimer $^+$
204	23	78	1	—	isoprene trimer $^+$
208	2	41	38	22	styrene dimer $^+$
218	3	14	—	—	$(CH_2-C(CH_3)=CH-CH_2)_3-CH_2^+$
258	1	20	—	—	$CH_2-C(CH_3)=CH-CH_2)_3CH_2C(CH_3)=CH^+$

However, in the case of polyisoprene α-bonds, although strengthened through the resonance from the double bond, are weakened by being adjacent to a tertiary carbon. Thus, α scissions to double bonds can also be expected to be highly effective. Peaks arising from an isoprene block of up to five monomer units were present in the spectra, indicating splitting of monomers and oligomers from the chain. However, only monomer peaks were observed for styrene. It is known that in vacuum or oxygen free atmosphere thermal degradation of polystyrene at elevated temperatures (below 300°C) is initiated by random scission of the main chain, to give primary and secondary macroradicals which depolymerize to the monomer [4, 12–15]. A similar thermal decomposition mechanism yielding mainly the monomer can be expected for the polystyrene blocks of the copolymer.

The base peak at 81 amu and intense peak at 95 amu may indicate that degradation of the isoprene block proceeded through chain scissions, followed by cyclization, yielding 1-methyl cyclopentene and 1-methyl cyclohexene.

~CH₂-CH₂-C(CH₃)=CH-CH₂-CH₂· → · CH₂-C(CH₃)=CH-CH₂-CH₂· .

82 amu

~CH-CH₂-CH₂-C(CH₃)=CH-CH₂-CH₂·→·CH₂-CH₂-C(CH₃)=CH-CH₂-CH₂·

96 amu

The ions at 81 and 95 amu may then be generated from these cyclic alkyenes during ionization, by electron impact in the ion source by H and CH₃ losses. In general, fragments produced by direct cleavage of C–C bonds further stabilized by H or CH₃ losses or H abstraction; i.e peaks at 175, 149, 135, 95 and 81 amu were more intense than the corresponding peaks at 176, 150, 136, 96 and 82 amu, and 190, 164, 150, 110 and 96; and peaks at 189, 175, 161, 135, 121, 93 and 81 amu were more abundant than peaks at 204, 190, 176, 150, 108 and 96 amu, respectively. However, it is not possible to conclude whether these processes occurred during thermal degradation and/or during electron impact ionization.

For a better understanding of the thermal behavior of the copolymer the ion–temperature profiles (variation of intensities as a function of temperature) of some selected peaks from each group were studied as depicted in the middle part of Fig. 1. Included in the

figure are also the ion–temperature profiles of polyisoprene (upper part) and polystyrene (lower part), and mass spectra recorded at their temperatures of maximum ion yields. As can be inferred from the figure, thermal decomposition of SIS started above 180°C and the maximum yield was obtained at 213°C. The peaks related to the styrene block (such as peaks at 77, 91 and 104 amu) showed a second weaker maximum at 227°C. Mass spectra recorded at 213 and 227°C are also given to stress the similarities with their corresponding homopolymers. Hence, it is clear that decomposition of the block copolymer takes place at two different temperature domains. This may be attributed to the different thermal stability of the isoprene and styrene blocks of the polymer chain. The cleavage of bonds in each block of the copolymer should be undoubtedly energetically similar to those in corresponding pure homopolymers. Tertiary carbons in the chain are points of instability. One may expect that the phenyl group lowers the stability more than the methyl group. However, another element of instability is the presence of double bonds introducing weakness in bonds which are in the β position to them. Decomposition occurred more readily in the isoprene block in accordance with this fact. The relative thermal stability, based on the temperature of half-life (T_h values also indicates the same trend [19]. The first maximum observed in the ion–temperature profiles of styrene related peaks, may be due to the decomposition of the units adjacent to the isoprene blocks at α positions to the double bonds. Yet there was also the possibility of the formation of benzene, toluene and some other alkyl substituted phenyls during the decomposition of the isoprene block, which would also produce 77 and 91 amu peaks. Actually the ratio of relative intensities of 77, 91 and 104 peaks at 213 and 227°C were not constant; 2.4, 1.3 and 0.5, respectively, indicating that they were produced either by different mechanisms or from different blocks.

