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Chemical Degradation of Poly(styrene disulfide) and Poly(styrene tetrasulfide) by Triphenylphosphine

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ABSTRACT: The chemical degradation of polysulfide polymers, viz., poly(styrene disulfide), PSD, and poly(styrene tetrasulfide), PST, has been achieved using triphenylphosphine, TPP. The reaction was monitored using ^{31}P NMR spectroscopy. The solubility analysis of the reaction residues reveals that while PSD degrades completely, PST on the other hand, undergoes complete degradation only when the concentration of TPP is increased. Moreover, the reaction of PST with TPP occurs at room temperature whereas PSD requires a higher temperature. The reaction products were analyzed using the direct pyrolysis mass spectrometric (DP-MS) technique, and their formation has been explained through an ionic mechanism.

Introduction

Polymers can be degraded by heat, radiation, mechanical energy, and chemicals. Among these, chemical degradation has been poorly studied. Chemical stability is necessary for a wider application of polymers. In spite of several applications of polysulfide polymers, such as adhesives, sealants, insulators, etc.,[1] studies on their chemical reactivity are very scarce in the literature. Such investigations are particularly attractive in assessing the stability of the S–S bond in different chemical environments. The reactivity of the S–S bond is also important from a biological point of view as it is present in the structures of many natural products and proteins.[2] Major reactions involving S–S linkages in such systems are bond cleavage by various species and disulfide interchange reactions. We report here how the widely used organic reagent triphenylphosphine (TPP) reacts with the S–S linkages in organic polysulfide polymers, namely, poly(styrene disulfide), PSD, and poly(styrene tetrasulfide), PST.

Experimental Section

The synthesis and characterization of both PSD and PST have been reported elsewhere.[3]

Desulfurization of Polymers. To PSD (0.168 g, 0.001 mol) in an NMR tube was added 5 mL of dry benzene. After complete dissolution, TPP (0.262 g, 0.001 mol) was added and the solution was mixed thoroughly. The progress of the reaction at different time intervals was monitored using ^{31}P NMR spectroscopy. The reaction was studied both at 30 °C and at 80 °C. For later studies, the reaction mixture was taken in a round bottom flask and refluxed over an oil bath.

PST was reacted with TPP under two different reactant ratios.

PST1. PST (0.058 g, 0.000 25 mol) and TPP (0.065, 0.000 25 mol) were taken in a 1:1 mole ratio.

PST2. PST (0.061 g, 0.000 26 mol) and TPP (0.130 g, 0.000 50 mol) were taken in a 1:2 mole ratio.

For both PST1 and PST2, the reaction was performed in the NMR tube itself at room temperature using benzene as solvent.

Analysis of the Reaction Products. After the reaction was over, the benzene solution was evaporated under vacuum and direct pyrolysis mass spectrometric (DP-MS) analysis of the residue was carried out to identify the products by heating the residue using a standard direct insertion probe for solid materials from 30 to 400 °C at a heating rate of 16 °C/min. Electron ionization was performed at 70 eV.

Measurements. ^{31}P-NMR experiments were carried out on a Bruker AC/(F) 200 NMR spectrometer; phosphoric acid which was used as the internal standard was taken in a sealed capillary tube and kept inside the NMR tube containing the reaction mixture. Mass spectrometric analyses were carried out on a JEOL-JMX-DX-303-GC-mass spectrometer.

Results and Discussion

^{31}P-NMR Spectroscopy. The ^{31}P-NMR spectra of the PSD–TPP reaction mixture at 30 °C and at different time intervals are given in Figure 1. The presence of only one peak at −6.0 ppm corresponding to TPP[3] indicates that no reaction has occurred at 30 °C even after 5 days. Figure 2 displays the ^{31}P-NMR spectra of the reaction mixture at different time intervals under reflux in benzene at 80 °C. In addition to the TPP peak, a new peak at 42.3 ppm appears, which is assigned to triphenylphosphine sulfide (TPPS) and is confirmed by comparing with the ^{31}P-NMR spectrum of pure TPPS.[4] With the increase in the time of reflux, the formation of TPPS increases (Figure 2). The peak at 25.4 ppm is due to triphenylphosphine oxide (TPPO).[4] Since the reaction was performed in air, partial oxidation of TPP could also have occurred, resulting in the formation of TPPO. Even in the desulfurization of simple trisulfides by TPP, formation of TPPO to some extent is observed.[5]

In PST (both PST1 and PST2), the reaction occurs immediately after mixing with TPP. This was confirmed from the ^{31}P-NMR spectrum (Figure 3) of the mixture immediately after mixing. The spectrum clearly reveals a large intense TPPS peak in comparison with that of the TPP. Like the PSD–TPP reaction, in the PST–TPP (both PST1 and PST2) reaction TPPO formation is also observed to some extent.

