Synthesis, Characterization, and Thermal Degradation Studies on Group VIA Derived Weak-Link Polymers

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ABSTRACT: Polymers containing group VIA derived weak links, viz. poly(styrene disulfide) (PSD), poly(styrene tetrasulfide) (PST), and poly(styrene diselenide) (PSDSE), have been synthesized. The polymers PSD and PST were characterized by NMR, IR, UV, TGA, and fast atom bombardment mass spectrometric (FABMS) techniques. The presence of different configurational sequences in PSD and PST were identified by ^{13}C NMR spectroscopy. PSDSE, being insoluble in common organic solvents, was characterized using solid-state ^{13}C NMR (CP-MAS) spectroscopy. Thermal degradation of polymers under direct pyrolysis–mass spectrometric (DP–MS) conditions revealed that all the polymers undergo degradation through the weak-link scission. A comparative study of the pyrolysis products of these polymers with that of poly(styrene peroxide) (PSP) revealed a smooth transformation down the group with no monomer (styrene or oxygen) formation in PSP to only styrene and selenium metal in PSDSE. This trend of group VIA is explained from the energetics of the C–X bond (X = O, S, and Se) which also seems to be important in addition to the weak X–X bond cleavage. In PSP and PSD, the behavior is also explained from the energetics of the alkoxy and thiyl radicals. The unique exothermic degradation in PSP compared to endothermic degradation in PSD and PSDSE is explained from the nature of the products of degradation.

Introduction

With the ever growing use of polymers, their stability and longevity are increasingly becoming important. Unavoidable interaction of aerial oxygen during the commercial synthesis of vinyl polymers leads to the insertion of the weak peroxy linkages in the backbone[1,2] which drastically influence the stability of polymers, even though the peroxy content in the chain may be very small. In this context investigations on the thermal stability of weak-link-containing polymers would be more rewarding compared to their structural studies where the low concentrations of the weak links may not be significantly revealing. Extensive studies have been carried out on the mode of insertion of peroxy linkages in polymers.[1,3] On the other hand, unfortunately, our understanding on the complex phenomena pertaining to the effect of weak links on the thermal stability and photostability of polymers is very poor.[4,5] Besides the peroxy links, other weak links of group VIA elements, namely, the disulfide and diselenide linkages, also affect the thermal stabilities of the polymers.[6–8] We report here a comparative study as to how the weak links of group VIA elements influence the thermal degradation behavior of polymers.

We have selected in the present study the copolymers of styrene with the elements of group VIA, namely, poly(styrene disulfide) (PSD), poly(styrene tetrasulfide) (PST), and poly(styrene diselenide) (PSDSE); they are all new polymers. A comparison on the pyrolytic comportment of these polymers has been attempted with another structurally similar polymer of this family, namely poly(styrene peroxide) (PSP), whose degradation mechanism has been previously studied in this laboratory.[9–11]

Experimental Section

Synthesis of Polymers. PSD was synthesized by condensing styrene dibromide with aqueous Na_2S_2 solution. Styrene dibromide was prepared using a reported procedure.[12] The aqueous solution of sodium disulfide was made by heating a mixture of sulfur (0.0048 mol, 0.1536 g) and sodium sulfide nonahydrate (0.0048 mol, 1.152 g) in water (10 mL) at 70 °C for 15 min with stirring. To this aqueous solution, styrene dibromide (0.004 mol, 1.0558 g) in chloroform (10 mL) was added. Tetrabutylammonium bromide was then added to the reaction mixture as a phase transfer catalyst. The mixture was stirred at room temperature for 24 h. The chloroform layer was separated, washed several times with water, and dried with anhydrous sodium sulfate. The polymer was precipitated as a white powder when the above chloroform solution was poured into a large excess of methanol; the polymer was subsequently vacuum dried.

PST was similarly synthesized by condensing the styrene dibromide with aqueous Na_2S_4. The aqueous solution of Na_2S_4 was made according to the reported procedure.[13]

Elemental analysis data of PSD and PST are as follows. Calcd for PSD: C, 57.14; H, 4.76. Found: C, 56.39; H, 4.48. Calcd for PST: C, 41.37; H, 3.45. Found: C, 42.14; H, 3.63.

PSDSE was made by condensing styrene dibromide with aqueous Na_2Se_2 solution. The aqueous solution of Na_2Se_2 was made by the reaction of sodium borohydride with elemental selenium under N_2 atmosphere.[14] Sodium borohydride (0.079 mol, 3.0 g) in water (25 mL) was added with stirring to selenium (0.038 mol, 3.0 g) suspended in 25 mL of water at room temperature. After the initial vigorous reaction subsided, an additional equivalent of selenium (0.038 mol, 3.0 g) was added. The reaction mixture was stirred for 15 min and then warmed briefly to complete the dissolution of selenium. The brownish red aqueous solution of Na_2Se_2 was then ready for use. To this aqueous sodium diselenide solution, styrene dibromide (0.038 mol, 10.03 g) in chloroform (10 mL) was added. Tetrabutylammonium bromide was also added subsequently. The reaction mixture was stirred under N_2 atmosphere at room temperature. After 1 h the polymer was formed as a black powder which was filtered and vacuum dried.