To clarify the results, the direct pyrolysis mass spectrometric analysis of related homopolymers have also been carried out. Maximum thermal decomposition yields from polyisoprene and polystyrene [5] were detected at 219 and 230°C, respectively, only a few degrees higher than the temperatures corresponding to the maxima present in the ion–temperature profiles of the thermal degradation products of the copolymer. These shifts to higher temperatures may be related to the molecular weights of the polymers in question. It is known that an increase in the molecular weight will, in turn, increase thermal stability. Some early results of our studies on the direct pyrolysis of monodispersed polystyrenes with different molecular weights had showed a dependency of temperature of maximum yield on molecular weights. Yet, the relation is not
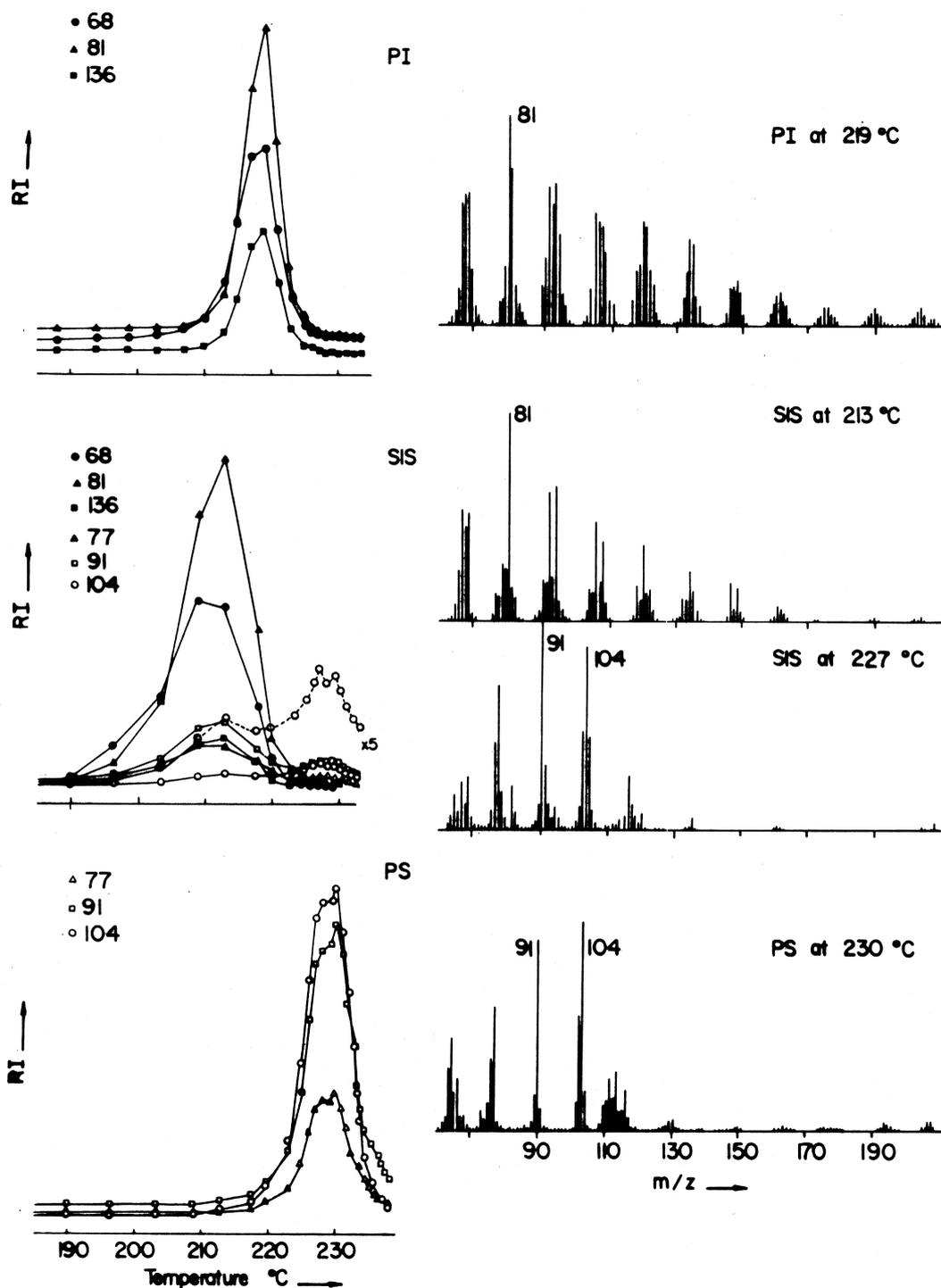
Fig. 1. Ion–temperature profiles of some characteristic fragments observed during the direct pyrolysis of polyisoprene (PI), styrene–isoprene–styrene block copolymer (SIS) and polystyrene (PS). On the right-hand side of the figure, mass spectra corresponding to maximum ion yields are also given. For SIS the two mass spectra given correspond to the two maxima observed in the ion–temperature profiles. The profile of the 104 amu peak corresponding to the styrene monomer ion in the copolymer is multiplied by a factor of five for better comparison with PS.

clearly justified at the moment and should also be studied at different heating rates.

The relative intensities of abundant and/or characteristic ions detected during the pyrolysis of polystyrene and polyisoprene at the temperatures corresponding to maximum yields, are given in Table 1 for comparison. Furthermore, the normalized mass spectrum of pyrolysis products of the copolymer at 227°C, the second maximum, is also included in the table. Notice that the pyrolysis mass spectra of the copolymer at 213 and 227°C are very similar to the mass spectra of related homopolymers. These results indicate that thermal characteristics of polyisoprene and polystyrene did not change in the copolymer. A similar behavior was observed for the styrene–butadiene–styrene block copolymer; styrene and butadiene blocks decomposed quite independently [21]. These results may be an evidence of the potential of the technique in the analysis of block copolymers.