The reactivity difference between PSD and PST toward TPP is very similar to that of the simple organic

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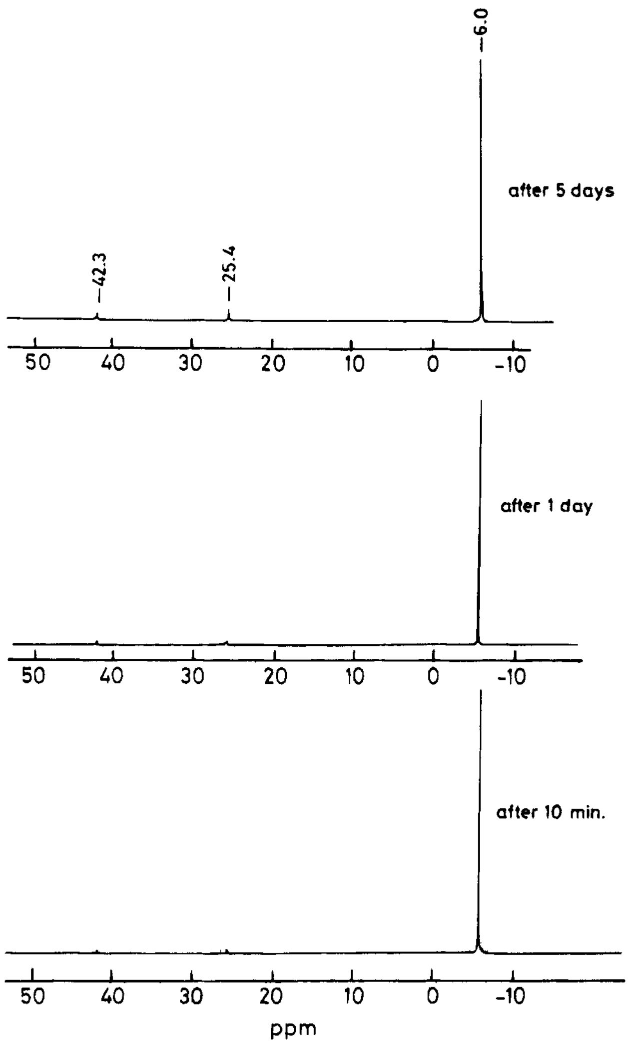


Figure 1. ^{31}P NMR spectra of the PSD–TPP reaction mixture (at 30 °C) recorded at different time intervals.

polysulfides–TPP reaction. For example, while benzyl disulfide does not undergo reaction with TPP (eq 1), benzyl trisulfide on the other hand reacts easily, forming the disulfide and TPPS (eq 2).[5]

$$\mathrm{PhCH_2SSCH_2Ph + PPh_3 \rightarrow Ph_3P^+{-}SCH_2Ph + PhCH_2S^- \nrightarrow PhCH_2SCH_2Ph + Ph_3PS} \quad (1)$$

$$\mathrm{PhCH_2SSSCH_2Ph + PPh_3 \rightarrow Ph_3P^+{-}SSCH_2Ph + PhCH_2S^- \rightarrow PhCH_2SSCH_2Ph + Ph_3PS} \quad (2)$$

The reason for the unreactivity of disulfides with TPP was attributed to the inability of the released mercaptide ion to displace phosphine sulfide from the sp^3-hybridized carbon.[5] The ^{31}P-NMR spectra of the mixtures of TPP with either PSD or PST (both PST1 and PST2) in benzene did not reveal the presence of significant amounts of the phosphonium salts. However, this does not preclude the existence of such species but merely indicates that they are too short-lived to accumulate in significant concentrations. It may be noted that nonrevelation of the presence of the phosphonium salt intermediate in the ^{31}P-NMR spectrum is also observed in the dibenzyl disulfide–TPP reaction.[5]

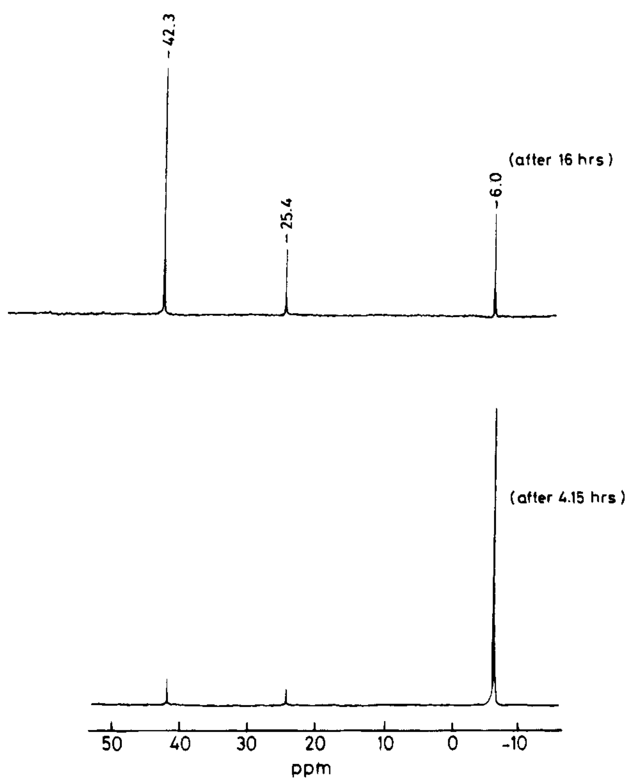


Figure 2. ^{31}P NMR spectra of the PSD–TPP reaction mixture at different time intervals under reflux at 80 °C.