Elemental analysis of PSDSE revealed that the polymer was mixed with a large amount of selenium metal.

Physical Measurements. ^{1}H and ^{13}C NMR spectra of both PSD and PST were recorded on a Bruker AC 200F NMR spectrometer as solutions in deuterochloroform and chloroform, respectively, with TMS as the internal standard. A capillary tube containing D_2O was placed inside the NMR tube which served as an external lock while recording the ^{13}C NMR spectrum. IR spectra in KBr pellets were recorded on a Hitachi 270–50 infrared spectrophotometer. UV spectral studies on polymer films were carried out on Hewlett-Packard 8452A diode array spectrophotometer. The polymer films were cast on the outer surface of a 1-cm quartz cell from a solution of the polymer in methylene chloride. The CP-MAS spectrum of the polymer PSDSE was recorded on a Bruker MSL solid-state NMR spectrometer operating at 75.47 MHz. The sample was spun in a Kel-F rotor at 3.46 kHz, and the spectral width employed was 25 kHz. The cross-polarization time was 1 ms, and the number

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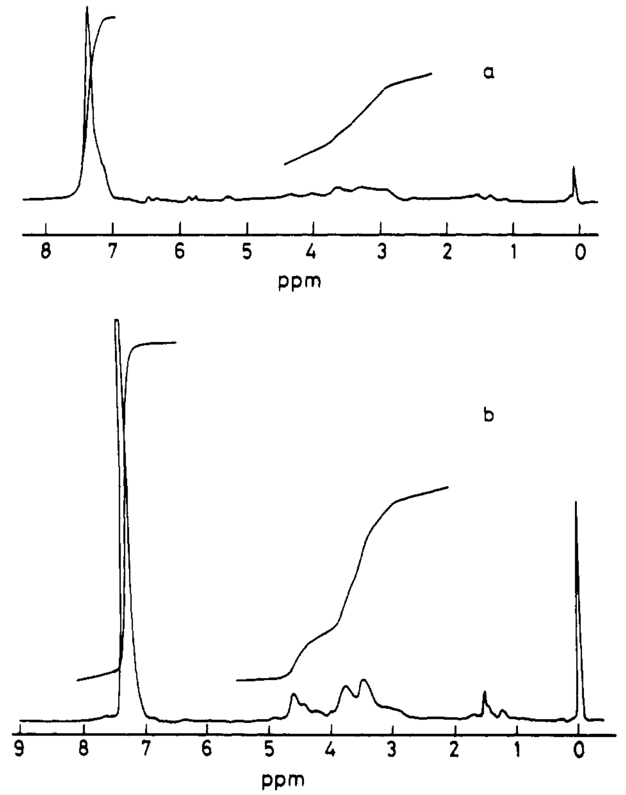
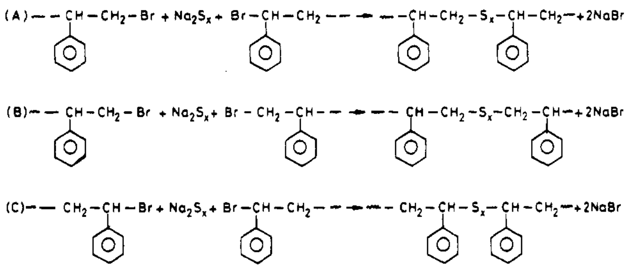


Figure 1. ^{1}H NMR spectrum of PSD (a) and PST (b) in $CDCl_3$.

Scheme I. Formation of Different Configurational Sequences: Head–Tail (A) Tail–Tail (B), and Head–Head (C) in PSD ($x = 2$) and PST ($x = 4$)



of scans was 17 664. Elemental analyses (C and H) were performed on a Heraeus elemental analyzer (CHN-O-Rapid). Thermogravimetric analysis was accomplished on a Perkin-Elmer TGS2 thermogravimetric analyzer at a heating rate of 20 °C/min. Pyrolysis was carried out using the direct insertion probe of a JEOL-JMS-DX-303-GC-mass spectrometer, heated from 50 to 400 °C at a heating rate of 16 °C/min. Electron impact (EI) mass spectra were obtained at 18 eV except for PSDSE. Chemical Ionization was performed using a Jeol D-300 mass spectrometer with methane as the reagent gas.

