Thermal Degradation Processes in Poly(xylylene sulfides) Investigated by Comparative Direct Pyrolysis MS and Flash Pyrolysis GC/MS Experiments

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ABSTRACT: The thermal degradation processes of two sulfur polymers, poly(xylylene sulfide) (PXM) and poly(xylylene disulfide) (PXD), were investigated in parallel by direct pyrolysis mass spectrometry (DPMS) and flash pyrolysis GC/MS (Py-GC/MS). Thermogravimetric data showed that these polymers decompose with two separate steps in the temperature ranges of 250−280 and 600−650 °C, leaving a high amount of residue (about 50% at 800 °C). The pyrolysis products detected by DPMS in the first degradation step of PXM and PXD were terminated by three types of end groups, $-CH_3$, $-CH_2SH$, and $-CH{=}S$, originating from thermal cleavage reactions involving a series of homolytic chain scissions followed by hydrogen transfer reactions, generating several oligomers containing some intact xylylene sulfide repeating units. The presence of pyrolysis compounds containing some stilbene-like units in the first degradation step has also been observed. Their formation has been accounted for with a parallel cleavage involving the elimination of H_2S from the PXM main chains. These unsaturated units can undergo cross-linking at higher temperatures, producing the high amount of char residue observed. The thermal degradation compounds detected by DPMS in the second decomposition step at about 600−650 °C were constituted of condensed aromatic molecules containing dihydrofenanthrene and fenanthrene units. These compounds might be generated from the polymer chains containing stilbene units, by isomerization and dehydrogenation reactions. The pyrolysis products obtained in the Py-GC/MS of PXM and PXD at 610 °C are almost identical. The relative abundance in the pyrolysate and the spectral properties of the main pyrolysis products were found to be in generally good agreement with those obtained by DPMS. Polycyclic aromatic hydrocarbons (PAHs) were also detected by Py-GC/MS but in minor amounts with respect to DPMS. This apparent discrepancy was due to the simultaneous detection of PAHs together with all pyrolysis products in the Py-GC/MS, whereas in DPMS they were detected in the second thermal degradation step without the greatest part of pyrolysis compounds generated in the first degradation step. The results obtained by DPMS and Py-GC/MS experiments showed complementary data for the degradation of PXM and PXD and, therefore, allowed the unequivocal formulation of the thermal degradation mechanism for these sulfur-containing polymers.

Introduction

The thermal decomposition processes that occur in aromatic and aliphatic polysulfides have received continued attention in the literature,[1−26] and some of us have been involved in the study of the thermal degradation processes of several sulfur polymers.[12−23]

Interest in thermal studies on sulfide polymers is justified by the extensive applications of these materials as engineering thermoplastics, adhesives, sealants, insulators, antioxidants, etc.[1]

Since the thermal cleavage of a polymer chain can be often inferred from the structure of the primary pyrolysis products formed, thermal degradation studies ought to focus on techniques that allow detection of the latter.

We have investigated here the thermal degradation products of two poly(xylylene sulfides) in parallel by direct pyrolysis mass spectrometry (DPMS)[2−4,27] and flash pyrolysis GC/MS (Py-GC/MS).[28,29]

The time scales of the two pyrolysis techniques are quite different, and we might expect that, in the case of thermally labile pyrolysis products, DPMS and GC/MS might be able to detect different compounds.[23] In Py-GC/MS, the residence time in the hot zone may be less than a second, whereas in DPMS, residence and transport times are in the order of milliseconds for probe pyrolysis (EI, CI), and even less for filament pyrolysis (DCI).[2−4,22]

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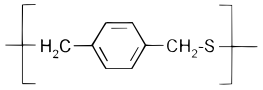
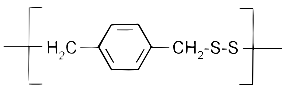
In the current literature, studies of polymer thermal degradation are usually carried out by only one of the above-described techniques (probably because very few laboratories are expert in both techniques), and this dualism may have generated some uncertainty about polymer pyrolysis. We have, therefore, started a project to perform comparative DPMS and Py-GC/MS studies, putting together the two pyrolysis techniques.

In a first study,[23] we have investigated poly(styrene disulfide) (PSD) and poly(styrene tetrasulfide) (PST). The time scales of the two pyrolysis techniques are quite different; therefore, significantly different products were detected in the pyrolysis of PSD and PST. Thus, compounds containing sulfur, styrene, and several cyclic styrene sulfides and diphenyldithianes were detected by DPMS, whereas a cyclic styrene sulfide and two diphenylthiophenes were observed by Py-GC/MS. These thiophene derivatives were absent among the compounds obtained by DPMS, because they are formed at high temperature from the further decomposition of the diphenyldithiane derivatives originating in the primary thermal degradation process of PSD and PST.[23]

In the present study, we have extended our investigations to poly(xylylene sulfide) (PXM) and poly(xylylene disulfide) (PXD) by comparative EI,CI-DPMS and Py-GC/MS experiments.



PXM



PXD

Experimental Section

Materials. Basic materials were commercial products appropriately purified before use. PXM and PXD were synthesized from xylylene dibromide and the corresponding Na_2S_x sulfides, as described previously.[24]

Thermogravimetry. A Perkin-Elmer thermal analyzer, TGS-2, was used to determine the thermal stability of the polymers. Experiments were carried out on about 2 mg of sample under nitrogen at a flow rate of 60 mL/min, at a heating rate of 10 °C/min up to 800 °C. The temperature at the maximum rate of polymer degradation (PDT) corresponds to the temperature (°C) at which DTG curves reach their maximum.

Direct Pyrolysis Mass Spectrometry. Pyrolysis mass spectra were obtained using a VG TRIO 1000 QMD mass spectrometer and Lab-Base software. Pyrolysis was carried out using the water-cooled standard direct insertion probe for solid materials, heated from 100 to 750 °C at a heating rate of 10 °C/min. Mass spectral scans were made continuously with a cycle time of 3 s, mass range 10–1000, and interscan time 3 s, and stored. Electron impact (EI) mass spectra were obtained at 18 eV. Chemical ionization (CI) was performed with isobutane as reagent gas (purchased from Matheson Gas Products). Source temperature was 200 °C.