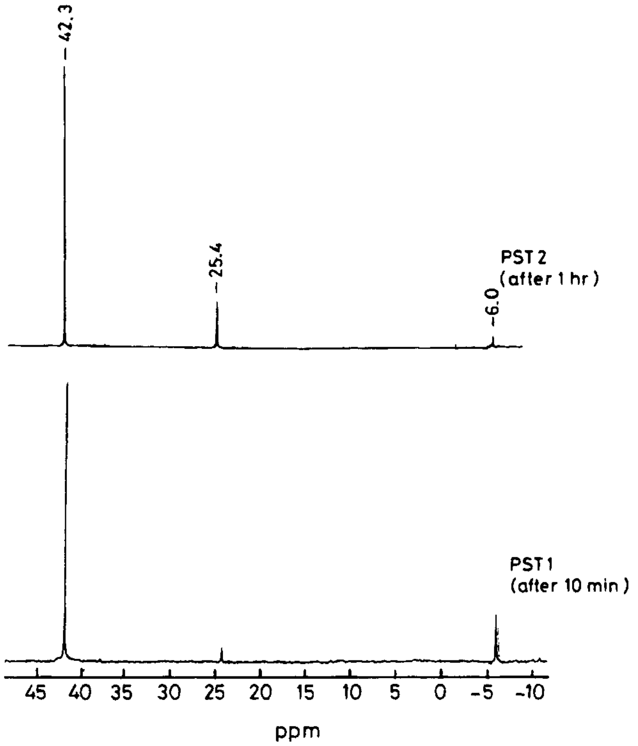


Figure 3. ^{31}P NMR spectra of the PST–TPP (both PST1 and PST2) reaction mixture recorded at room temperature.

Solubility. After the reaction was over, the benzene solution was evaporated under vacuum. The residue thus obtained was tested for its solubility in acetone. While the PSD–TPP reaction residue and the PST2 reaction residue were soluble in acetone, the PST1 reaction residue was insoluble in the same medium. It should be noted here that both the pure homopolymers PSD and PST are not soluble in acetone. On the basis

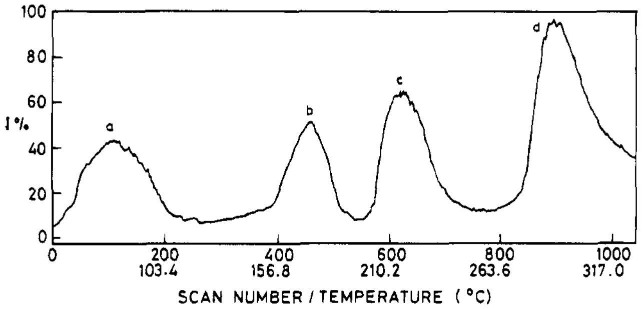
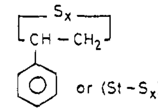
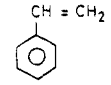
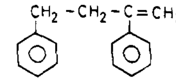


Figure 4. Total ion current (TIC) of the PSD−TPP reaction residue.

of the solubility data, it is inferred that while PSD has undergone complete degradation to smaller products, PST degrades completely only under PST2 reaction conditions.

Mass Spectrometry. In the direct pyrolysis mass spectrometric (DP-MS) method, the samples are introduced via the direct insertion probe of the mass spectrometer and the temperature is increased gradually. This mode of analysis is advantageous, as the sample is gradually heated under high vacuum and any volatiles formed during heating will be removed immediately from the hot zone and subsequently ionized and detected. The succession of such removal will depend upon the vapor pressure of the species present, i.e., the high molecular weight fragments will generally be removed at relatively higher temperatures. Unlike the GC−MS technique where there is every possibility of high molecular weight or polar compounds getting stuck in the column, in this method no such transport problem will arise since the heating is achieved very close to the ion source. Hence in the DP-MS method the compounds with different vapor pressures will evaporate at different temperatures, resulting in the total ion chromatogram (TIC) consisting of multiple single ion chromatograms (SICs) of the individual compounds. However, a problem arises when compounds of similar vapor pressures are present. In such a case the mass spectrum will be a mixture of the molecular ions and fragment ions of the individual components, thus making the spectrum complex. Many low molecular weight cyclic compounds, formed during polymerization reactions, have been detected by this MS distillation procedure.[6]

Table 1. Molecular Ions of the Reaction Products of PSD and PST with TPP Detected in the DP-MS Analysis

Structural assignments		PSD−TPP (M^+)	PST1 (M^+)	PST2 (M^+)
 or (St−S_x)	$x = 1$	136	136	136
	$x = 2$	168	168	168
	$x = 3$		200	200
	$x = 4$		232	232
Ph_3PS		294	294	294
S_n	$n = 2$		64	
	$n = 3$		96	
	$n = 4$		128	
	$n = 5$		160	
	$n = 6$		192	
	$n = 8$		256	
		104	104	104
		208		

PSD−TPP Reaction Residue. The TIC and mass spectra corresponding to the peak maxima of the individual SICs of the PSD−TPP reaction residue are given in Figures 4 and 5, respectively. The structural assignments of the molecular ions are displayed in Table 1. There are four SICs (represented as a, b, c, and d in Figure 4) in the TIC, reflecting that four major products are formed in the reaction. TPPS is the first compound to evaporate since the mass spectrum corresponding to the peak maxima of the first SIC contains the molecular ion peak of TPPS (*m*/*z* 294) as the base peak (Figure