Results and Discussion

^{1}H and ^{13}C NMR Spectroscopy. The proton NMR spectra (Figure 1) of both PSD and PST were found to be similar. The ^{1}H NMR spectrum (recorded in $CDCl_3$) of both PSD and PST showed a broad absorption in the range 2.8–4.8 ppm for the CH and CH_2 protons along with the phenyl absorption at 7.0–7.4 ppm. The broad poorly resolved and merged CH and CH_2 peaks in the ^{1}H NMR spectra of both PSD and PST at 2.8–4.8 ppm can arise from two possibilities: firstly, when an aqueous solution of sodium disulfide or sodium tetrasulfide is made, to some extent it contains other sulfide anions, like mono, tri, etc.,[15] which will also get inserted into the polymer backbone during polymerization; secondly due to the different configurational sequences, i.e., head–head, head–tail, and tail–tail structures (Scheme I), present in the polymer. Besides, redistribution of different configurational sequences also occurs in the presence of aqueous sodium polysulfide.[15]

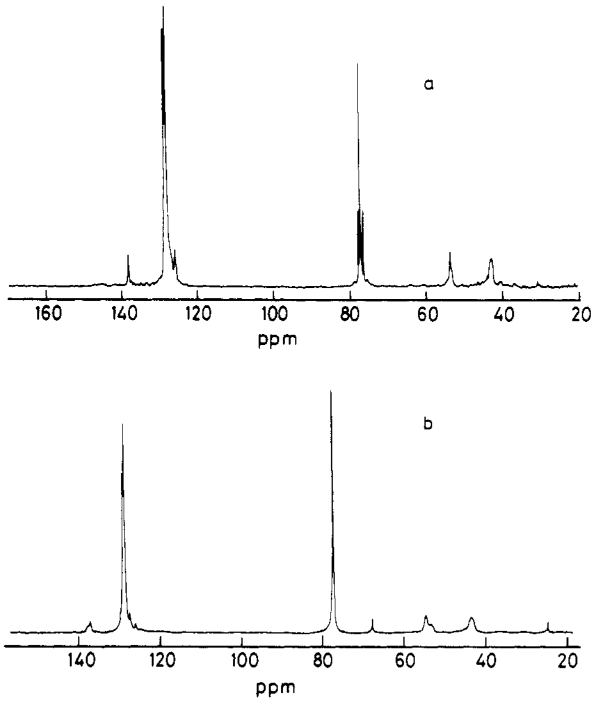


Figure 2. ^{13}C NMR spectra of PSD (a) and PST (b) recorded in $CHCl_3$. A capillary tube containing D_2O was kept inside the NMR tube for locking purpose.

The ^{13}C NMR spectrum (in $CHCl_3$) was recorded in both the off-resonance and broad band mode. In PSD (Figure 2a) the CH phenyl carbon resonances are found between 128.5 and 128.9 ppm with the aromatic quaternary carbon resonance at 138.5 ppm. The other two absorptions at 54.0 and 43.1 ppm are due to the backbone carbon atoms of CH and CH_2 groups, respectively. The ^{13}C NMR spectrum of PST (Figure 2b) revealed the phenyl CH carbons absorbing between 126.0 and 130.08 ppm, with the aromatic quaternary carbon absorption between 136.7 and 138.5 ppm. The CH and CH_2 carbons of the PST backbone are found to absorb at 54.4 and 43.3 ppm, respectively. The peak at 76 ppm in both the spectra is due to $CHCl_3$.

The presence of different configurational sequences in both PSD and PST (Scheme I) was studied using ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of PST (Figure 2b) shows a broad aromatic quaternary carbon peak with a fine splitting. Two peaks were also observed for the backbone CH carbon, but the CH_2 carbon was found to be insensitive to the existence of configurational sequences. These observations clearly reveal the presence of configurational sequences in PST. Surprisingly, the ^{13}C NMR spectrum of PSD (Figure 2a) did not show the presence of configurational sequences. Since the methods of synthesis of PSD and PST are similar, it is most likely that PSD also has configurational sequences similar to PST. However, its nonrevealation in the ^{13}C NMR spectrum is not understandable at present.

It may be pointed out that PSD synthesis has been attempted earlier by Todorova et al.[16] Unlike our ^{1}H NMR data which shows merging of CH and CH_2 protons, their data are well separated. The above difference in ^{1}H NMR spectrum seems to be due to the low molecular weight of the polymer which they would have veritably obtained as against the high molecular weight they have reported. This would have happened due to the presence of (α-chloroethyl)benzene in the reaction mixture which is a chain stopper. The merging of CH and CH_2 peaks in ^{1}H NMR seems to be characteristic of this system, because both

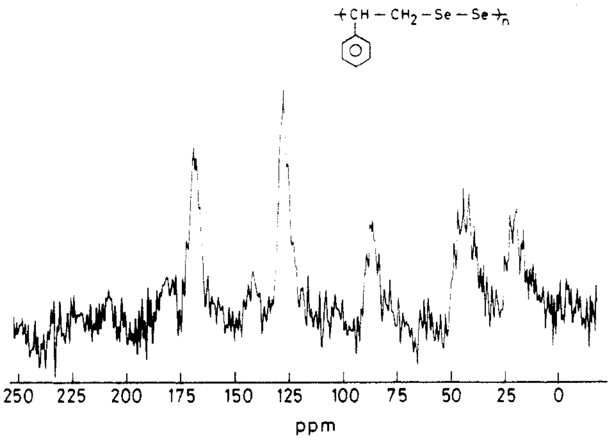


Figure 3. ^{13}C CP MAS NMR spectrum of PSDSE.