Pyrolysis-GC/MS. Flash pyrolysis experiments were performed using a FOM-4LX Curie-point pyrolysis unit[30] directly connected to the injector of a Hewlett Packard 5890 Series II gas chromatograph. Polymer samples were pressed on flattened ferromagnetic wires with a KBr press as described by Venema and Veurinink.[31] The on-line flash pyrolysis experiments were performed by inductive heating of the sample-coated wires in 0.l s to their Curie temperature, at which it was held for 10 s. The Curie temperatures used were 358 (nickel) and 610 °C (iron/nickel alloy). The gas chromatograph, equipped with a cryogenic unit, was programmed from 0 (5 min) to 320 °C (15 min) at a rate of 3 °C/min. Separation of the pyrolysis products was achieved using a fused-silica capillary column (25 m × 0.32 mm) coated with CP Sil-5 (film thickness, 0.45 μm). Helium was used as carrier gas. The compounds were detected either using FID or by mass spectrometry using a VG Autospec Ultima mass spectrometer (cycle time, 1 s; mass range, 45–900; ionization energy, 70 eV).

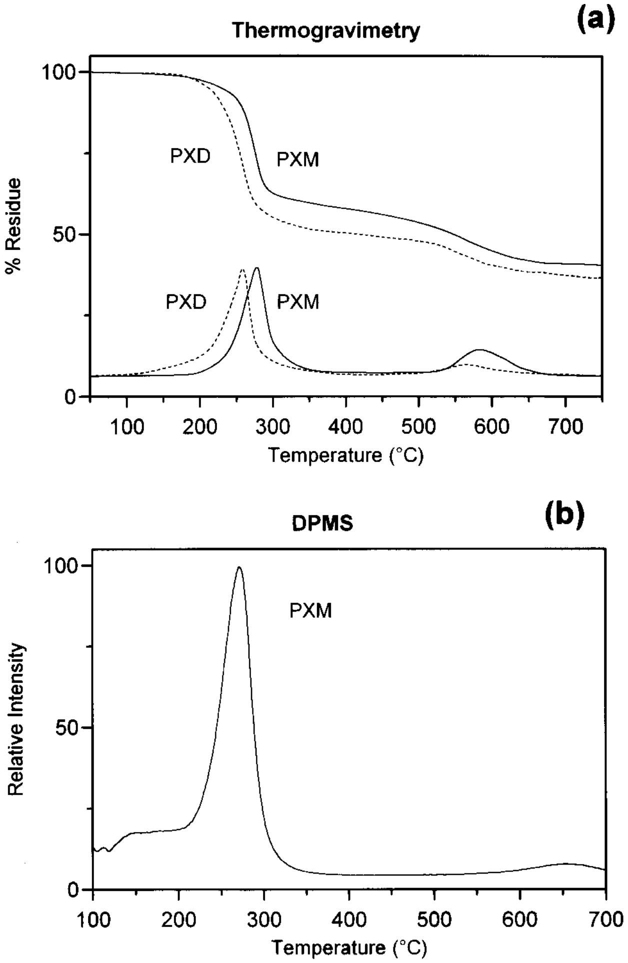


Figure 1. (a) Thermogravimetric and derivative thermogravimetric curves of PXM and PXD, obtained at 10 °C/min under N2 flow. (b) Total ion current curve of PXM obtained by DPMS at 10 °C/min.

Results and Discussion

Thermogravimetry. The thermal stability of PXM and PXD has been investigated by thermogravimetry (TG). The TG and DTG curves of PXM and PXD (Figure 1a) show that the maximum rate of thermal decomposition occurs at 280 and 250 °C, respectively. The weight loss starts at about 200 °C and levels off from 300 to about 550 °C. A second step of thermal degradation takes place at about 600 °C, and the total weight loss comes to about 50–60% at 800 °C.

The high amount of char residue left at high temperatures by these polymers contrasts with their relatively low thermal stability. A high amount of char residue is, instead, typical of bridged aromatic polymers, such as PPS, PES, PPO, and PEK, which are believed to form graphite-like, cross-linked and condensed polyaromatic structures during the pyrolysis process.[21,22]

Direct Pyrolysis Mass Spectrometry. In this technique,[2–4,27] the polymer samples are heated inside the ion source of the MS with the same linear temperature program used in the TG runs (10 °C/min), so that the total ion current (TIC) curves obtained by DPMS are nearly superimposable with the DTG curves.

In fact, the TIC curves of PXM and PXD (Figure 1b) have a similar shape of the differential DTG curves,

