Stabilization of Thermal Degradation of Poly(methyl methacrylate) by Polysulfide Polymers

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ABSTRACT: The thermal degradation of poly(methyl methacrylate) (PMMA) in the presence of polysulfide polymers, namely, poly(styrene disulfide) (PSD) and poly(styrene tetrasulfide) (PST) was studied using thermogravimetry (TG) and direct pyrolysis-mass spectrometric (DP-MS) analysis. Both PSD and PST were found to stabilizethe PMMA degradation, which was explained by both radical recombination and a chain-transfer mechanism. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 2149–2156, 1997

INTRODUCTION

Polysulfide polymers, due to their good environment and low-temperature properties, find extensive applications as adhesives, sealants, and insulators.[1] Although the simple low molecular weight disulfides and tetrasulfides are known to be good chain-transfer agents and retarders of radical polymerization, respectively,[2–7] the use of their polymeric counterparts for chain-transfer study has been realized only recently from our laboratory.[8] Because of their chain-transfer behavior, polysulfide polymers can also be used as stabilizers for most of the vinyl polymers, which undergo thermal degradation by a radical mechanism. Studying the thermal degradation of poly(methyl methacrylate) (PMMA) assumes importance due to its wide variety of applications such as automotive lenses and reflective devices. Although additives such as red phosphorus, nafions, transition-metal halides, tin compounds, and simple disulfides have been tried as stabilizers of the thermal degradation of PMMA,[10,11] no reports are available on the utility of polysulfide polymers in this regard. Here, we chose to study the effect of poly(styrene disulfide) (PSD) and poly(styrene tetrasulfide) (PST) on the thermal degradation of PMMA. These polymeric additives would have the added advantage of curtailed migration and evaporation normally encountered with simple additives.

EXPERIMENTAL

Preparation of PMMA

A commercial methyl methacrylate (MMA) monomer was purified by washing with 10% NaOH solution, dried over sodium sulfate, and vacuum-distilled. Polymerization of MMA was carried out using an azobisisobutyronitrile (AIBN) initiator (AIBN/MMA mol ratio 1 : 400) at 60°C for 1 h in a sealed glass ampule after being thoroughly degassed and filled with nitrogen. The reaction mixture was poured into a large amount of methanol to precipitate the PMMA. The PMMA was further purified by washing several times with methanol and finally dried under a vacuum. The PSD and PST were prepared as described elsewhere.[12]

Preparation of Blends

PMMA/PSD and PMMA/PST blends were prepared by stirring chloroform solutions of the two

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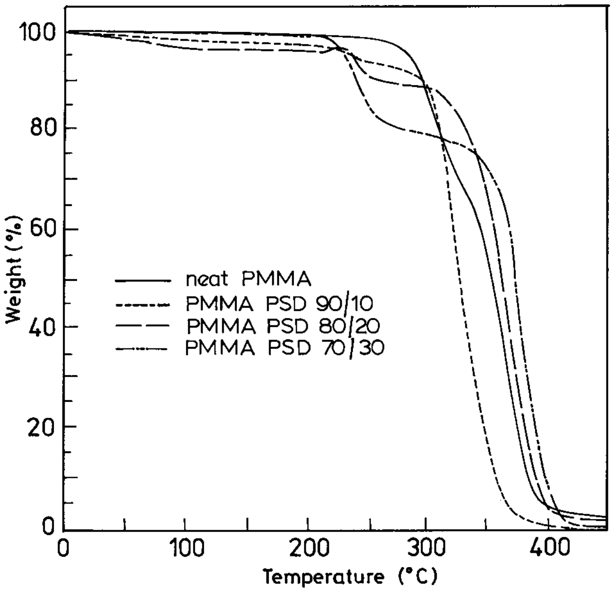


Figure 1 TG curves of neat PMMA and PMMA/PSD blends.

polymers in three different compositions (90/10, 80/20, and 70/30 w/w) at room temperature for 30 min and the solvent was evaporated to obtain the blend.

Thermogravimetry (TG)/Differential Thermogravimetry (DTG)

TG/DTG analysis was done on a TA2000-951TGA thermogravimetric analyzer at a heating rate of 10°C/min in a N_2 atmosphere using 5 mg of the sample.

Mass Spectrometry

Pyrolysis of the blends (0.1 mg) was carried out using a direct insertion probe which is inserted directly into the source chamber of a VG MICROMASS 7070H mass spectrometer. The samples were heated from 30 to 400°C at a rate of 16°C/min. Electron ionization (EI) was performed at 18 eV at a scan speed of 1 s/decade at 220°C. The source temperature is maintained at around 200°C.