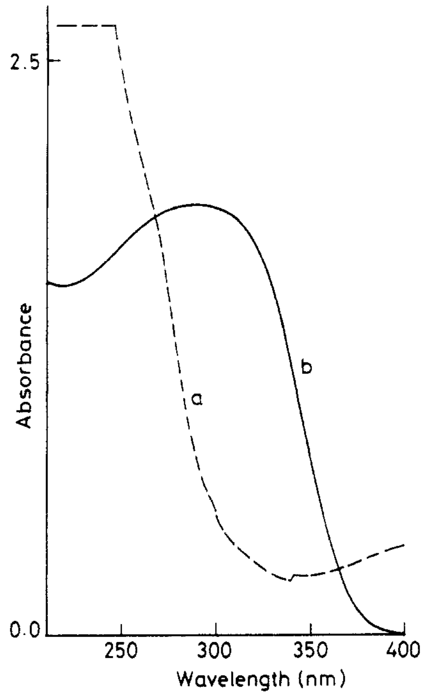


Figure 4. UV absorption spectra of PSD (a) and PST (b) films.

PSD and PST exhibit similar NMR pattern. Interestingly a similar poorly resolved and merged CH and CH_2 ^1H NMR spectrum has also been reported by Blight et al. for a particular fraction of styrene polysulfide.[17]

Since the PSDSE was not soluble in any common organic solvents, solid-state ^{13}C NMR (CP-MAS) spectrum (Figure 3) was recorded. Phenyl absorption at 126.6 ppm along with CH at 43.9 ppm and CH_2 at 19.1 ppm was observed. The peaks at 85.6 and 166.4 ppm are found to be due to the spinning side bands.

UV Spectroscopy. UV absorption spectra of PSD and PST showed a distinctly different pattern (Figure 4). While the absorption ended at 300 nm for PSD, it continued up to 390 nm in PST. In simple alkyl polysulfides, a similar effect is observed,[18] like for example in benzyl disulfide the absorption is observed up to around 300 nm but for benzyl tetrasulfide the absorption extends up to 350 nm with a shoulder around 300–350 nm.[19] The occurrence of such a bathochromic shift in the UV spectra with increase in the number of sulfur atoms between the organic moiety is attributed to the strong sulfur–sulfur conjugation involving the d orbitals.[20] Since the UV absorption ends at 300 nm, it is concluded that the presence of higher sulfide linkages like tri, tetra, etc. are negligible in PSD. Hence, the broad ^1H NMR spectrum of PSD at 2.8–4.8 ppm can be attributed only to the different configurational sequences present in the polymer backbone.

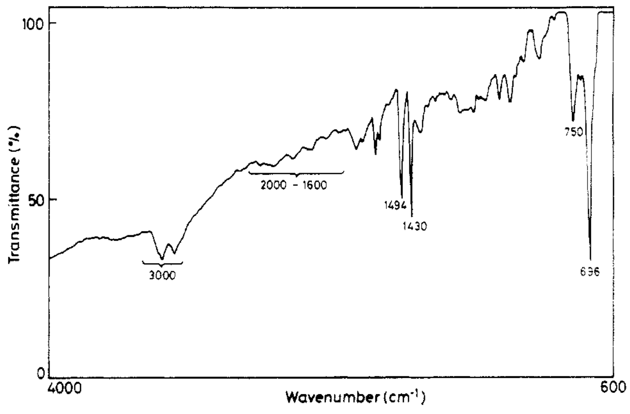


Figure 5. IR spectrum (KBr pellet) of PST.

