

Articles

Thermal Degradation Processes in Polysulfide Copolymers Investigated by Direct Pyrolysis Mass Spectrometry and Flash Pyrolysis–Gas Chromatography/Mass Spectrometry

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ABSTRACT: This is the first report on the analysis of random block polysulfide copolymers containing different amounts of repeating units in the copolymer backbone, which has been studied by direct pyrolysis mass spectrometry (DPMS) and by pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS). The homopolymers such as poly(ethylene sulfide) (PES), poly(styrene sulfide) (PSS), and two random copolymers, viz., poly(ethylene sulfide-*x*-*co*-styrene sulfide-*y*) [copolymer I ($x = y = 0.5$) and copolymer II ($x = 0.74$, $y = 0.26$)] were investigated by both DPMS and Py–GC/MS (except copolymer II) techniques. In the case of copolymer I, the thermal degradation products of SE₁, SE₂, S₂, and S₂E (S = styrene sulfide, E = ethylene sulfide) were detected in DPMS, whereas the formation of SE₁ and SE₂ were observed by Py–GC/MS technique. However, for copolymer II, SE₃ was also found along with SE₁, SE₂, S₂, and S₂E in DPMS. The formation of additional product (SE₃) observed in copolymer II could be due to an increase in the block length formed during copolymerization. Further, a comparative study on thermal degradation of PES, poly(ethylene disulfide) (PEDS), and poly(ethylene tetrasulfide) (PETS) were investigated by Py–GC/MS. The pyrolysis products detected by both DPMS and Py–GC/MS indicates that the thermal decomposition of these polymers yield cyclic sulfides through an intramolecular exchange or by backbiting processes. The linear products with thiol and vinyl groups were also observed by Py–GC/MS along with the cyclic products via carbon hydrogen transfer reaction.

Introduction

The characterization of types of copolymers and sequence arrangements of subunits in condensation polymers cannot be easily ascertained by usual methods, including NMR, which has been widely used as a powerful tool for the characterization of vinyl copolymers.

Mass spectrometry is another technique which finds prevalent application to characterize the polymers.¹ Among the mass spectrometry techniques, the thermal degradation of polymers has been probed by direct pyrolysis mass spectrometry (DPMS) and pyrolysis gas chromatography/mass spectrometry (Py–GC/MS) techniques.

Although the DPMS and Py–GC/MS studies on the homopolymers and alternating copolymers of condensation polymers have been reported^{2–4} earlier, these techniques have not been explored to characterize the random block copolymers to the best of our knowledge.

The active study on thermal degradation of polysulfide polymers has been investigated by several authors.^{3–27} The interest in thermal degradation study

on polysulfide polymers is due to its extensive applications in adhesives, sealants, insulators, etc⁵ and also is due to the interest in understanding the primary and secondary thermal degradation mechanisms.

In the present study, the analysis of random block polysulfide copolymers such as poly(ethylene sulfide-*x*-*co*-styrene sulfide-*y*) [copolymer I ($x = y = 0.5$), copolymer II ($x = 0.74$, $y = 0.26$)] and their corresponding homopolymers PES and PSS are investigated by both DPMS and Py–GC/MS techniques (except copolymer II). Indeed, these techniques are mainly focused to gain an insight into the influence of random incorporation of comonomer into the copolymer that affects the thermal degradation products. We have also extended our investigation to PES, poly(ethylene disulfide) (PEDS), and poly(ethylene tetrasulfide) (PETS, the first synthetic elastomer manufactured commercially in the United States) to study how the sulfur rank present in the polymer backbone affects the thermal degradation products of the corresponding polymers by Py–GC/MS technique. Hitherto, no reports are available on a comparative study of the thermal degradation of PES, PEDS, and PETS.

Experimental Section

Materials. Basic materials were appropriately purified before use.

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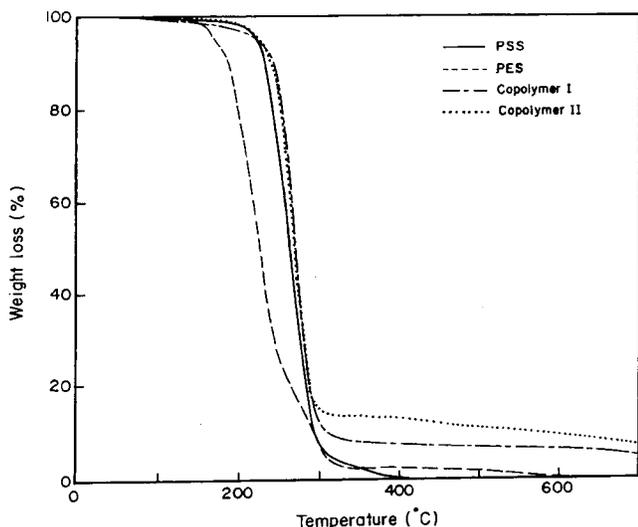


Figure 1. TG traces of homo- and copolymers.