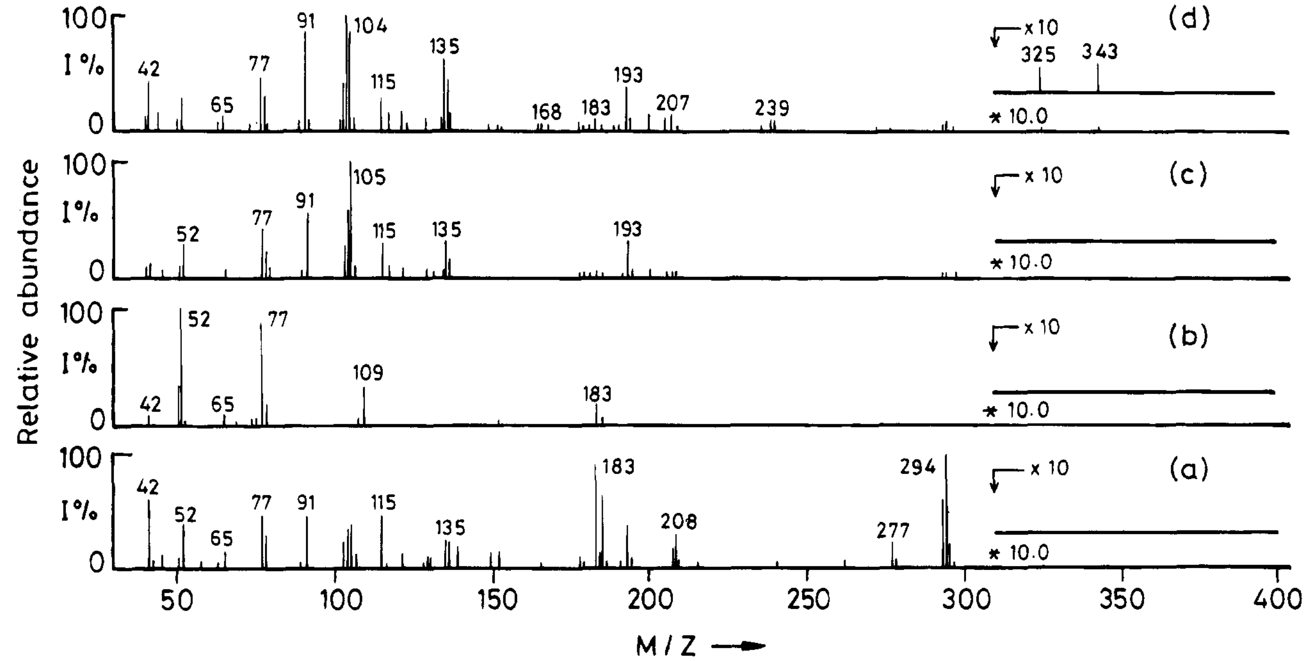


Figure 5. Mass spectra corresponding to the individual peak maxima observed in the TIC of the PSD−TPP reaction residue.

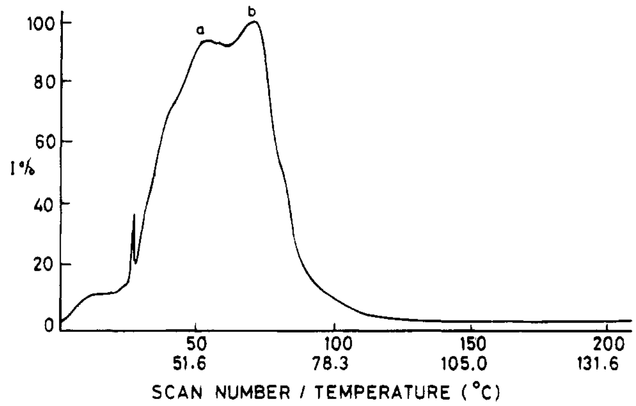


Figure 6. Total ion current of the PST1 reaction residue.

5a). This assignment is based on the comparison with the mass spectrum of the authentic TPPS sample.[7] We are not able to identify the second product since the peak corresponding to the maximum mass is *m*/*z* 109, which is a fragment ion (Figure 5b). The individual mass spectra corresponding to the peak maxima of the third and fourth SICs (Figure 5c,d) both conform to the presence of a mixture of styrene (*m*/*z* 104), styrene dimer (*m*/*z* 208), styrene sulfide (*m*/*z* 136), and a cyclic disulfide having the structure (St$-S_2$) (St = styrene unit) (*m*/*z* 168). To some extent the molecular ion peaks corresponding to styrene, styrene sulfide, and styrene dimer are also seen in the mass spectrum of the first SIC (Figure 5a) along with that of TPPS, reflecting that although TPPS evaporates to a major extent, the above three products also evaporate along with it to some extent.

The mechanism by which all these products are formed from PSD is given in Scheme 1. First, the formation of a phosphonium salt occurs followed by the mercaptide–disulfide interchange to give the cyclic disulfide which subsequently undergoes desulfurization by reacting with TPP to yield the styrene sulfide and TPPS. The styrene sulfide formed in turn undergoes desulfurization by TPP to yield styrene and TPPS. Under refluxing conditions, the styrene monomer formed dimerizes to yield the styrene dimer. Desulfurization of cyclic disulfides and episulfides by TPP is known in the literature.[8,9] Also to be noted is that the mercaptide–disulfide interchange reaction is very common among polysulfide polymers.[1]

PST1 Reaction Residue. The TIC of the PST1 reaction residue (Figure 6) is very different from the PSD–TPP reaction residue (Figure 4) in that no individual SICs are present here. But in the TIC two peak maxima are observed (a and b in Figure 6). This is due to the overlap of two SICs. From the mass spectrum corresponding to the two peak maxima (Figure 7a,b), the individual products were identified (Table 1). Apart from the cyclic disulfide, styrene sulfide, styrene, and TPPS (they are also formed in the PSD–TPP reaction), the other observed products include sulfur ((S_2, *m*/*z* 64), (S_3, *m*/*z* 96), (S_4, *m*/*z* 128), (S_5, *m*/*z* 160), (S_6, *m*/*z* 192), and (S_8, *m*/*z* 256)) and other cyclic sulfides having the structure (St$-S_x$) (x = 3 (*m*/*z* 200) and 4 (*m*/*z* (232)). Comparison of the mass spectra (Figure 7a,b) revealed that the peak at *m*/*z* 294 (molecular ion peak of TPPS) has a higher intensity in the first spectrum (Figure 7a) than in the second (Figure 7b). From these data, it is concluded that first TPPS evaporates to a major extent followed by the other compounds.