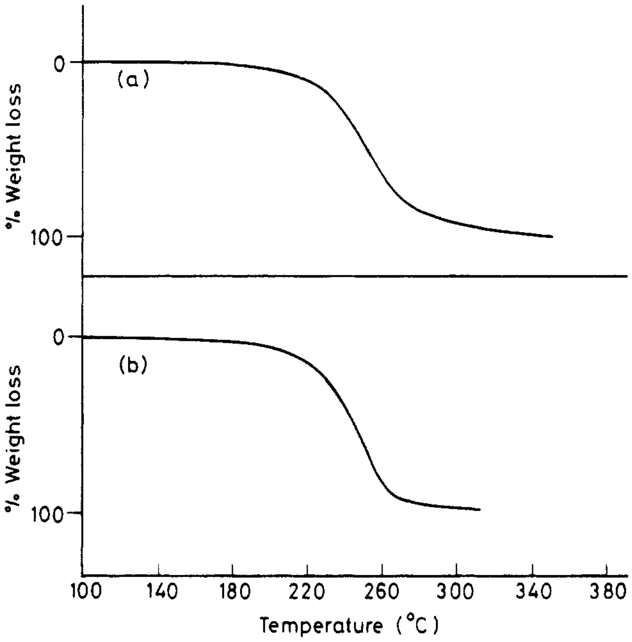


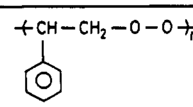
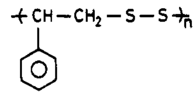
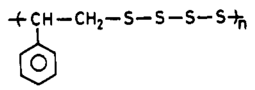
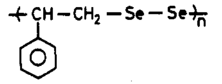
Figure 6. Dynamic TGA traces of PSD (a) and PST (b).

IR Spectroscopy. Like ^1H NMR, the IR spectra (Figure 5) of both PSD and PST are similar (IR spectrum of PSD is not presented). This is due to the fact that both C–S and S–S vibrations are very weak, and the vibrations of only the organic moiety are observed. IR bands around 3000, 1494, and 1452 cm^{-1}, showed the presence of phenyl group, with overtones from 1600 to 2000 cm^{-1}, and strong bands at 696 and 723 cm^{-1} revealed that the phenyl group is monosubstituted.

Thermogravimetry. The thermal stabilities of PSD and PST were studied from the thermograms recorded under N_2 atmosphere at a heating rate of 20 °C/min (Figure 6). Temperatures of the onset of polymer degradation are given in Table I. It is found that both PSD and PST are more stable compared to PSP. TG analysis of PSDSE was not performed due to the presence of a large amount of selenium metal mixed with the polymer.

Mass Spectrometry. In the direct pyrolysis–mass spectrometric (DP–MS) technique,[21] the sample is introduced through the direct insertion probe, and the temperature is gradually increased up to a point at which thermal degradation of the polymer occurs; the emanated volatiles are then ionized and detected. Under these conditions the mass spectrum of the polymer will be generally a mixture of compounds produced from pyrolysis. For detailed mechanistic information on the process of thermal degradation, the mass spectra are scanned repetitively during pyrolysis, stored, and analyzed. The advantage of examining such successive scans consists in

Table I. Structure and TGA Data of the Polymers Containing Group VIA Linkages

code	structure	T_{onset}[a] (°C)
PSP	 $-\!\!\!\!(\mathrm{CH(C_6H_5)-CH_2-O-O})_n$	110[b]
PSD	 $-\!\!\!\!(\mathrm{CH(C_6H_5)-CH_2-S-S})_n$	220
PST	 $-\!\!\!\!(\mathrm{CH(C_6H_5)-CH_2-S-S-S-S})_n$	220
PSDSE[c]	 $-\!\!\!\!(\mathrm{CH(C_6H_5)-CH_2-Se-Se})_n$	

[a] Temperature of onset of decomposition was found from the initial weight loss in the TGA curve. [b] Reference 11. [c] Since the sample is mixed with significant amount of selenium metal, it is difficult to identify the onset of decomposition.

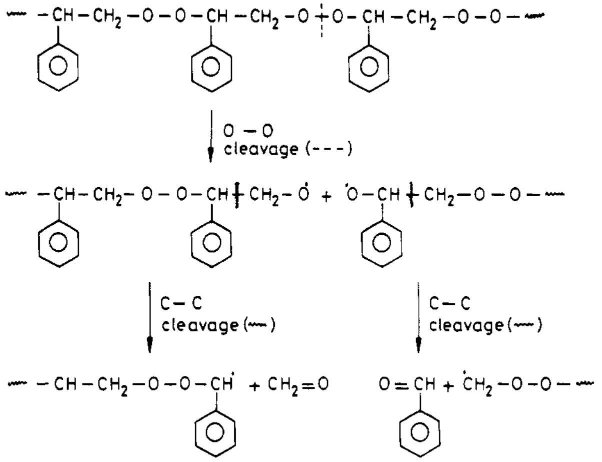
the possibility of identifying eventual differences among the spectra and to assign them to different processes of thermal degradation occurring at different temperatures. A general advantage of this technique is that the pyrolysis is achieved under high vacuum and therefore the thermal degradation products formed are volatilized and removed readily from the hot zone. Besides, the low probability of molecular collisions coupled with rapid detection reduces the occurrence of secondary reactions to a large extent and, hence, primary pyrolysis products are exclusively detected which are important in studying the primary thermal degradation mechanism. Furthermore, since pyrolysis is accomplished very close to the ion source, the problem of transport does not exist and the fragment of high mass, often essential for the structural characterization of the polymer, can be detected which are generally lost in other techniques. The only disadvantage of this method is that the molecular ions of the thermally formed products are always mixed with the fragment ions generated due to the electron impact. By use of soft ionization techniques, like chemical ionization mass spectrometry (CI-MS) in the positive mode, the molecular ions are identified by the characteristic MH^+ ion peak.