Synthesis of Copolymers. The PSS and copolymers I and II were synthesized by interfacial polycondensation using sodium sulfide from styrene dibromide or a mixture of styrene dibromide and ethylene dibromide. A typical procedure for the synthesis of copolymer I is as follows. To a solution of Na_2S (0.9365 g, 0.012 mol) in 10 mL of water was added 10 mL of CHCl_3 solution containing ethylene dibromide (0.9395 g, 0.005 mol) and styrene dibromide (1.32 g, 0.005 mol), followed by

the addition of tetrabutylammonium bromide (0.0644 g, 0.0002 mol) as a phase transfer catalyst. The mixture was stirred for 24 h. The CHCl_3 layer was separated, washed several times with water to remove sodium bromide, and dried over anhydrous sodium sulfate. Then the CHCl_3 solution was poured into a large excess of methanol to precipitate the copolymer. The copolymer was further purified from oligomers by repeated reprecipitation using chloroform and methanol as solvent and nonsolvent, respectively. Finally, it was dried to a constant weight in a vacuum. The characterization of the above polymers by IR, NMR, and copolymer composition has been reported.²⁸ The compositions of the copolymers were determined by comparing the area of the phenyl peaks with the total backbone proton peaks and the reactivity ratios were $r_1 = 0.33$ (styrene sulfide) and $r_2 = 3.50$ (ethylene sulfide) [Finemann–Ross method]. The PES, PEDS, and PETS were synthesized by using a reported procedure.²⁹

Thermogravimetry (TG). A Seiko thermal analyzer, model SSC 5200H, was used to determine the thermal stability of the polymers. Experiments were carried out using 2 mg of sample, under nitrogen atmosphere at a flow rate of 100 mL/min, at a heating rate of 20 °C/min.

DP–MS. Pyrolysis was carried out using the direct insertion probe of a VG MICRO-MASS 7070H mass spectrometer, at a heating rate of 32 °C/min. Electron ionization (EI) was maintained at 18 eV. Chemical ionization (CI) was performed using a SHIMADZU MS-Q5050 instrument with methane as the reagent gas.

Py–GC/MS. Flash pyrolysis experiments were carried out using a Curie-point pyrolysis unit directly connected to the injector of Hewlett-Packard 5890 gas chromatograph. The on-line pyrolysis experiments were performed by inductive heat-

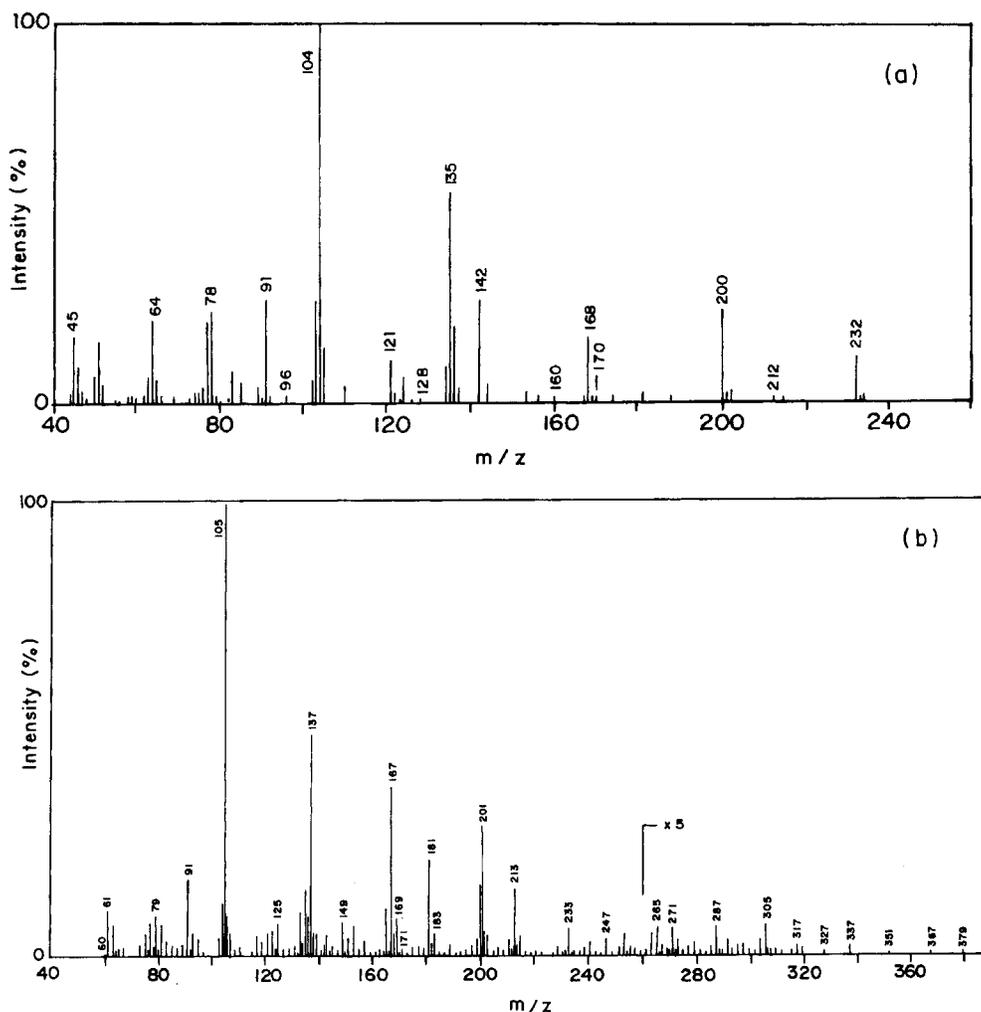


Figure 2. DPMS of PSS: (a) EI and (b) methane CI.