PST2 Reaction Residue. The TIC of the PST2 reaction residue is presented in Figure 8. Although no individual SICs are present in the TIC, from the pattern of the TIC there appears to be an overlap of three SICs whose peak maxima are represented as a, b, and c in Figure 8. The individual mass spectra corresponding to the three peak maxima are given in Figure 9. From

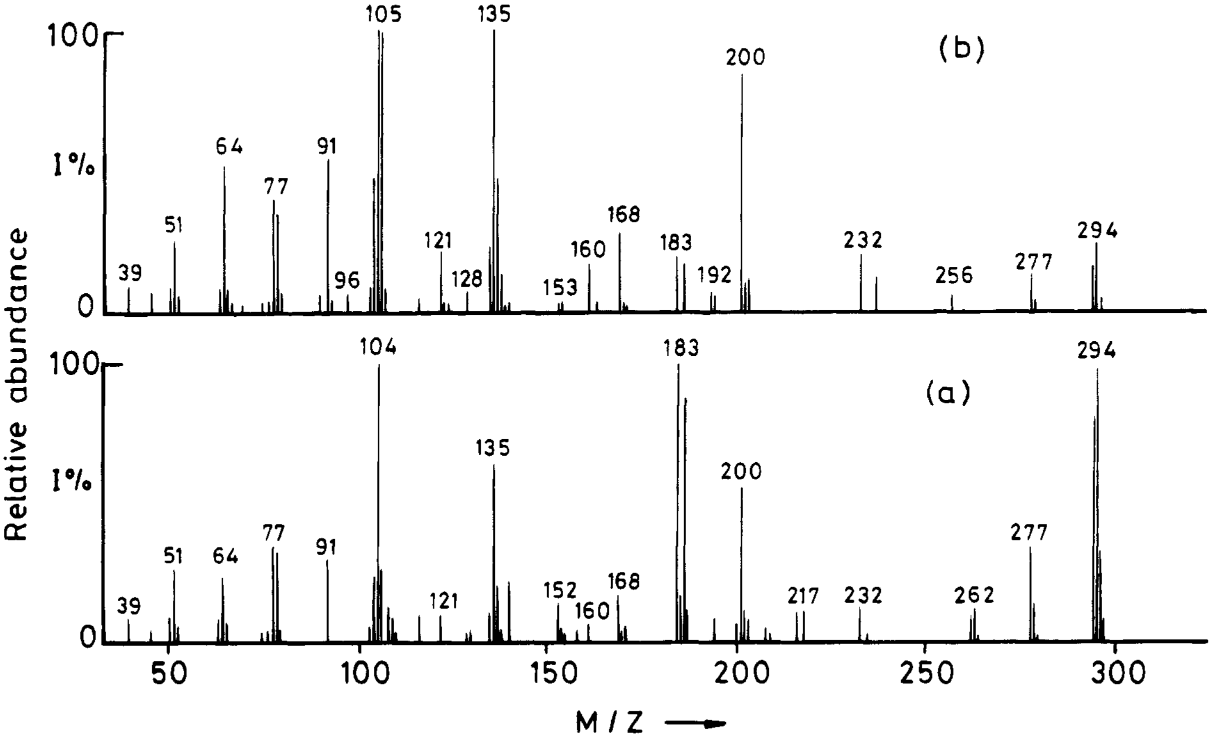
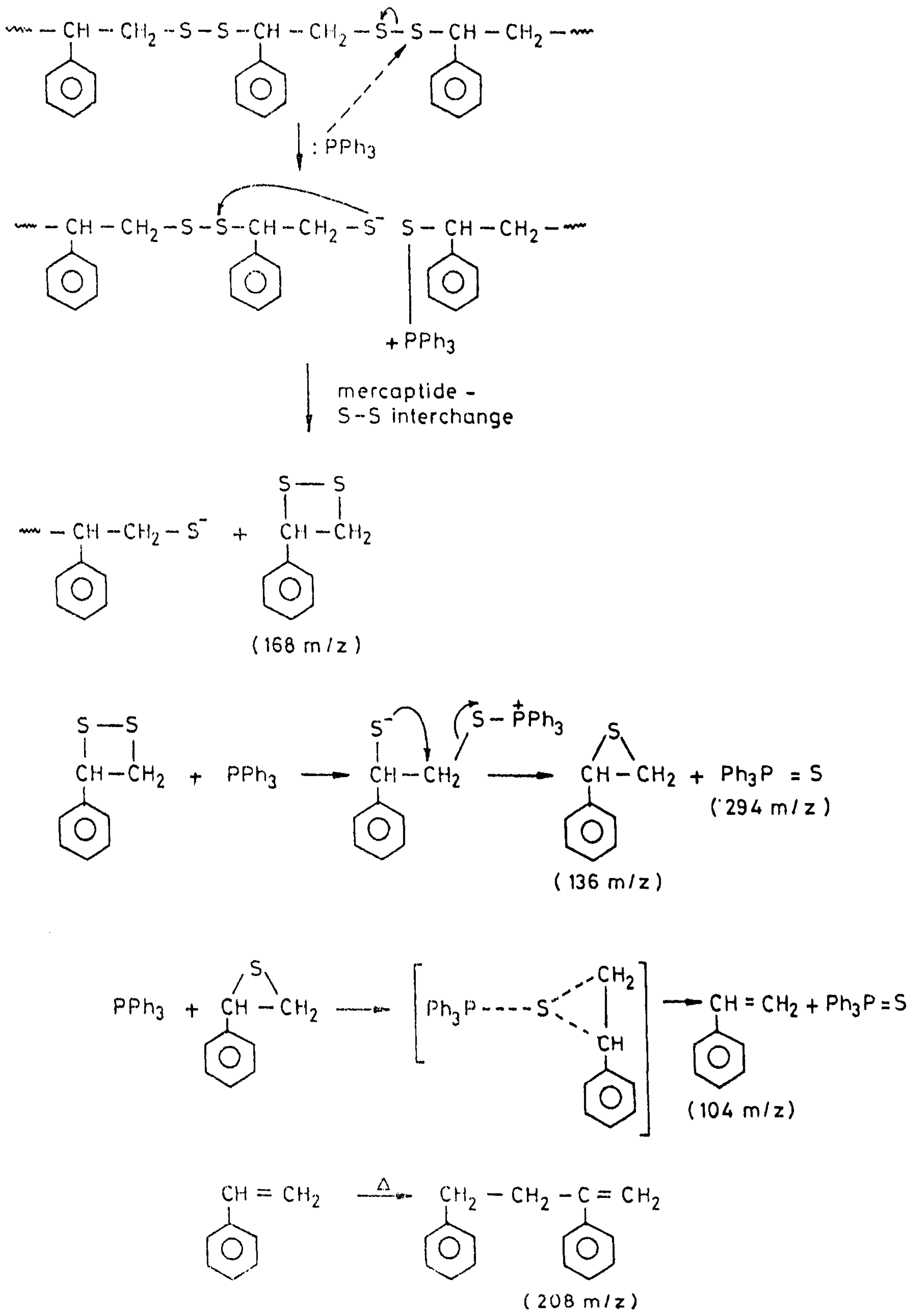