During condensation polymerization, the formation of cyclic oligomers also occurs to some extent. EI/CI-MS is suitable for the detection of such low molecular weight impurities present in the polymer samples since they are volatile under the high vacuum of the mass spectrometer at relatively low temperatures at which polymers do not degrade.[22] The oligomers are usually detected as separated peaks in the total ion current (TIC) curves much before the evolution of the products originating from the polymer pyrolysis. However, some of the higher molecular weight cyclic oligomers may not be volatile, and hence they are not seen by the MS distillation method. To overcome this problem, fast atom bombardment mass spectrometry (FABMS) is used where oligomers with a molecular weight up to about 1500 can be easily detected without heating the polymer sample.[23]

FABMS analysis has been done for both PSD and PST and they are not found to be mixed with any oligomers.

PSP. The DP-MS studies on PSP have been carried out in this laboratory, and it is observed that benzaldehyde and formaldehyde are the major products of degradation.[24] Under Py-GC conditions the same products are also formed in large amounts.[9] The rate controlling step in PSP degradation is the O-O bond cleavage resulting in the alkoxy radicals[9-11,25-28] which subsequently decompose to form benzaldehyde and formaldehyde (Scheme II).

Scheme II. Thermal Degradation Mechanism of PSP[a]



[a] (〰) and (- - -) represent the bonds which are broken for that particular reaction.

PSD. The electron impact (EI) and methane chemical ionization (CI) mass spectra of the pyrolysis products of PSD are reported in parts a and b of Figure 7, respectively. The structural assignments of the molecular ion peaks appearing in both the spectra are given in Table II. In the CI spectrum (Figure 7b) the peaks at *m/z* 105 and 137 are assigned to MH^+ ions of styrene and stryene sulfide, respectively. Since sulfur is not ionized by methane plasma, peaks due to sulfur is not detected in the CI spectrum. However, a peak at *m/z* 64 in the EI spectrum (Figure 7a) clearly revealed the formation of sulfur (S_2) as one of the major degradation products. The pathway by which the formation of styrene, styrene sulfide, and sulfur occurs from PSD is shown in Scheme III. Since styrene is formed in large amounts (base peak), it is inferred that the weakest bond in the polymer backbone is the C-S bond. This is also true in simple organic disulfides where the C-S bond is found to be much weaker than the S-S bond.[29] The formation of S_2 from PSD is easily expounded from the fact that when sulfur is heated, S_2 is the major product.[30]

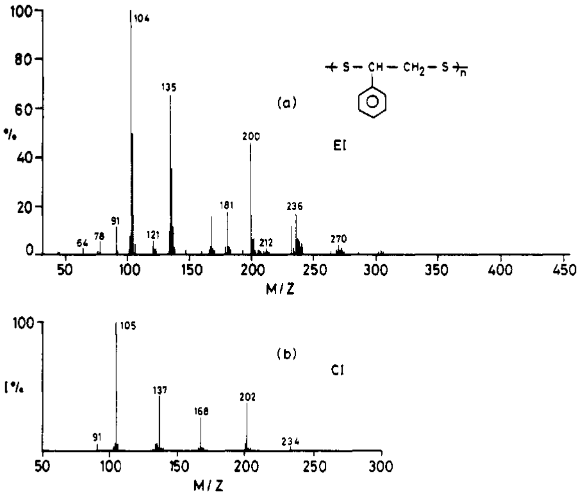
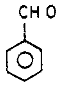
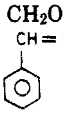
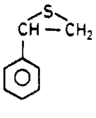
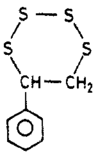


Figure 7. Mass spectra of PSD: (a) EI and (b) methane CI.