Table 1. Pyrolysis Products Detected in the DPMS of PSS, PES, and Copolymers I and II

| PSS | Copolymers I and II |
|---|---|
| Sn 64 (2), 96 (3), 128 (4), 160 (5) Ph-CH=CH ₂ 104 Ph-CH-CH ₂ 136 (1), 168 (2), Sn 200 (3), 232 (4), 264 (5), 296 (6) HS-CH-CH ₂ -SH 170 Ph Ph-CH-CH-Ph 212 S S Ph Ph 273 (MH ⁺) | Sn 64(2), 96 (3), 128(4), 160 (5) Ph-CH=CH ₂ 104 Ph-CH-CH ₂ 136 (1), 168 (2), Sn 200 (3), 232 (4) 264 (5), 296 (6) HS-CH-CH ₂ -SH 170 Ph Ph-CH-CH-Ph 212 S S Ph Ph $\left[\text{CHCH}_2\text{S} \right]_x \left[\text{CH}_2\text{CH}_2\text{S} \right]_y$ Ph Ph Copolymer I (x, y) Copolymer II (x, y) 60 (0, 1), 120 (0, 2) 60 (0, 1), 120 (0, 2) 180 (0, 3), 196 (1, 1) 180 (0, 3), 196 (1, 1) 240 (0, 4), 256 (1, 2) 240 (0, 4), 256 (1, 2) 272 (2, 0), 336 (2, 1) 272 (2, 0), 300 (0, 5) 316 (1, 3), 336 (2, 1) 360 (0, 6) $\text{H} \left[\text{CHCH}_2\text{S} \right]_x \left[\text{CH}_2\text{CH}_2\text{S} \right]_y \text{H}$ Ph Ph Copolymer I (x, y) Copolymer II (x, y) 122 (0, 2), 182 (0, 3) 122 (0, 2), 182 (0, 3) 198 (1, 1), 242 (0, 4) 198 (1, 1), 242 (0, 4) 258 (1, 2), 302 (0, 5) 258 (1, 2), 274 (2, 0) 318 (1, 3) 302 (1, 5), 318 (1, 3) |
| PES $\left[\text{CH}_2\text{CH}_2\text{S} \right]_n$ 60 (1), 120 (2), 180 (3) 240 (4), 300 (5), 360 (6), 420 (7) Ph = Phenyl group | |

ing of the sample-coated wires at 700 °C. The separated products were analyzed by a mass spectrometer.

Results and Discussion

TG. The TG traces of homo- and copolymers are presented in Figure 1. The thermal stability of PES is

less compared to that of PSS and copolymers I and II. The DPMS analysis was performed at the temperature corresponding to maximum rate of polymer decomposition observed in TG analysis.

DPMS. In the DPMS technique, polymers are introduced via the direct insertion probe, and the temperature is increased gradually up to a point at which thermal degradation reactions occur; the volatile products thus formed are ionized and then detected. The advantage of this technique is that the pyrolysis is achieved very close to the ion source and hence primary degradation products are identified by this technique.

PSS. The EI and methane CI mass spectra of the PSS recorded at 270 °C are displayed in Figure 2, parts a and b, respectively, and the primary degradation products formed are presented in Table 1. Styrene forms the base peak and its formation is reported in the literature.²⁴ Sulfur shows peaks due to S₂ (*m/z* 64), S₃ (*m/z* 96), S₄ (*m/z* 128), S₅ (*m/z* 160), and peaks due to styrene sulfide(s) (*m/z* 136, 168, 200, 232) are also present in the spectrum.

PES. In the case of PES, the pyrolysis products (Table 1) observed are similar to one reported by Montaudo et al.¹⁸ (Figure is not presented here).

Copolymers I and II. Figures 3 and 4 [a (EI) and b (CI)] show the DPMS of copolymers I and II, respectively, recorded at 270 °C, and the products are listed in Table 1. The polymeric chain consists of styrene sulfide and ethylene sulfide as repeating units. The reactivity ratio analysis indicates that the copolymer contains random blocks of ethylene sulfide and styrene sulfide. Hence, we expect three kinds of pyrolysis products correspond to (i) ethylene sulfide blocks, (ii) styrene sulfide blocks, and (iii) a hetero-linkage that con-