Figure 7. Mass spectra corresponding to the peak maxima observed in the TIC of the PST1 reaction residue.

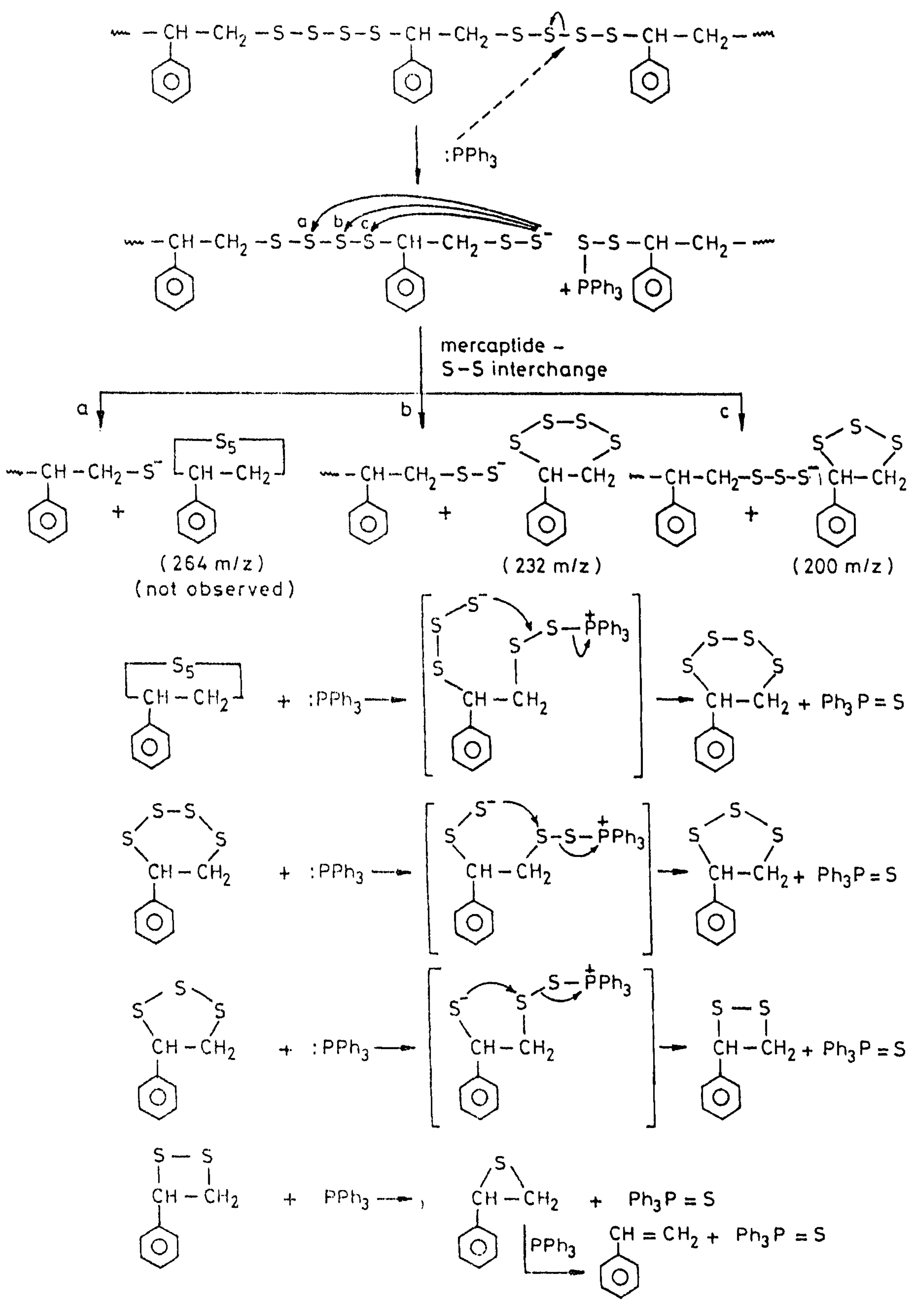
Scheme 1. Mechanism of the PSD–TPP Reaction