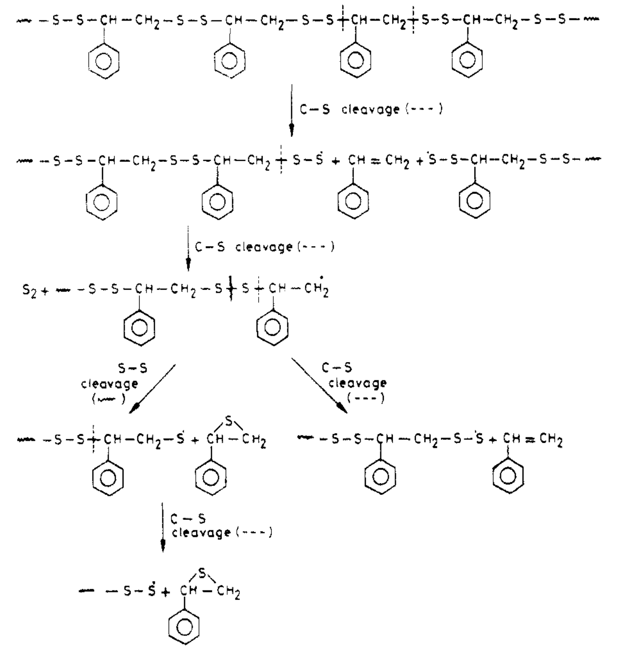
PST. The EI and CI mass spectra of the pyrolysis products of PST are shown in parts a and b of Figure 8, respectively. Analysis of these spectra reveals that along with styrene, styrene sulfide, and sulfur, a new compound, with *m/z* 232 in the EI spectrum and appearing at *m/z* 233 in the CI spectrum, is also formed which is assigned to a cyclic tetrasulfide (Table II). The evolution of these products from PST can be explained on the basis that the

Table II. Molecular Ions of the Thermal Degradation Products Observed in the DP-MS of Polymers Investigated

products	PSP	PSD		PST		PSDSE[c]
	M^+	M^+	MH^+	M^+	MH^+	M^+
	106[b]					
CH_2O	30[b]					
		104	105	104	105	104
		136	137	136	137	
S_2		64		64		
				232	233	
Se, Se_2						80, 156

[a] It may be noted here that since PSDSE is mixed with a considerable amount of Selenium metal, the DP-MS spectrum contains the fragment ions of Se_8 as well. [b] Reference 24.

Scheme III. Thermal Degradation Mechanism of PSD[a]



[a] (﹏) and (- - -) represent the bonds which are broken for that particular reaction.

central S–S bond, which is being weaker in a tetrasulfide compared to a disulfide,[31] cleaves and initiates the degradation process (Scheme IV). According to the chemistry of thiyl radicals, tetrasulfide ($RS_4^•$), trisulfide ($RS_3^•$), and disulfide ($RS_2^•$) radicals have similar energies.[32] It implies that the interconversion among $RS_4^•$, $RS_3^•$, and $RS_2^•$ can easily occur. This logic is clearly visible in Scheme IV where the transformation of these radicals from one to another readily occurs. Further, since S_2 is the most stable product,[30] the trisulfide radical will rearrange to form S_2 and monosulfide radical; the latter rearranges to styrene sulfide.

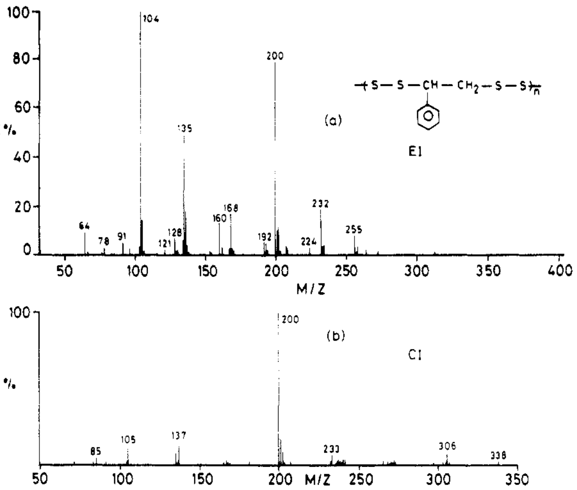
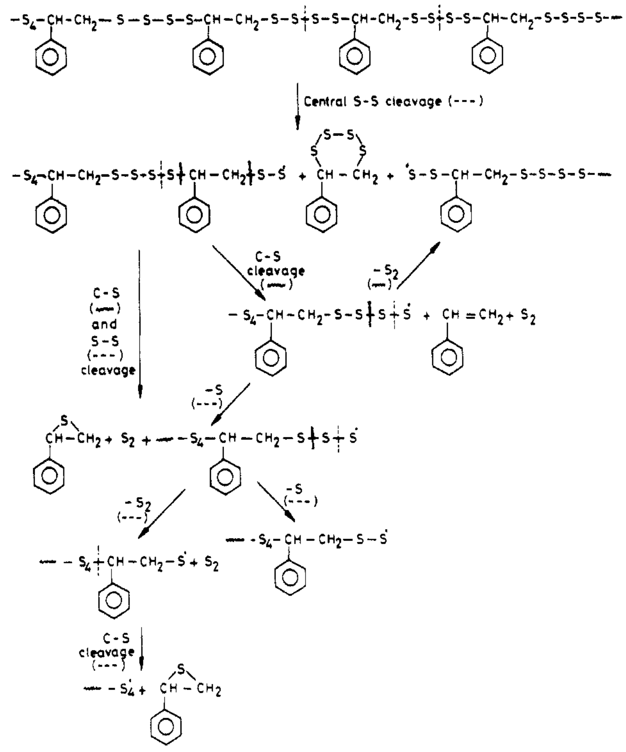


Figure 8. Mass spectra of PST: (a) EI and (b) methane CI.