3.2. Indirect pyrolysis

Indirect pyrolysis of SIS copolymer indicated the formation of styrene as the major product. The relative intensities of the most characteristic ions above 50 amu and their assigned chemical formulae at 469°C corresponding to maximum product yield are collected in Table 2. All the ions observed showed a similar trend as a function of temperature (Fig. 2). Relative intensities of the fragments were quite different compared with those observed from the direct pyrolysis of both SIS copolymer and related homopolymers. The peaks assigned to styrene block were noticeably abundant contrary to direct pyrolysis results and expectations because of the composition of the copolymer.

Table 2
The relative intensities (RI) of the charcteristic peaks observed at 469°C with the assigned chemical formulae during the indirect pyrolysis of SIS

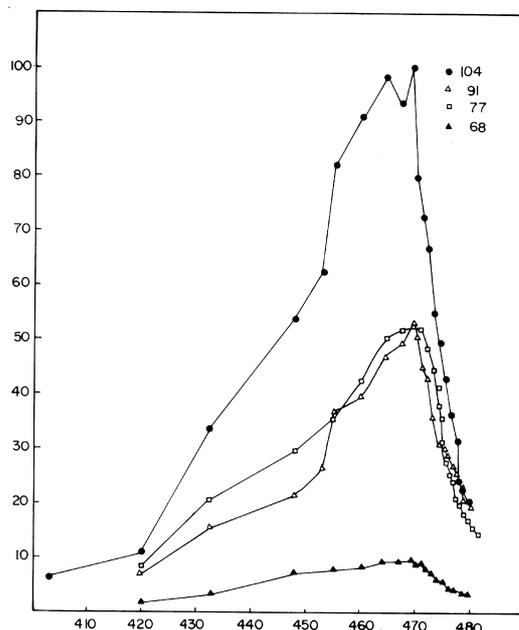| m/z	RI	Chemical formula
67	305	$CH_2 = C(CH_3)\text{-}CH = CH^+$
68	98	isoprene monomer $^+$
77	516	$C_6H_5^+$
78	572	$C_6H_6^+$
81	126	$C_5H_7\text{-}CH_2^+$
82	56	$C_5H_7\text{-}CH_3^+$
91	533	$C_7H_7^+$
95	33	$C_6H_9\text{-}CH_2^+$
96	21	$C_6H_9\text{-}CH_3^+$
104	1000	styrene monomer $^+$
118	52	$C_6H_5(CH_3)\text{-}CH = CH_2^+$

Fig. 2. Ion–temperature profiles of some characteristic fragments observed during the indirect pyrolysis of SIS.

Only low molecular weight, volatile and stable products can be detected with the use of the indirect pyrolysis technique. Under these conditions secondary reactions are more effective. Taking into account the very low yields of fragments characteristic of the isoprene sequence, it can be deduced that not only 1-methylcyclopentene and 1-methyl cyclohexene but also benzene, toluene and even styrene were produced during the thermal degradation of the isoprene block, by cyclization and H-elimination and/or abstraction reactions. These results supported direct pyrolysis findings; products arising from the isoprene block yielded ions that are primarily characteristics of the styrene block, such as fragments at 77 and 91 amu. However, indirect pyrolysis of polyisoprene mainly yielded the monomer. One may think that the styrene block somehow activates the formation of benzene, toluene and styrene from the isoprene block. Some indirect pyrolysis experiments were carried out using polyisoprene (85%) and polystyrene (15%) blends. Yet different thermal degradation paths were followed by the two homopolymers in the mixture in this case. No evidence for the effect of styrene-based products on polyisoprene degradation products can be obtained from these data. However, it may be expected that the effect should be different in the copolymer in the presence of chemical interactions between the two homopolymers.

4. Conclusion

Thermal degradation of the SIS copolymer occurred at a temperature range of 190–235°C under direct pyrolysis conditions. Two maxima, at 213 and 227°C, were observed in ion-temperature profiles. The characteristic ions diagnostic to polyisoprene reached their maximum values at 213°C, whereas the ones that could only be due to the decomposition of the styrene block had a maximum at 227°C. Each block showed a very similar thermal behavior with the corresponding homopolymer. Isoprene block degradation proceeded through random chain scissions at α and β positions, followed by cyclization, yielding 1-methyl cyclopentene and 1-methyl cyclohexene. The splitting of monomers and low molecular weight oligomers was also detected. A radical depolymerization mechanism was associated with the styrene block. The direct pyrolysis MS method seems to be a powerful technique in the thermal analysis of block copolymers.

Indirect pyrolysis results indicated that secondary reactions were very effective, yielding mainly styrene, toluene, benzene, 1-methyl pentene and 1-methyl hexene, when degradation occurred in a closed reactor. Thermal stability and/or decomposition products arising from different blocks could not be differentiated with the use of indirect pyrolysis MS findings. However, it can also be used to support the direct pyrolysis results.

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