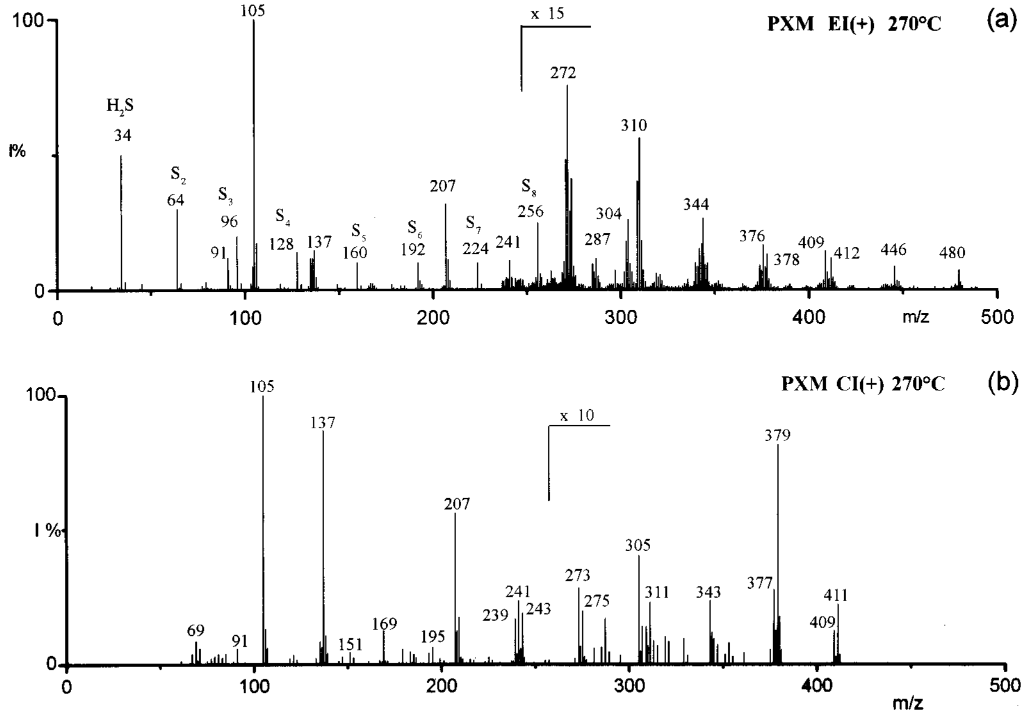
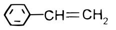
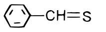
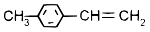
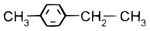
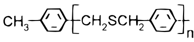
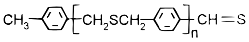
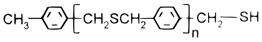
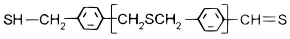
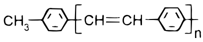
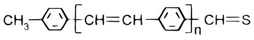
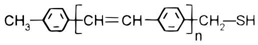
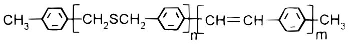
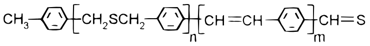
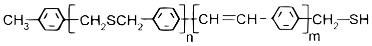
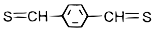
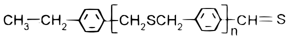
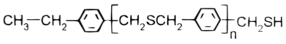
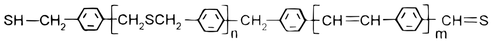
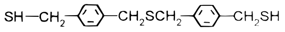
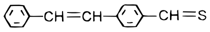
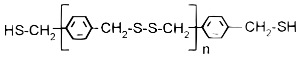
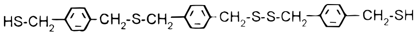
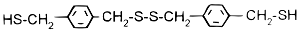
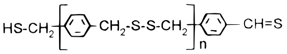
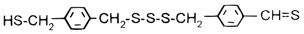
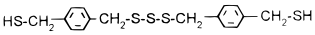
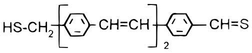
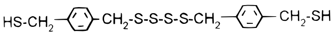
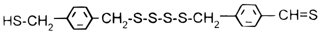


Figure 2. Mass spectra of pyrolysis compounds detected at 270 °C in the DPMS of PXM: (a) EI, 18 eV; (b) isobutane CI.

Table 1. Pyrolysis Compounds Detected in the DPMS of PXM and PXD in the Temperature Range of 250−350 °C

H_2S	34
S_n	64(2),96(3),128(4),160(5),192(6),224 (7),256 (8)
	104
	122
	118
	120
	106(0),242(1),378(2)
	136(0),272(1),408(2)
	138(0),274(1),410(2)
	168(0),304(1)
	208(1),310(2),412(3)
	238(1),340(2),442(3)
	240(1),342(2),444(3)
	344(1,1);480(2,1);446(1,2)
	374(1,1);476(1,2)
	376(1,1);478(1,2)
	166
	150(0),286(1)
	152(0),288(1)
	372(0,2)
	306
	224
	170(0), 338(1)
	440
	338
	336(1), 474(2)
	368
	370
	406
	402
	400

showing two separate decomposition steps in the temperature ranges of 250−280 and 600−650 °C.

The pyrolysis mass spectra of PXM and PXD were recorded by using both EI and CI ionization modes. Pyrolysis products appear as molecular ions (M^+) in EI spectra and as protonated molecular ions (MH^+) in the CI spectra; thus, it is possible to distinguish them from fragment ions.

The 18 eV EI and the isobutane CI mass spectra of the thermal degradation products, evolved at the TIC maximum (270 °C) of PXM, are shown in Figure 2. The structural assignments of the most intense molecular ions are given in Table 1. It can be noted that all pyrolysis compounds detected have $-CH_3$, $-CH_2SH$, and $-CH{=}S$ as end groups.

The base peak in Figure 2 are due to the ion at *m/z* 105, which corresponds to *p*-xylene. *p*-Xylene gives the tropilium-type ion by EI and does not give the protonated ion in our CI conditions.

The ion at *m/z* 137, corresponding to the MH^+ ion of *p*-methylthiobenzaldehyde, is present in the CI spectrum (Figure 2b) with higher intensity with respect to the EI spectrum (Figure 2a). Some of the ions appearing in the spectra can be assigned to pyrolysis com-