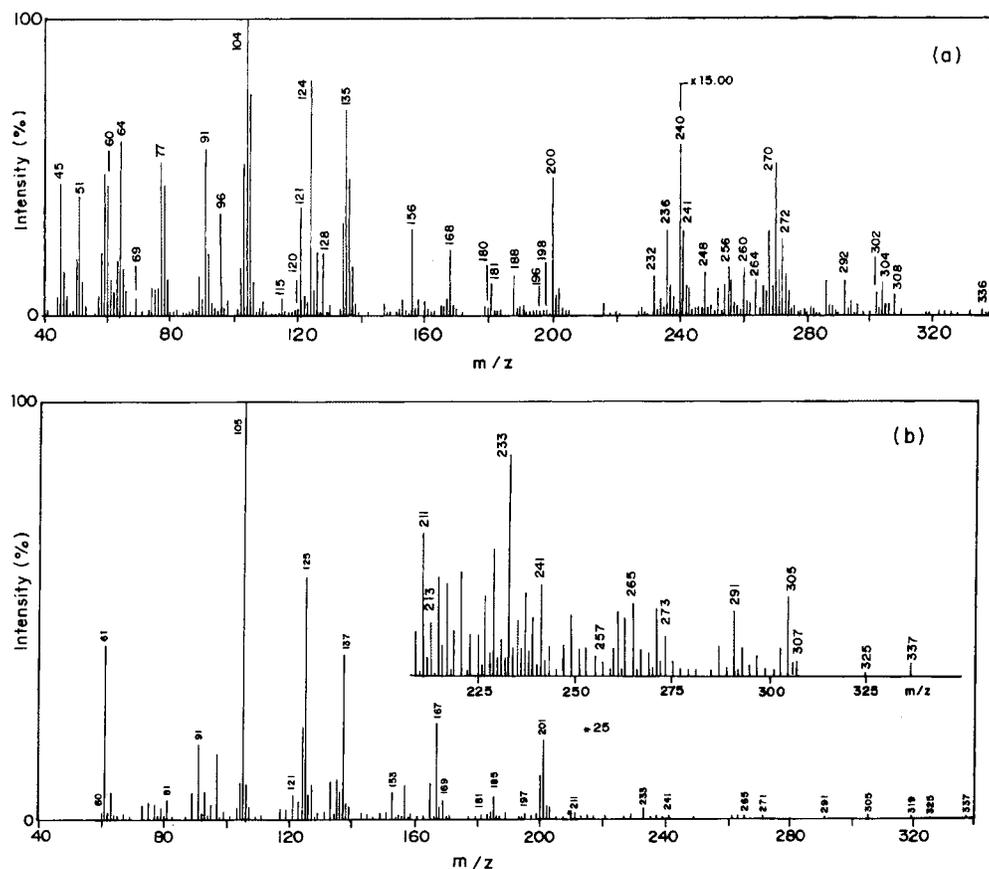


Figure 3. DPMS of copolymer I: (a) EI and (b) methane CI.

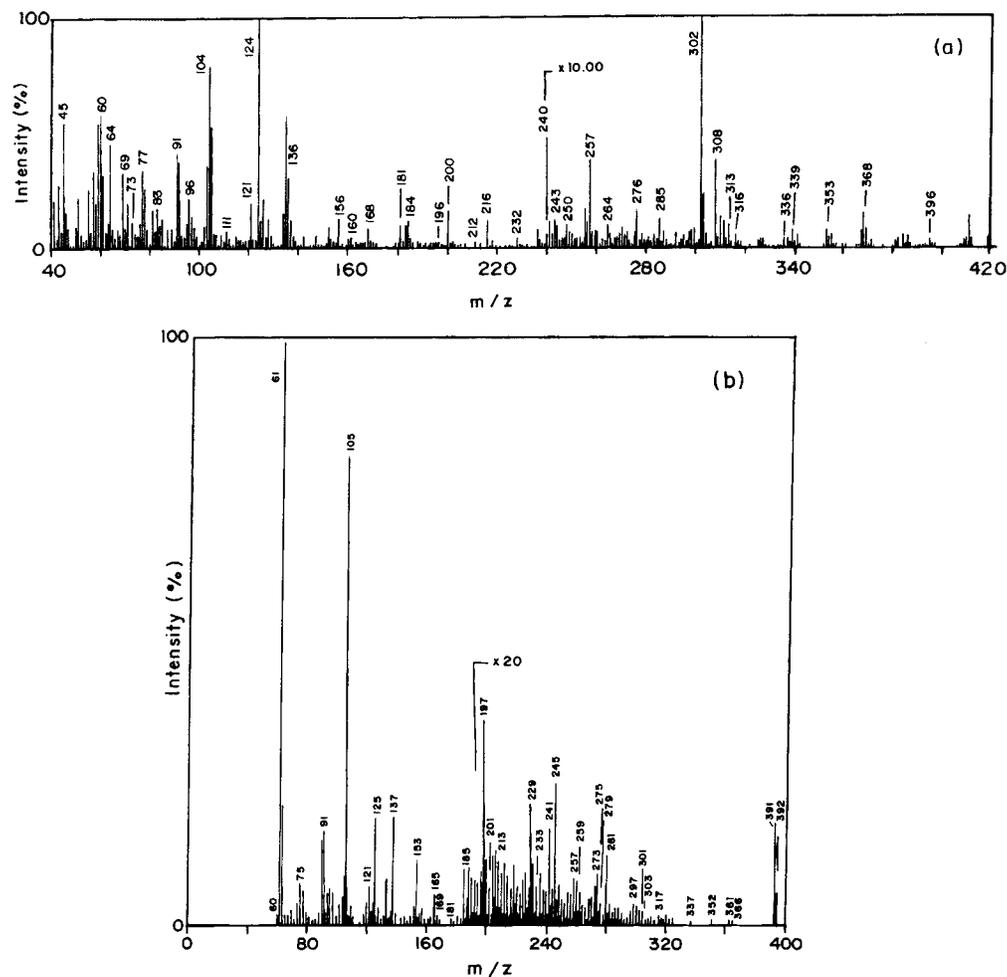
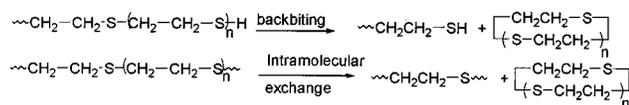


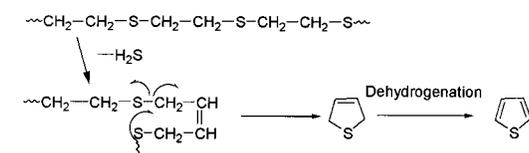
Figure 4. DPMS of copolymer II: (a) EI and (b) methane CI.