RESULTS AND DISCUSSION

TG/DTG

Figures 1 and 2 represent the TG curves of neat PMMA and its blends with different weight compositions of PSD and PST, respectively. The PMMA shows a two-step degradation: The first weight loss between 240 and 320°C corresponds to the degradation starting at the vinylidine chain end[13] [Scheme 1, eq. (1)], while the second weight loss, between 320 and 440°C, is due to the random initiation[13] followed by unzipping of the PMMA chain [Scheme 1, eq. (2)].

The TG curves of the blends of PMMA with either PSD (Fig. 1) or PST (Fig. 2), at different weight compositions, show a similar trend: a two-step degradation—the first step occurring between 200 and 300°C, and the second, in the range of 300–440°C. Also, it was found that with increase in the concentration of PSD or PST in the blend the weight loss of the first step of degradation increases while that of the second step proportionately decreases.

For neat PMMA, Kashiwagi et al.[13] reported DTG peak temperatures at 270 and 360°C, corresponding to the first and the second steps of degradation, respectively, at a heating rate of 2°C/min. Since higher heating rates tend to increase the peak temperature of the degradation, in the present study also, the first and the second DTG peak temperatures of neat PMMA shift to 305 and 378°C (Fig. 3), respectively, at a heating rate of 10°C/min.

Mass Spectrometry

In the DP-MS technique, the sample is introduced through the direct insertion probe and the tem-

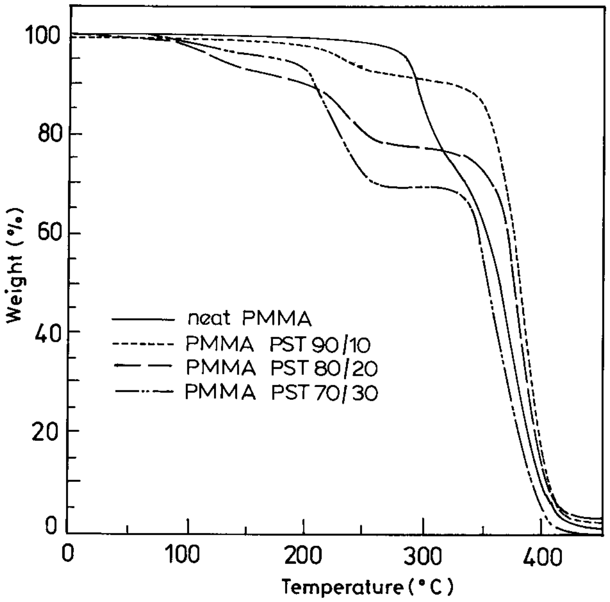
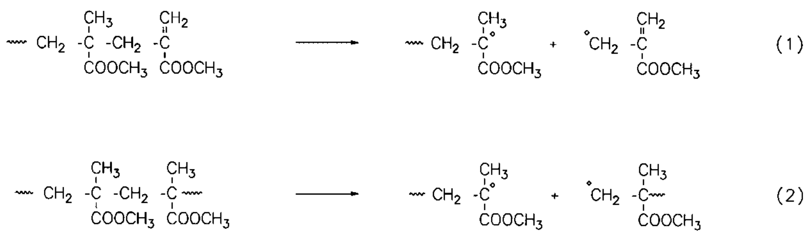


Figure 2 TG curves of neat PMMA and PMMA/PST blends.

Mechanism of thermal degradation of PMMA



Scheme 1

perature is gradually increased up to a point at which thermal degradation of the polymer occurs; the emanated volatiles are then ionized and detected. Combination of linear heating and EI in the mass spectral analysis of the polymers allows total ion current (TIC) and single ion current (SIC) curves to be obtained. The TIC profile which records the ion current of the total amount of volatile products evolved from a polymer degradation is directly related to the DTG trace.[14] Generally, DTG and TIC curves match but sometimes they may not due to the difference in the experimental conditions, where a high vacuum is applied in the DP-MS technique and an inert atmosphere is used in the TG analysis.[15]

To study the interaction of PSD and PST with PMMA, the DP-MS of the blends of PMMA/PSD and PMMA/PST were obtained. The TIC of all the samples are shown in Figures 4 and 5, respectively. The corresponding DTG curves for the blends are also displayed in Figures 4 and 5. It is clearly seen that in all the cases the TIC peak maxima is shifted to lower temperature compared to the corresponding DTG peak temperature. As mentioned earlier, this temperature shift can arise due to the high pressure in the MS instrument and a similar behavior was observed earlier for a different polymer.[15]