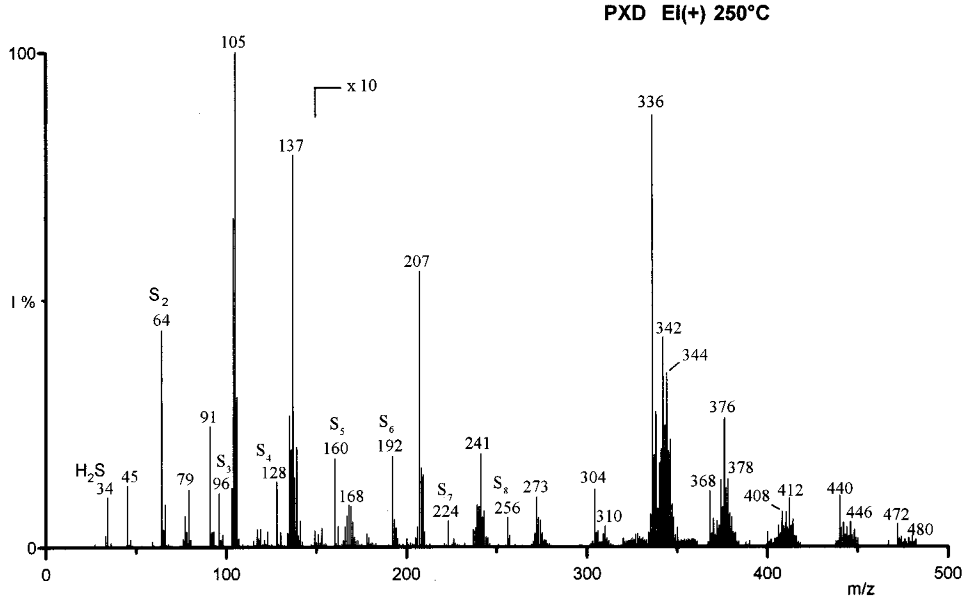
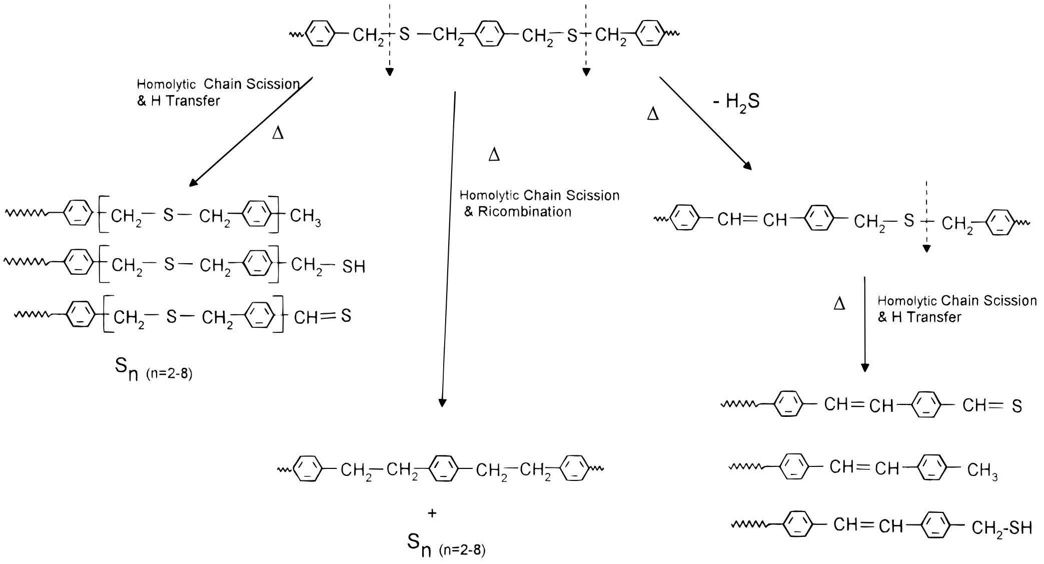


Figure 3. EI 18 eV pyrolysis mass spectrum of PXD obtained by DPMS at 250 °C.

Scheme 1. Thermal Degradation Processes of PXM and PXD in the Temperature Range of 250−350 °C



pounds containing intact xylylene sulfide units. Ions bearing a stilbene-like structure have also been detected with noticeable intensity, together with ions containing both units in the chain (Table 1).

Peaks at *m/z* 64, 96, 128, 160, 196, 228, and 256 are present (although with low intensity) in the EI mass spectrum in Figure 2a and show nominal mass and isotopic distribution typical of pure sulfur species, S_2−S_8, respectively. Sulfur is also evolved as H_2S (peak at *m/z* 34 in Figure 2a).

Pure sulfur species are absent in the CI mass spectrum of PXM (Figure 2b) because they are not ionized by the isobutane CI plasma.[22]

The EI mass spectrum of poly(xylylene disulfide) (Figure 3) obtained at 250 °C (temperature at the TIC maximum) shows pretty much the same thermal degradation products of PXM, except for the last 10 compounds listed in Table 1, which contain the xylylene disulfide bridge charactecistic of PXD, and except for the higher intensity of the peaks corresponding to pure sulfur species.

The pyrolysis products detected by DPMS in the first degradation step of PXM and PXD (Table 1) can originate from the two types of thermal cleavage reactions, as shown in Scheme 1. It is believed that a first type of thermal cleavage occurs by a homolytic chain scission at the C−S bond, followed by hydrogen transfer reactions, which generate several oligomers containing the xylylene sulfide repeating units, each terminated by three types of end groups: $-CH_3$, $-CH_2SH$, and $-CH{=}S$. The latter type of end group (i.e., thioaldehyde) has already been found among the pyrolysis products of other sulfur polymers.[16] Pure sulfur species may arise from this process or by an alternative route, which may also produce ethylene groups along PXM and PXD chains (Scheme 1).

Pyrolysis compounds containing stilbene units may be formed through a different cleavage process, which involves the elimination of H_2S from the poly(xylylene sulfide) main chain (Scheme 1). These units can quickly undergo isomerization and cross-linking to form thermally stable polycyclic aromatic structures, which produce the high amount of char residue observed for PXM and PXD (see below).

Although the thermal degradation processes in Scheme 1 appear to occur almost simultaneously, the evolution

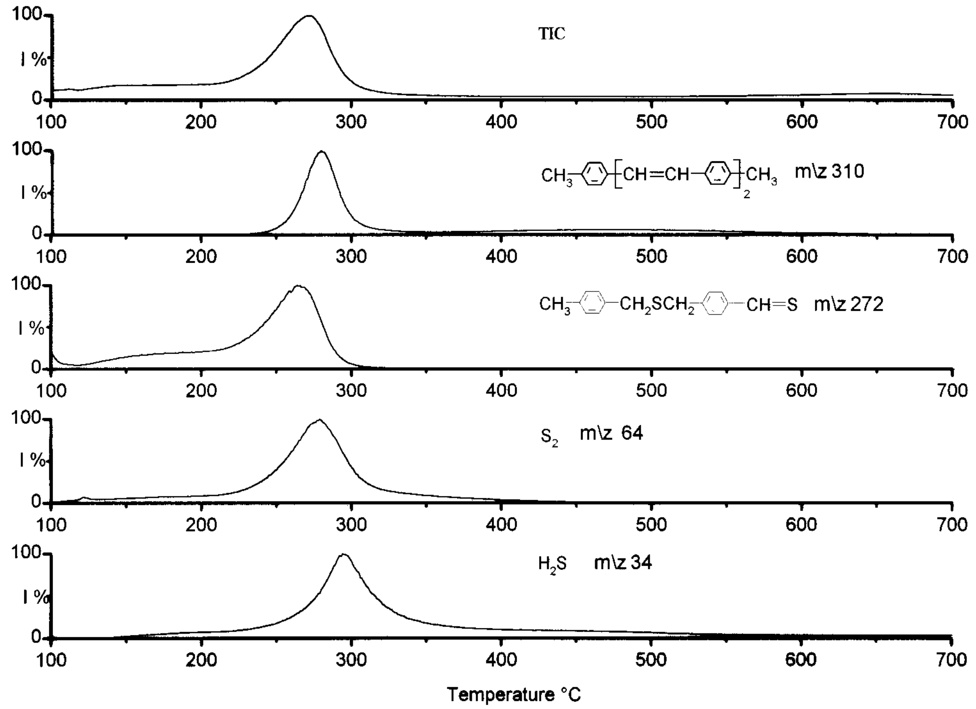


Figure 4. Total ion current curve and temperature–time-resolved evolution profiles of the ions at *m/z* 34, 64, 272, and 310 obtained by DPMS of PXM.