the mass spectra (Figure 9), the individual compounds identified (Table 1) were the same as observed in the PST1 reaction residue except for the sulfur. Analysis of the mass spectra reveals that the intensity of the peaks corresponding to the molecular ions of styrene, styrene sulfide, and other cyclic sulfides decreases on going from Figure 9a to Figure 9c. It implies that except for TPPS (*m*/*z* 294), other compounds evaporate initially under DP-MS conditions.

Comparison of the mass spectra of the PST1 and PST2 reaction residues shows the following differences. Firstly, the peaks due to sulfur observed in the PST1 reaction residue mass spectra are completely absent in the mass spectra of the PST2 reaction residue. From

Scheme 2. Mechanism of the PST–TPP Reaction



this, it is inferred that free sulfur is not at all formed when the TPP concentration is increased. Secondly, it is observed that TPPS, which evaporates first in the PST1 reaction residue under DP-MS conditions, evaporates only after other reaction products of the PST2 reaction have evolved. This is also reflected in the single ion current of the individual compounds formed from the PST1 reaction residue (Figure 10).

Based on the mass spectral analysis the following mechanism (Scheme 2) has been proposed for the PST–TPP (both PST1 and PST2) reaction. Like the PSD–TPP reaction, here also first the formation of a phos-

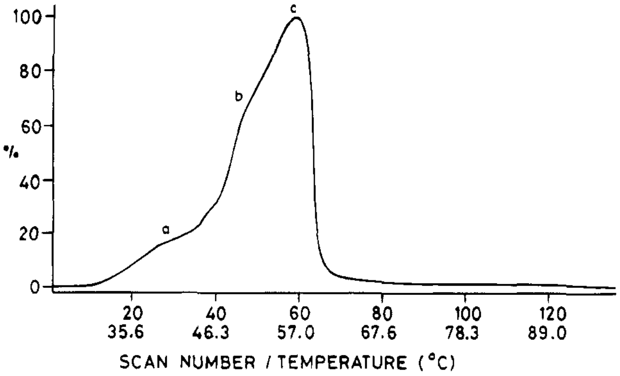


Figure 8. Total ion current of the PST2 reaction residue.

phonium salt occurs by the attack of TPP at the central S–S bond[10] of PST followed by mercaptide–polysulfide exchange to form the cyclic compounds which in turn undergo desulfurization by TPP, finally yielding styrene and TPPS. The molecular ion peak of the cyclic sulfide (St–S_5) (*m*/*z* 264) is not observed either in the PST1 or in the PST2 reaction residues. It is assumed here that this cyclic sulfide is very unstable due to seven-membered ring structure and reacts rapidly with TPP to form the more stable six-membered ring cyclic sulfide (St–S_4) (*m*/*z* 232) and TPPS.

Thermal Degradation vs Chemical Degradation Processes. The use of the DP-MS method in separating the mixtures, based on the differences in the vapor pressure of individual components has already been discussed earlier. However, nonvolatile polymers decompose thermally under DP-MS conditions to form the primary degradation products. During the analysis of the reaction residues by the DP-MS method, the thermal degradation process may occur if any unreacted polymer is present. In such an event, the analysis would be complicated and becomes unreliable. Hence, it is necessary to clearly distinguish between thermal degradation and the simple distillation process. The possibility of the former occurring in the present study is ruled out due to the following reasons.

Both neat PSD and PST have a thermal decomposition temperature of about 220 °C.[3] Since PSD reacts with TPP at 80 °C and PST at room temperature itself and when these reaction temperatures are compared with the thermal decomposition temperatures of the individual polymers, the occurrence of thermal degradation is ruled out.

Let us now examine the product-evolving temperatures of the reaction mixture. It is observed that for the PSD–TPP reaction residue the molecular ions of styrene, styrene sulfide, styrene dimer, and triphenylphosphine sulfide all appear before 103 °C (Figure 4); for PST1 the temperature range extends up to 78.3 °C (Figure 6 and 10), and for PST2 it is only up to 62.3 °C (Figure 8). Since these product-evolving temperatures are much lower than the thermal decomposition temperatures of neat PSD and PST, it further proves that the polymers are degraded only through the chemical reaction with TPP.