The EI spectrum of neat PMMA shows an intense peak at m/z 100 due to the molecular ion of the MMA monomer. The EI mass spectra of the

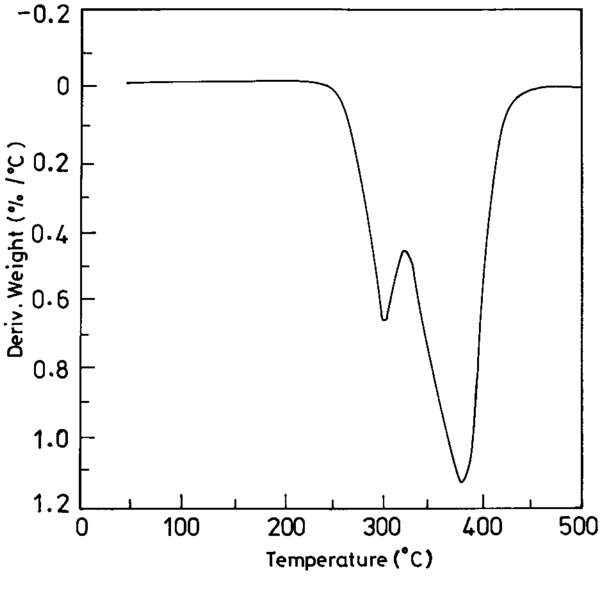


Figure 3 DTG curve of neat PMMA.

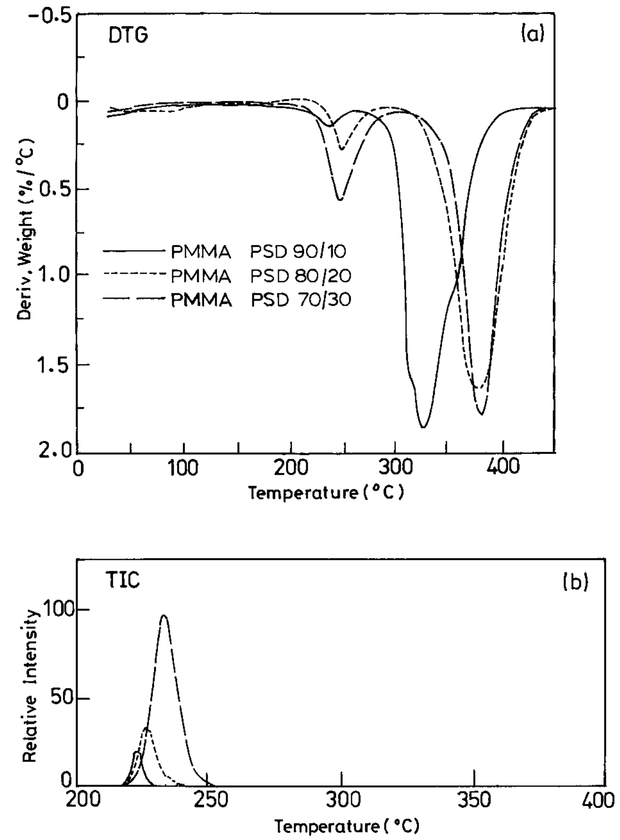


Figure 4 Comparison between (a) DTG curves and (b) TIC curves of PMMA/PSD blends.

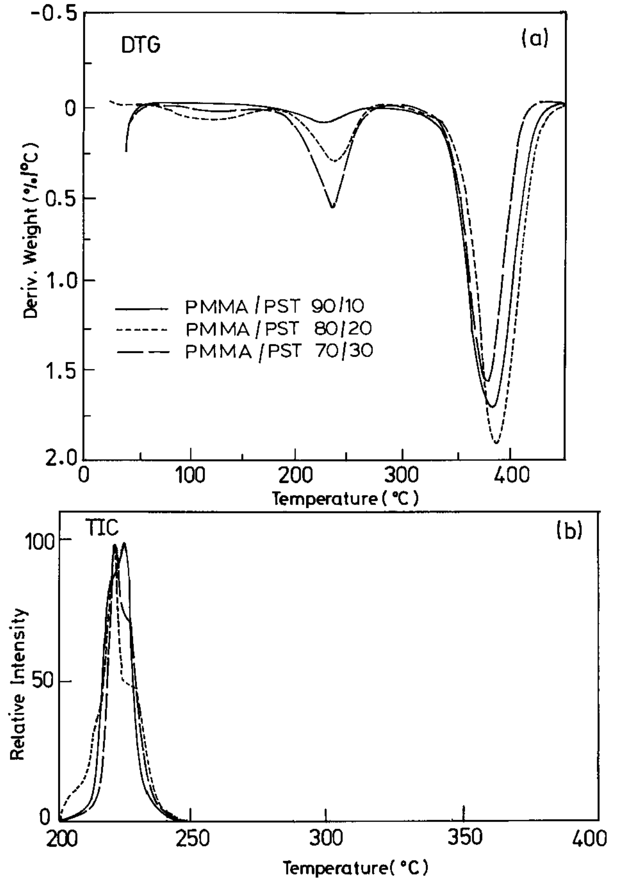


Figure 5 Comparison between (a) DTG curves and (b) TIC curves of PMMA/PST blends.