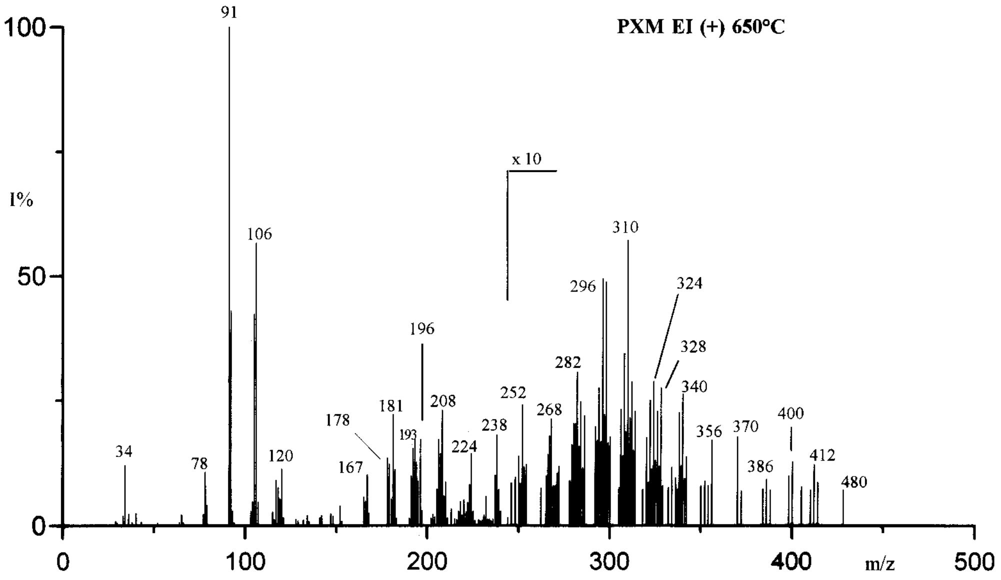


Figure 5. EI 18 eV pyrolysis mass spectrum of PXD obtained by DPMS at 650 °C.

profiles of the single pyrolysis species show that the formation of stilbene units occurs slightly later with respect to pyrolysis compounds with the original structures of PXM and PXD.

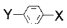
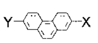
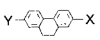
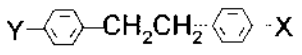
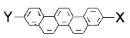
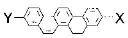
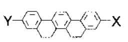
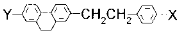
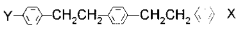
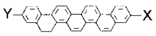
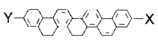
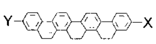
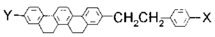
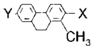
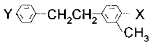
Inspection of the temperature-time-resolved single-ion curves of the pyrolysis compounds evolved in the DPMS of PXM (Figure 4) shows that pyrolysis compounds bearing the original repeating unit of PXM, e.g., the ion at *m/z* 272, have an early evolution profile with respect to ions with stilbene units, e.g., the ion at *m/z* 310. The evolution profiles of the pure sulfur species are coincident with the TIC trace (in Figure 4 is showed only the ion at *m/z* 64 as an example), whereas the maximum of the evolution profile of H_2S is shifted toward higher temperature (about 300 °C) with respect to sulfur.

Therefore, these data indicate that the initial weight loss observed in the TG curves (Figure 1) is due to the initial formation of compounds bearing the repeating units of PXM or PXD and that sulfur species are generated by pyrolysis in the first thermal degradation stage. The presence of residual impurities of pure sulfur species in PXM and PXD samples can be excluded because, under our DPMS conditions (high vacuum and slow heating rate),[3,15,32–34] they would evolve at lower temperature before polymer degradation.

When the temperature increases slightly, the elimination of H_2S from the PXM backbone becomes favored, and compounds bearing the stilbene unit are generated. Since the latter may quickly aromatize and cross-link, the weight loss from PXM and PXD is almost stopped on going to higher temperature (Figure 1a).

TG traces in Figure 1a show that, at about 600–650 °C, PXM and PXD experience another weight loss. In Figure 5 is shown the EI mass spectrum of the thermal degradation products of PXM generated at 650 °C, and

Table 2. Pyrolysis Compounds Detected in the DPMS, at 650 °C, of PXM and PXD

	X,Y					
Stucture	H,H	H,CH_3	H,C_2H_5	CH_3,CH_3	CH_3,C_2H_5	C_2H_5,C_2H_5
	78	92	106	106	120	134
	178	192	206	206	220	234
	180	194	208	208	222	236
	182	196	210	210	224	238
	278	292	306	306	320	334
	280	294	308	308	322	336
	282	296	310	310	324	338
	284	298	312	312	326	340
	286	300	314	314	328	342
			410	410		
	384	398	412	412		
	386	400	414	414	428	
	388					
						250
						252

the tentative structural assignments of the most intense molecular ions are reported in Table 2. It can be noted that these pyrolysis compounds show condensed aromatic structures with H, CH_3, and C_2H_5 as end groups, which may be generated by the homolytic chain scission and hydrogen transfer of ethyl units generated in the first degradation step (Scheme 2).