Scheme 1. Thermal Degradation Mechanism of PES, PSS, and Copolymers I and II

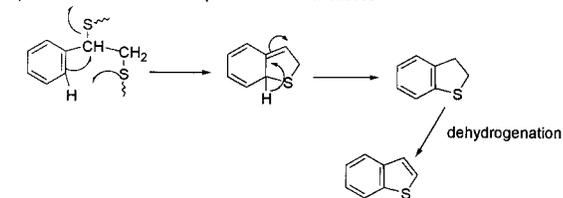
a) Formation of Oligomers



b) Formation of Thiophene and its derivatives



c) Formation of Benzo b thiophene and its derivatives



nects both the blocks. The formation of ethylene sulfide oligomers may be assumed from the ethylene sulfide block present in copolymer through backbiting reaction or by an intramolecular exchange process, and it is illustrated in Scheme 1a. The formation of styrene sulfide dimer can be assumed from the styrene sulfide block.

Apart from the pyrolysis products that corresponds to individual blocks, we are also observed the peaks

(Figure 3 and Table 1) due to hetero-linkage [as M^+ in EI at m/z 196(SE), 256(SE_2), and 336 (S_2E)] of cyclic oligomers and open chain compounds (as M^+ in EI at m/z 198, 258, and 318) originates from the copolymer backbone (Figure 3a). The formation of the above products is confirmed by CI (Figure 3b) mass spectra as protonated molecular (MH^+) ions.

In the case of copolymer II, the sequence such as SE_3 (m/z 316) was observed along with the pyrolysis products observed for styrene sulfide block, ethylene sulfide block, and copolymer I. It is well-known that the sequence length distribution is broader for more reactive monomer during copolymer formation; hence, we have observed broader oligomer distribution for ethylene sulfide units during thermal degradation of both the copolymers I and II (Table 1). The concentration of ethylene sulfide units is higher in copolymer II; therefore, it implies sequence length up to hexamer for ethylene sulfide block and tetramer (SE_3) for hetero-oligomers (Figure 4, parts a and b).

Py-GC/MS. In Py-GC/MS technique, the polymer is pyrolyzed by rapid heating of the probe in an inert atmosphere of the pyrolysis chamber, and the pyrolysis products are separated prior to the MS analysis. An advantage of this technique is that the individual analysis of the isomeric products separated by GC is possible.

PES. The Py-GC/MS pyrogram of PES recorded at 700°C is shown in Figure 5. Thiophene forms the base peak, and the formations of other products are listed in

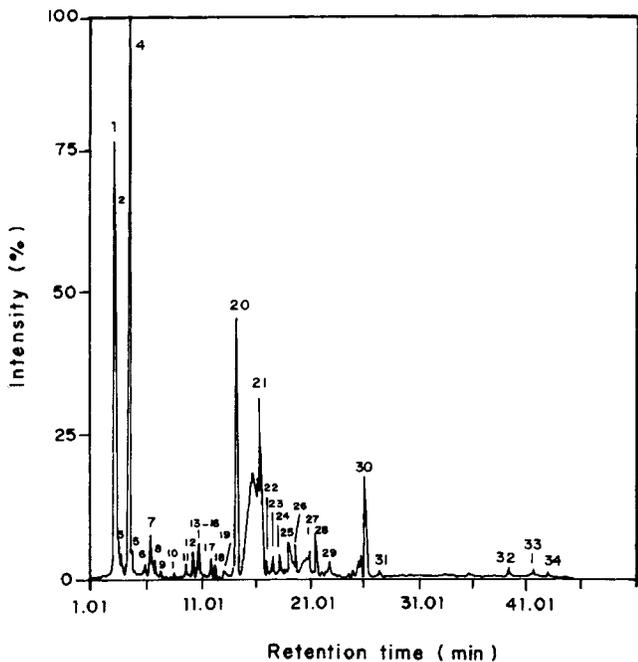


Figure 5. Gas chromatograms of the flash pyrolysates (Curie temperature, 700 °C) of PES.