Attention may also be drawn to the fact that in the DP-MS analysis of neat PSD and PST, sulfur is formed as one of the thermal decomposition products.[3,11] The very fact that sulfur peaks are missing in the mass spectra of both PSD–TPP and PST2 reaction residues clearly reveals that no thermal degradation has occurred in these two cases. However, when the TPP is not present in sufficient amounts, which happens under PST1 reaction conditions, the polymer does not chemically degrade completely. As a result some thermal degradation may also occur which is evident from the presence of sulfur peaks in the PST1 reaction residue mass spectra.

Lastly, a cyclic trisulfide having the structure (St–S_3) (*m*/*z* 200), which was formed as one of the thermal decomposition products of neat PSD,[11] was found to be completely absent in the EI-MS of the PSD–TPP reaction residue. This also goes to show the occurrence

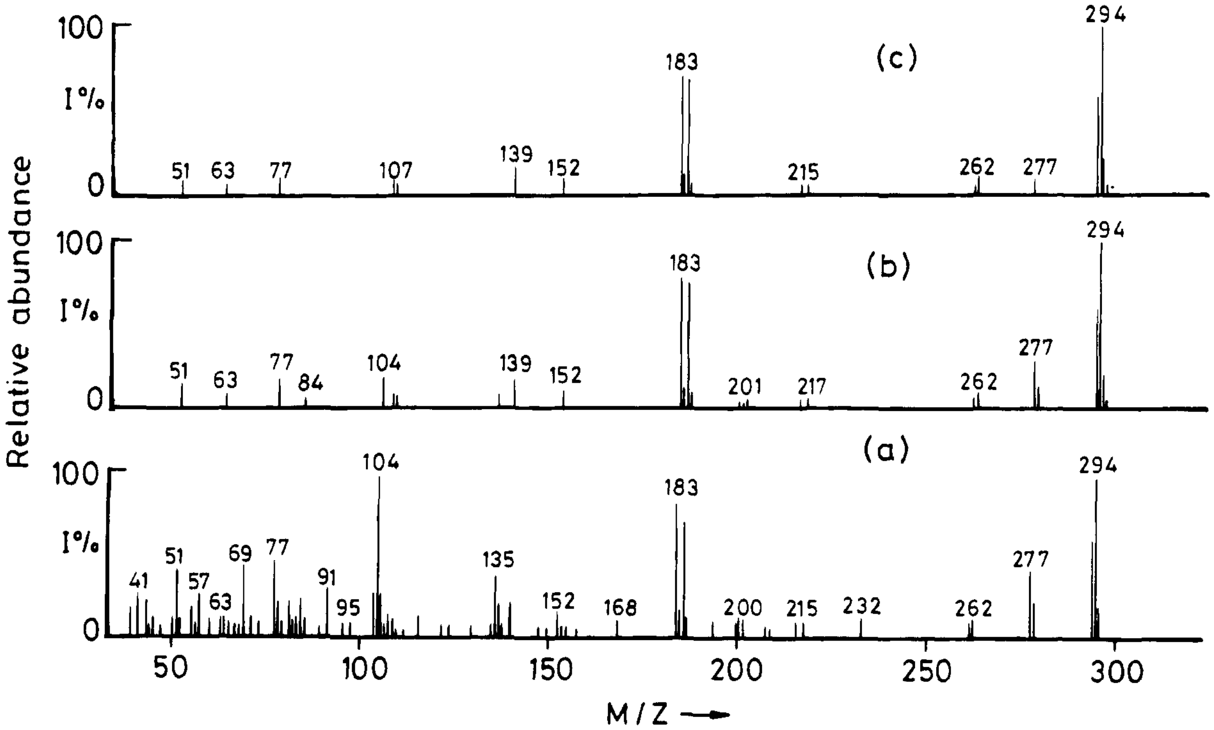


Figure 9. Mass spectra corresponding to the peak maxima observed in the TIC of the PST2 reaction residue.

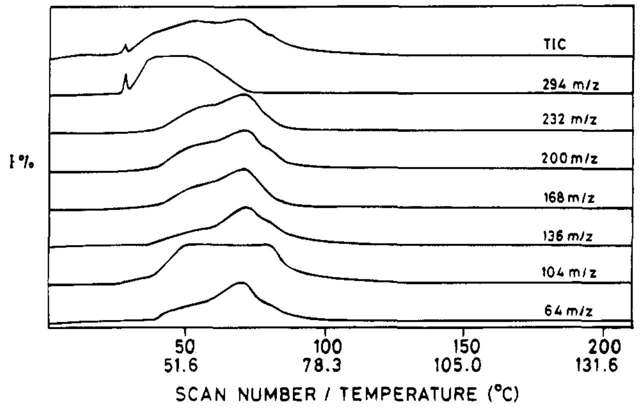


Figure 10. SIC curves of the individual compounds observed in the DP-MS analysis of the PST1 reaction residue.

of chemical degradation and the absence of thermal degradation in the PSD−TPP reaction.

Conclusions

The chemical reactivity of PSD and PST toward TPP has been studied by ^{31}P-NMR spectroscopy, and the reaction products have been analyzed using DP-MS technique. While PSD did not react with TPP at room temperature, PST (PST1 and PST2) reacted spontaneously with TPP at room temperature, forming the degradation products. Formation of the products was explained by an ionic mechanism which first involves the generation of a phosphonium salt intermediatefollowed by mercaptide interchange with the S−S bond. Solubility analysis as well as DP-MS data on PST1 and PST2 reaction residues revealed that PST is completely degraded only when the concentration of TPP is increased.

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