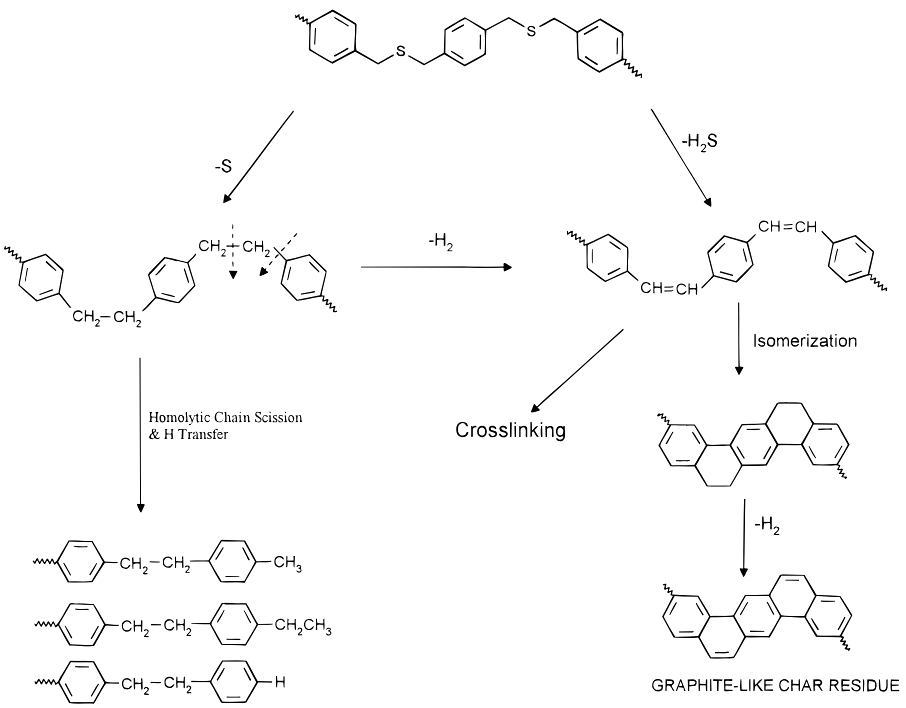
The two most intense peaks in Figure 5 are due to the ions at *m/z* 91 (tropylium ion) and 106, corresponding to toluene and ethylbenzene, respectively. Of course, the ion at *m/z* 91 can arise from the EI fragmentation of other alkyl aromatics as well as from toluene. The other peaks in the spectrum are assigned to condensed aromatic molecules that may be generated from the isomerization of stilbene units to dihydrophenantrene and the successive aromatization, as described in Scheme 2. An alternative route might be the direct aromatization of stilbene units with H_2 loss. However, it is well known that stilbene itself generates phenanthrene by isomerization to dihydrophenanthrene and subsequent dehydrogenation.[35-38] Dihydrophenanthrene has been found when stilbene was irradiated in the absence of oxygen.[36]

The analysis of the evolution profiles of the single species lends support to this interpretation. In Figure 6 is reported the TIC curve of PXM in the temperature range 400−700 °C, together with the evolution profiles of the ions at *m/z* 298, 296, 294, and 292, corresponding to pyrolysis compounds with an increasing degree of aromatization. It can be noted that pyrolysis compounds containing dihydrophenanthrene units are evolved at an earlier stage with respect to the pyrolysis compounds containing phenanthrene units. In fact, the ion at *m/z* 292, which corresponds to a molecule containing only aromatic units, shows the evolution maximum at the highest temperature (700 °C, Figure 6).

The second stage of weight loss, occurring at 600−650 °C (Figure 1a), is therefore due the volatilization of imperfect fragments of graphite-like structures generated in the aromatization process of the char residue. When the aromatization and cross-linking reactions are completed, the residue becomes resistant to temperature, and this accounts for the high amount of char residue left in the second stage of weight loss (Figure 1a).

Elemental Analysis of the Char Residue. From the structures drawn in Table 2, it can be seen that sulfur-containing compounds are absent in the spectrum recorded at 650 °C, suggesting that sulfur has been stripped off from the decomposing polymer, together

Scheme 2. Thermal Degradation Processes of PXM and PXD in the Temperature Range of 600−650 °C



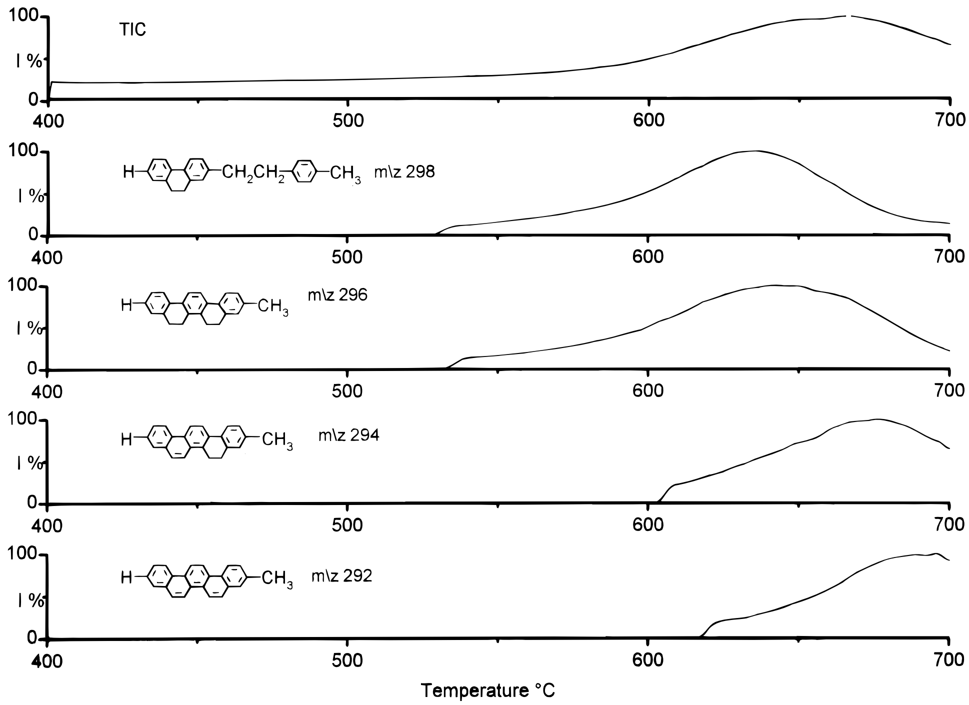


Figure 6. Total ion current curve and temperature−time-resolved evolution profiles of the ions at *m/z* 298, 296, 294, and 292, obtained by DPMS of PXM, in the temperature range of 400−700 °C.

with the volatiles generated at lower temperature.