Table 2. Flash Pyrolysis-GC/MS Products of PES and PSS Observed at 700 °C^a

| peak no | $-(CH_2CH_2S)_n-$ | m/z | peak no | $-(CH_2CH_2S)_n-$ | m/z | Peak no | PSS | m/z |
|---------|-----------------------------|-----|---------|--------------------------------------|-----|---------|--|-----|
| 1 | <chem>H3CC=CCH3</chem> | 54 | 18 | <chem>S</chem> | 116 | 35 | <chem>S=C=S</chem> | 76 |
| 2 | <chem>C(S)H-CH2</chem> | 60 | 19 | Isomer of 18 | 116 | 36 | <chem>c1ccccc1</chem> | 78 |
| 3 | <chem>S=C=S</chem> | 76 | 20 | <chem>S</chem> | 120 | 37 | <chem>c1ccccc1C</chem> | 92 |
| 4 | <chem>c1ccsc1</chem> | 84 | 21 | <chem>CH3SCH=CHSCH3</chem> E or Z | 120 | 38 | <chem>c1ccccc1CC</chem> | 106 |
| 5 | <chem>HSCH2CH2SH</chem> | 94 | 22 | <chem>c1ccsc1</chem> | 124 | 39 | <chem>c1ccccc1C=C</chem> | 102 |
| 6 | <chem>c1ccsc1</chem> | 86 | 23 & 24 | <chem>CH2=CHSCH=CHSCH=CH</chem> | 142 | 40 | <chem>c1ccccc1C=C</chem> | 104 |
| 7 | <chem>c1cc(C)sc1</chem> | 98 | 25 & 26 | <chem>H3C-S-S-CH3</chem> | 152 | 41 | <chem>c1ccccc1S</chem> | 110 |
| 8 | <chem>c1cc(C)sc1</chem> | 98 | 27 | <chem>c1cc2ccsc2c1</chem> | 146 | 42 | <chem>c1ccccc1C(C)C</chem> | 120 |
| 9 | <chem>c1ccsc1</chem> | 88 | 28 | <chem>c1cc2ccsc2c1</chem> | 140 | 43 | Unidentified | 120 |
| 10 | Unidentified | 108 | 29 | Unidentified | 152 | 44 | <chem>c1ccc2c(c1)sc(C)cc2</chem> | 134 |
| 11 | <chem>c1cc(C)sc1</chem> | 112 | 30 | <chem>H3C-S-S-CH3</chem> | 180 | 45 | <chem>c1ccc2c(c1)sc(C)cc2</chem> | 136 |
| 12 | <chem>3HC-c1cc(C)sc1</chem> | 112 | 31 | <chem>c1cc2ccsc2c1</chem> | 166 | 46 & 47 | <chem>c1ccc2c(c1)sc(C)cc2</chem> | 136 |
| 13 | <chem>c1cc(C)sc1</chem> | 110 | 32 & 33 | Unidentified | 430 | 48 | Unidentified | 156 |
| 14 | Isomer of 12 | 112 | 34 | <chem>c1cc2ccsc2c1</chem> | 178 | 49 | Unidentified | 183 |
| 15 | <chem>c1cc(C)sc1</chem> | 110 | | | | 50 | <chem>Ph-c1ccc2c(c1)sc(C)cc2-Ph</chem> | 236 |
| 16 | <chem>c1ccsc1</chem> | 120 | | | | 51 | <chem>Ph-c1ccc2c(c1)sc(C)cc2-Ph</chem> | 236 |
| 17 | <chem>c1ccsc1</chem> | 118 | | | | 52 | Unidentified | 236 |
| | | | | | | 53 | <chem>Ph-c1ccc2c(c1)sc(C)cc2-Ph</chem> | 236 |
| | | | | | | 54 | <chem>Ph-c1ccc2c(c1)sc(C)cc2-Ph</chem> | 240 |

^a Peaks 1–34: PES. Peaks 35–54: PSS.

Table 2. Episulfide, thiophene, thiol-substituted thiophene, and alkyl- and vinyl-substituted thiophenes were formed as the major products, which indicates that formation of cyclics is favored during thermal degradation of PES. The formation of thiophenes and alkyl-substituted thiophenes are due to the elimination of hydrogen sulfide, cyclization followed by dehydrogenation reaction. The loss of hydrogen from 2,5-dihydrothiophene to form thiophene has been reported in the literature.³⁰ Some of the product formations are illustrated in Scheme 1. Apart from these, a few linear

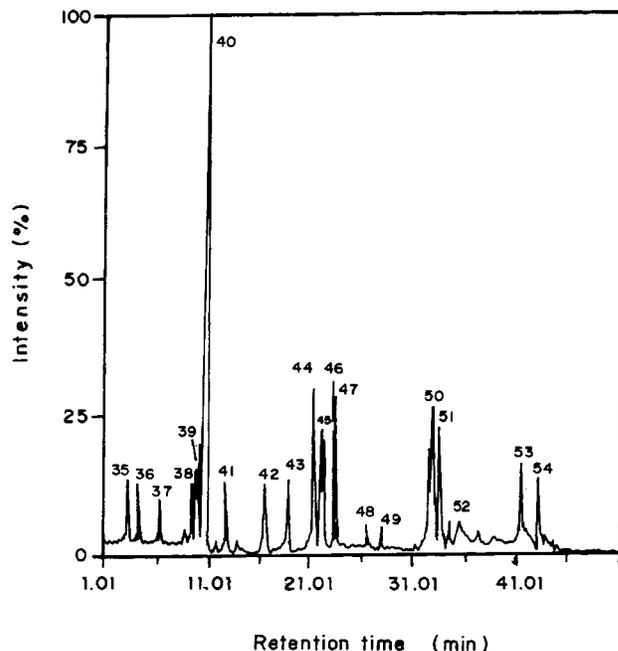


Figure 6. Gas chromatograms of the flash pyrolysates (Curie temperature, 700 °C) of PSS.