Scheme IV. Thermal Degradation Mechanism of PST[a]



[a] (﹏) and (- - -) represent the bonds which are broken for that particular reaction.

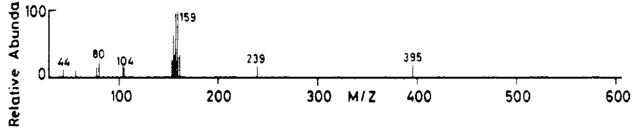


Figure 9. EI-MS (70 eV) spectrum of PSDSE.

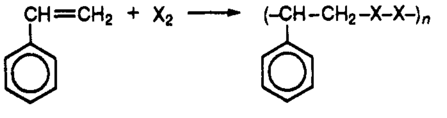
PSDSE. The PSDSE is very unstable compared to the other polymers of the group. The mass spectrum of PSDSE in shown in Figure 9. The major products are styrene and selenium metal. A majority of the simple diselenides on pyrolysis (eq 1) first form the monoselenides and then on continued heating yield organic compounds devoid of selenium.[33] In PSDSE a similar mechanism is most likely to operate, first forming the monoselenide and finally the styrene and selenium. In this polymer the initiation of degradation is most probably through the Se–Se cleavage.

$$RSeSeR \rightarrow RseR \rightarrow RR \qquad (1)$$

Due to the high instability of the C–Te and Te–Te bonds, poly(styrene ditelluride) could not be synthesized; its degradation pattern will hopefully be similar to PSDSE.

Group Behavior. The trend in the formation of pyrolysis products down the group VIA can be interpreted from the bond energy of C–X (X = O, S, and Se) in the polymer backbone. Since the C–O bond is strongest in PSP, we obtain aldehydes (formaldehyde and benzaldehyde) exclusively and there is no evidence for the formation of styrene monomer or oxygen. In PSD and PST the C–S bond is relatively weaker than the C–O bond of PSP and, hence, the formation of styrene and sulfur occurs along with the other thio compounds. In PSDSE, the C–Se, being the weakest in the group, results in the formation of styrene and selenium metal exclusively. The group behavior of these polymers can also be explained from the energetics of the radicals produced. Unlike PSP, the PSD and PST do not form corresponding thioaldehydes because thiyl radicals (RS$^\bullet$) differ significantly from the alkoxy radicals (RO$^\bullet$). Despite the proximity of sulfur and oxygen in the periodic table the energetics associated with the formation of >C=S are much less favorable than that of >C=O.[32]

Consider now the energetics of the degradation process. It is assumed here that thermochemically all these polymers can be produced from their respective monomers, i.e., styrene and the respective group VIA elements (eq 2).



(2)

X = O, S, and Se

In PSDSE we get back the selenium metal and styrene monomer; the degradation has to be necessarily endothermic since the polymerization process is exothermic. In contrast, the degradation products of PSP are entirely different from the monomers styrene and oxygen and it is perhaps a unique candidate in the group exhibiting unusual exothermic degradation.[34] The PSD, which falls between oxygen and the selenium in the group, shows an intermediate behavior where the degradation products are a mixture of monomers and thio compound. The DSC studies revealed that the PSD degradation is endothermic.

Conclusions

The present investigation exhibits a novel approach to understand the mechanism of polymer stability by deliberately introducing the weak links into the backbone. The most commonly found weak links in the polymers are the peroxy linkages which get inadvertently incorporated into the backbone during radical polymerization of vinyl monomers. A comparative study on the alternating copolymers of styrene and group VIA weak linkages, namely, peroxide, disulfide, tetrasulfide, and diselenide, has been made to get a general image of their pyrolytic behavior, which originates at the weak links. The spectrum of the pyrolytic products in these polymers, which differ significantly, revealed an interesting transformation down the group with respect to the monomer formation. In PSP neither styrene is formed nor oxygen is evolved. But in PSDSE only the monomers styrene and selenium metal are obtained. The PSD and PST show a mixed product spectrum which contains sulfur compounds in addition to the monomers styrene and sulfur. The unique exothermic degradation of PSP compared to other members can be attributed to the product formation, where the monomers are completely absent. The diverse nature of the products in these group VIA polymers emanates from the reactivity of the alkoxy radicals and thiyl radicals which differs significantly.

It is hoped that these studies may be useful for a better understanding of the general mechanism of degradation of commercial polymers where the weak links are often present.

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Supplementary Material Available: EI-MS (70 eV) spectrum of PSP (1 page). Ordering information is given on any current masthead page.

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