To ascertain if sulfur is still contained in the char residue, elemental analysis was performed on the residue obtained by heating a PXM sample in a TG apparatus up to 800 °C.

The analytical results for the original sample of PXM were as follows. Calcd for $(C_8H_8S)_n$: C, 70.6; H, 5.9; S, 23.5. Found: C, 71.7; H, 5.7; S, 22.9.

For the char residue of PXM, the following analytical results were found: C, 91.8; H, 1.5; S, 6.6. The carbon and hydrogen data indicate, therefore, that a marked aromatization has occurred in the residue, with formation of polycyclic aromatic structures. The sulfur content of the PXM char residue is drastically reduced: only 30% of the original sulfur was retained in the residue.

A similar behavior has been observed[21] in the case of another aromatic sulfur polymer, poly(phenylene sulfide), where the residue obtained at high temperature was found to have a graphite-like structure, from which the bonded sulfur tends to be almost completely extruded.

Flash Pyrolysis GC/MS. The thermal degradation behavior of the two sulfur polymers, PXM and PXD, was also studied by flash pyrolysis in combination with gas chromatography (GC) and mass spestrometry (MS) in order to achieve separation and identification of the low-molecular-weight products formed. Flash pyrolysis was performed at two different temperatures, 358 and 610 °C. Mass spectrometry was run in the EI mode at 70 eV.

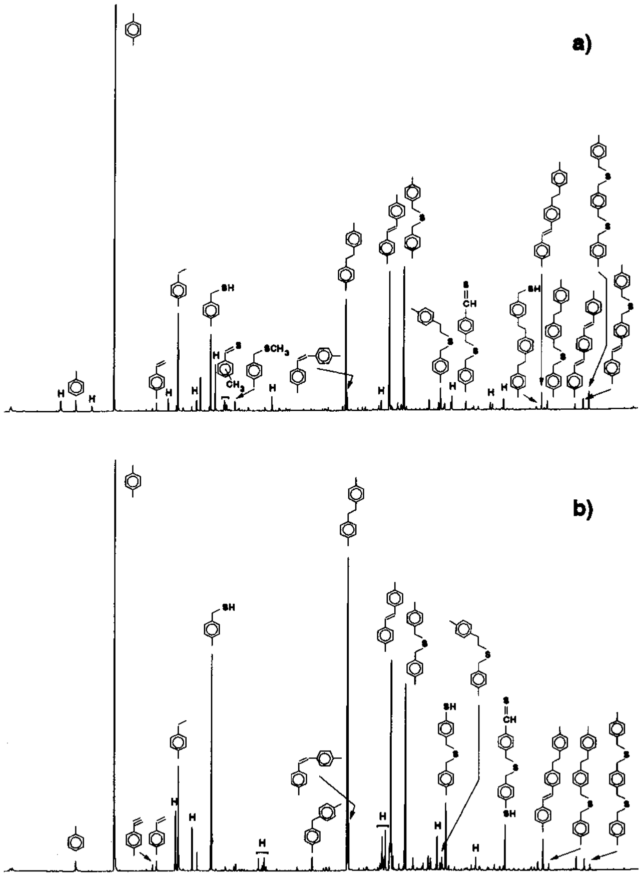
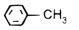
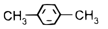
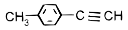
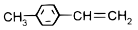
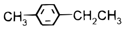
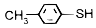
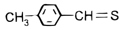
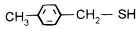
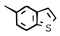
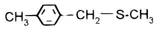
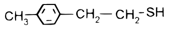
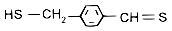
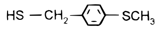
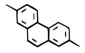
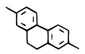
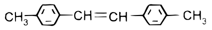
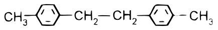
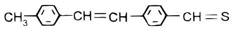
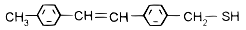
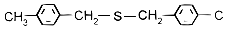
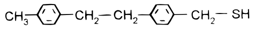
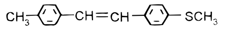
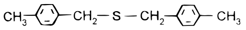
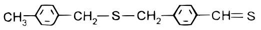
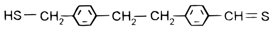
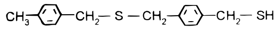
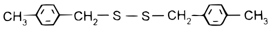
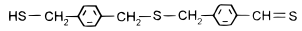
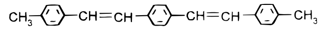
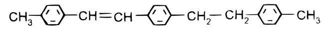
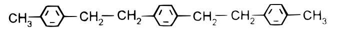
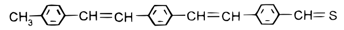
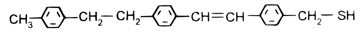
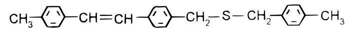
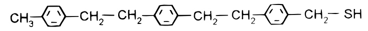
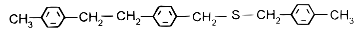
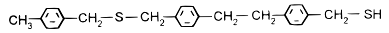
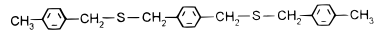
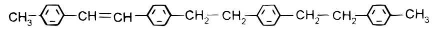
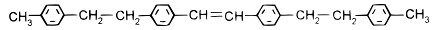


Figure 7. Gas chromatograms of the flash pyrolysates (Curie temperature, 610 °C) of (a) PXM and (b) PXD. Halogen-containing compounds are indicated by "H".