products, such as 2-butyne, CS_2 , and 1,2-ethanedithiol, are also observed. The formation of ethanedithiol is attributed to the carbon-hydrogen transfer reactions.¹⁸ It is to be noted here that Machon et al.⁹ observed linear products such as the thiol and vinyl end group as the major products and cyclic episulfides as the minor products. In the present study, we have observed that the formation of cyclics is the major products, in contrast to Machon et al. The major difference in the product formation could possibly be due to the poor resolution of the instrument in the earlier studies. The formation of cyclics from polysulfide polymers^{18,31} and the thiophene from dimethyl sulfide³² and diethyl disulfide³³ on pyrolysis also support our observations. Similar observation is reported in an earlier study on vinyl polymers.³⁴

PSS and Copolymer I. The Py-GC/MS pyrograms corresponding to PSS and copolymer I are presented in Figures 6 and 7, respectively. In both the homopolymer (PSS) and copolymer, styrene forms the base peak, and the formation of other products are displayed in Tables 2 and 3, respectively. The formation of diphenylthiophene isomers from styrene sulfide units could be explained as follows: From head-to-tail poly(styrene sulfide) units, 2,4-diphenylthiophene is expected as a pyrolysis product, whereas 3,4- and 2,5-diphenylthiophenes are anticipated products from head-to-head and tail-to tail poly(styrene sulfide) units. The loss of sulfur from 2,5-diphenyl-1,4-dithiadene to form 2,4-diphenylthiophene has been reported in the literature.³⁵

In the case of copolymer I, the peaks due to ethylene sulfide and thiophene could have originated from the thermal degradation of ethylene sulfide units in the copolymer backbone. The products such as styrene, styrene sulfide, diphenylthiophenes, and some of the other products are assumed to originate from the styrene sulfide units in the backbone of the copolymer. The peaks between 57 and 61 can be accounted for the hetero-linkage of the copolymer I (see Figure 6 and Table 3). The formations of SE_1 and SE_2 during thermal degradation detected by DPMS are also observed by Py-GC/MS.

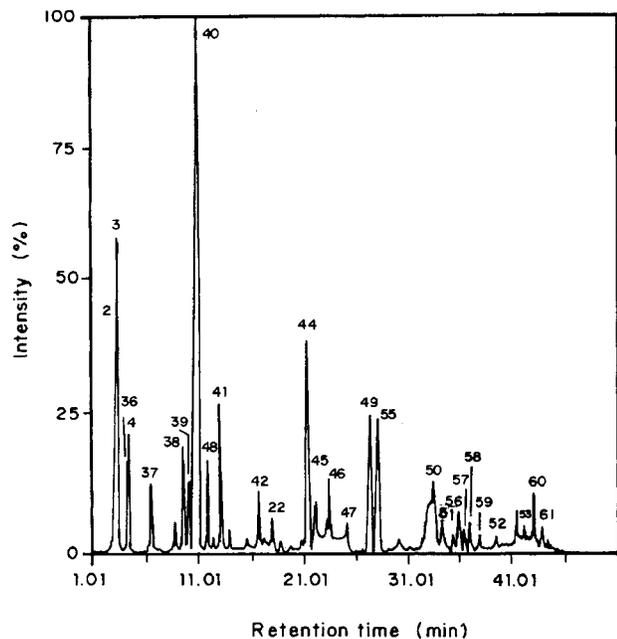


Figure 7. Gas chromatograms of the flash pyrolysates (Curie temperature, 700 °C) of copolymer I.

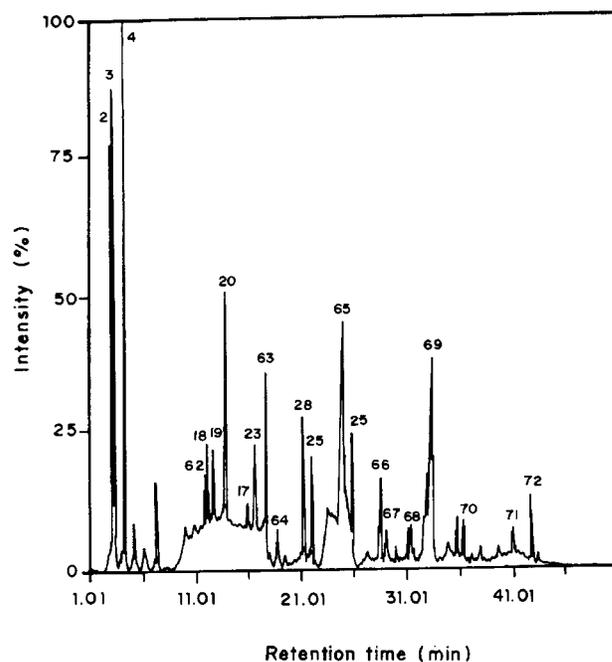


Figure 8. Gas chromatograms of the flash pyrolysates (Curie temperature, 700 °C) of PEDS.

Table 3. Flash Pyrolysis–GC/MS Products of Copolymer I, PEDS, and PETS Observed at 700 °C^a

| Peak no. | Copolymer I | m/z | Peak no. | PEDS | m/z | Peak no. | PETS | m/z |
|----------|--------------|-----|----------|--|-----|----------|--------------------------------------|-----|
| 55 | | 160 | 62 | | 118 | 73 | Unidentified | 138 |
| 56 | | 178 | 63 | $-\text{CH}_2\text{CH}_2\text{S}_3-$ | 124 | 74 | Unidentified | 162 |
| 57 | | 196 | 64 | | 152 | 75 | Unidentified | 154 |
| 58 | | 190 | 65 | $-\text{CH}_2\text{CH}_2\text{S}_4-$ | 156 | 76 | $-\text{CH}_2\text{CH}_2\text{S}_8-$ | 188 |
| 59 | Isomer of 58 | 190 | 66 | Unidentified | 188 | 77 | $-\text{S}_6-$ | 192 |
| 60 | | 210 | 67 | Unidentified | 172 | 78 | Unidentified | 200 |
| 61 | | 256 | 68 | $-\text{CH}_2\text{CH}_2\text{S}_5-$ | 188 | 79 | $-\text{CH}_2\text{CH}_2\text{S}_8-$ | 220 |
| | | | 69 | $-(\text{CH}_2\text{CH}_2\text{S}_3)_2-$ | 184 | 80 | Unidentified | 188 |
| | | | 70 | Unidentified | 206 | | | |
| | | | 71 | $-\text{S}_8-$ | 256 | | | |
| | | | 72 | Unidentified | 208 | | | |

^a Peaks 2–4, 22, 36–42, 44–53 (see Table 1), and 55–61: copolymer I. Peaks 2–4, 17–20, 23, 25, 28 (see Table 1), and 62–72: PEDS. Peaks 1–4, 13, 17, 18, 20, 23, 25, 28, 34 (see Table 1), 63, 65, and 73–80: PETS.

When we compare homopolymers (PES and PSS) with copolymer (Tables 2 and 3), the thermal degradation of the copolymer favors the formation of styrene sulfide units cleaved products. It is noteworthy to mention that the substituted thiophenes are absent in the copolymer I pyrogram, which could be due to the random placement of styrene sulfide units that disturbs their formation.

PEDS and PETS. The Py–GC/MS pyrograms of PEDS and PETS recorded at 700 °C are displayed in Figures 8 and 9 respectively, and the products formed are listed in Table 3. Here also, thiophene forms the base peak, and some of the products that are formed in PES are also formed in PEDS and PETS. The formation of thiophene and its derivatives could be rationalized by thermally induced loss of hydrogen sulfide and sulfur. In the case of PEDS and PETS (except peak no 13 in

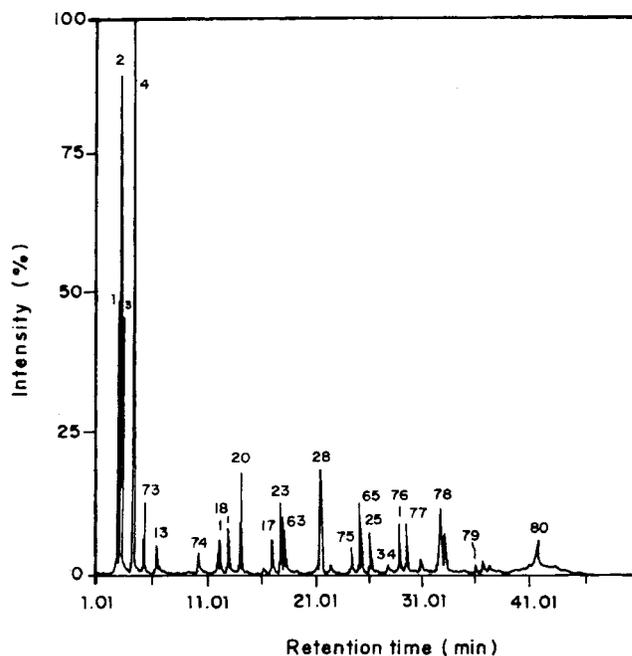


Figure 9. Gas chromatograms of the flash pyrolysates (Curie temperature, 700 °C) of PETS.

PETS) the alkyl- and vinyl-substituted thiophenes are completely absent, whereas they are present in PES pyrogram. Alternatively, higher sulfur rank containing cyclic products were formed in the case of PEDS and PETS.

Conclusions

The homopolymers and random block copolymers were investigated by both DPMS and Py–GC/MS techniques. It is interesting to mention here that the amount of comonomer in the copolymer plays a vital role in thermal degradation analysis. This observation is consolidated in DPMS mode that oligomers formed from ethylene sulfide block (up to hexamer for copolymer II

and tetramer for copolymer I) and hetero-linkage segment (up to tetramer for copolymer II and trimer for copolymer I).

In copolymer I, SE, S₂, SE₂ and S₂E were observed in DPMS, whereas SE and SE₂ were detected in Py-GC/MS mode. The absence of S₂ and S₂E could be due to their thermal lability in Py-GC/MS mode, where the possibility of the primary pyrolysis products formed were likely to undergo secondary thermal degradation. However, the formation of diphenylthiophenes suggest that initially formed styrene sulfide dimer, a primary degradation product, could have undergone secondary thermal degradation in Py-GC/MS.

We believe that the incorporation of styrene sulfide in to the copolymer backbone have the significant effect in thermal degradation products. The absence of substituted thiophenes in Py-GC/MS explains that the presence of styrene sulfide units disturb their formation during thermal degradation. The thiophene derivatives observed in PES are absent in PEDS and PETS which indicates the influence of sulfur rank on the thermal degradation products.

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