Figure 7 shows the gas chromatograms of the flash pyrolysates (Curie temperature, 610 °C) of PXM and PXD, respectively. Analysis of the pyrolysis products by MS revealed that the composition of the pyrolysates of both polymers is almost identical. Clearly, both pyrolysates are dominated by 1,4-dimethylbenzene (*p*-xylene). Low-molecular-weight aromatic products (i.e., benzene, styrene, and 4-ethyl-1-methylbenzene) as well as elemental sulfur (S_8) were absent in the pyrolysate. Toluene was detected in trace amounts. In general, the pyrolysates are composed of products bearing the repeating units of PXM and PXD with $-CH_3$, $-CH_2SH$, and $-CH{=}S$ end groups. An overview of the main pyrolysis products, together with their spectral properties and their relative abundances in the pyrolysate, is

Table 3. Molecular Ions and Base Peaks of Pyrolysis Compounds Detected in the Py-GC/MS (610 °C) of PXM and PXD

	91	92	tr.
	91	106	+++
	115	116	tr.
	118	118	+
	91	120	++
	91	124	tr.
	135	136	tr.
	105	138	++
	147	148	tr.
 or 	105	152	tr.
	167	168	+
	105	184	tr.
	206	206	+
	193	208	+
 (Z and E)	208	208	++
	105	210	++
	238	238	tr.
 (Z and E)	240	240	tr.
	105	242	++
	105	242	+
	207	254	tr.
	105	256	+
	105	272	tr.
 or 	239	272	+
	105	274	+
	104	304	tr.
 (E/E)	310	310	+
 (Z and E)	207	312	+
	209	314	tr.
	340	340	tr.
 (Z and E)	105	344	tr.
 (Z and E)	207	344	++
	312	346	tr.
	105	346	++
	105	378	++
	105	378	tr.
 (Z or E)	207	416	tr.
 (Z or E)	311	416	tr.

given in Table 3, and it reveals a generally good agreement with the results obtained by DPMS. Thus, upon pyrolysis, the sulfur linkages present in the polymers are partly evolved as low-molecular-weight sulfur-containing compounds, but obviously most sulfur species are trapped in the condensed residue remaining on the ferromagnetic wire and on the Pyrex glass tube in the pyrolysis unit. Halogen-containing compounds (Cl, Br) were ubiquitous among the pyrolysis products. Presumably, they can be ascribed to end groups deriving from the synthesis of the sulfur polymers, which involves the use of halogenated compounds.[24]

Analysis of the main pyrolysis products (as summarized in Table 3) reveals that the intense m/z 105 fragment in both the CI and EI spectra of the DPMS experiments can be only partly ascribed to 1,4-dimethylbenzene. Compounds bearing the repeating units of PXM and PSX also contribute substantially to this specific mass fragment.

The thermogravimetry experiments (Figure 1a) showed that the maximum rate of thermal decomposition takes place between 250 and 280 °C, much lower than the Curie temperature of 610 °C used for flash pyrolysis. Therefore, PXM was subjected to flash pyrolysis using a Curie temperature of 358 °C (Figure 8). The composition of the pyrolysate obtained at this lower temperature is virtually identical to that of the flash pyrolysate of 610 °C (cf. Figure 7a). The relatively higher amount of 1,4-dimethylbenzene in the 610 °C pyrolysate can be ascribed to a prolonged degradation of PXM at higher temperatures, which corresponds with the second weight loss between 600 and 650 °C as observed in the TG data (Figure 1a).

Formation of PAHs in the Pyrolysis Processes. Polycyclic aromatic hydrocarbons (PAHs) were detected by Py-GC/MS among the pyrolysis products, i.e., dimethyldihydrophenanthrene and dimethylphenanthrene (Table 3). These polycyclic aromatic products were found to be minor constituents of the pyrolysate. Moreover, penta- and hexacyclic aromatic compounds were not found to be present in the flash pyrolysates. Instead, DPMS data show clearly the presence of PAHs, up to heptacyclic PAHs (Table 2), in the second thermal degradation stage.

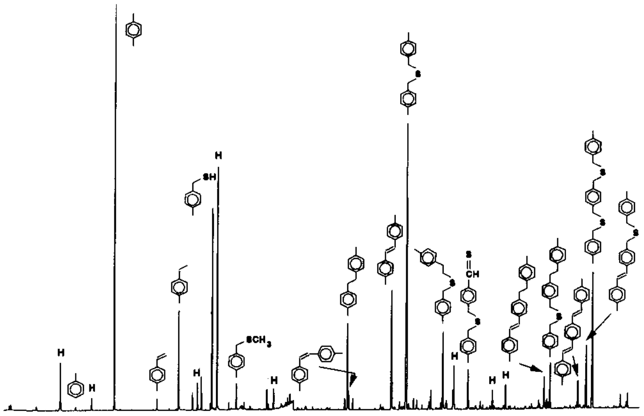


Figure 8. Gas chromatograms of the flash pyrolysate (Curie temperature, 358 °C) of PXM. Halogen-containing compounds are indicated by "H".

This discrepancy might be attributed to several different factors. First, the flash pyrolysis conditions used (i.e., heating of the ferromagnetic wire to its Curie temperature in <0.1 s) inhibit the formation of polycyclic aromatic products. This implies that the generation of stilbene units upon flash pyrolysis of the PXM and PXD polymers is less favored in comparison with DPMS, probably due to higher heating rates. Furthermore (Scheme 2), the stilbene units should have a *Z*-configuration to enable the cyclization and aromatization reactions leading to the formation of PAHs. This configuration seems to be thermodynamically least stable, altough the *Z* and *E* configurations are in equilibrium, and the consumption of form *E* will shift the equilibrium. The Py-GC/MS data show that the abundance of (*Z*) 1,2-(4-methylphenyl)ethene is approximately 4 times lower than that of its E-isomer (cf. Figure 7). Therefore, the relatively slow heating rates of the DPMS method are thought to favor the cyclization and aromatization reactions outlined in Scheme 2, leading to the formation of relatively higher concentrations of PAHs.

Alternatively, it may be thought that the higher molecular weight aromatic compounds are retained either in the pyrolysis unit or on the GC column. The latter explanation, however, can account only in part for the lower amounts of PAHs encountered in the flash pyrolysates, since the detection of high-molecular-weight PAHs (e.g., perylene) has been reported.[39]

Furthermore, in Py-GC/MS experiments, the PAHs are detected together with all the other pyrolysis products, whereas in DPMS, the PAHs are detected only in the second thermal degradation stage, i.e., on a pyrolysate fraction that does not contain the greatest part of the products evolving in the first pyrolysis stage of PXM and PXD, and this makes easier their detection.

It can be concluded that the results obtained by the DPMS and Py-GC/MS experiments show complementary data for the degradation products of PXM and PXD and, subsequently, shed light over the degradation mechanisms of these sulfur-containing polymers.

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