PMMA/PSD or PMMA/PST blends were similar and, hence, a representative mass spectrum of PMMA/PSD (90/10 w/w) is displayed in Figure 6. Table I lists the structures of all the degradation products formed from the blends of PMMA with PSD or PST. The degradation of neat PSD[12] or PST[12] yield styrene (*m*/*z* 104), sulfur (*m*/*z* 64), styrene sulfide (*m*/*z* 136), and other cyclic styrene di-, tri-, and tetrasulfides (*m*/*z* 168, 200, and 232, respectively). Since the EI mass spectra were recorded at 220°C, the peak corresponding to the ion at *m*/*z* 100 was not observed in the spectra.

A typical SIC of the individual compounds generated from the degradation of the PMMA/PSD blend is reported in Figure 7. Similar SICs were also obtained for the other blends. From this, it is clear that in the blends the first step involves the degradation of PSD (or PST) to various products such as styrene, sulfur, styrene sulfide, a cyclic disulfide, a cyclic trisulfide, and a cyclic tetrasulfide. The evolution of MMA starts only after all the PSD or PST degradation products are evolved (Fig. 7).

Stabilization of PMMA Degradation by PSD/PST

The SICs of MMA generated from neat PMMA as well as from the blends of PMMA/PSD and PMMA/PST are displayed in Figure 8. It clearly shows that the evolution of MMA has shifted to above 240°C in all the blends as compared to the MMA evolution occurring at 210°C in the neat PMMA. The mechanism of stabilization by PSD is given in Scheme 2. In the first stage, the PSD degrades[12] at the C—S bond, forming the —$S_2^{\bullet}$ [Scheme 2, eq. (3)], which undergoes further cyclization to form the products such as styrene, sulfur, and cyclic sulfides[12] [Scheme 2, eq. (4)] as well as PMMA degrading at the chain end, form-

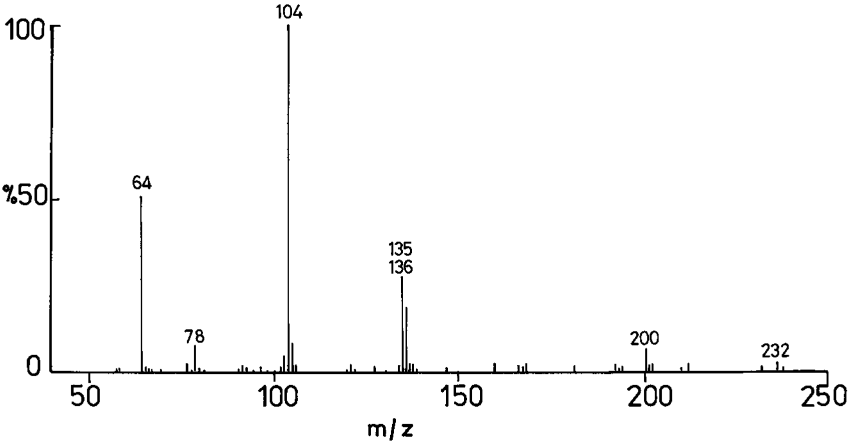
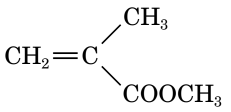
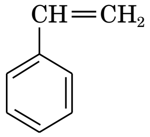
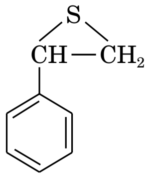
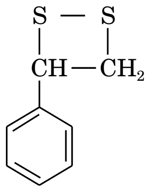
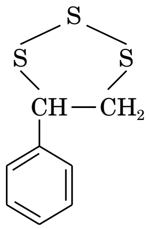
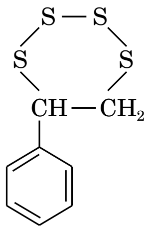


Figure 6 EI mass spectrum (18 eV) of the pyrolysis products of the PMMA/PSD (90/10 w/w) blend recorded at 220°C.

Table I Structures of the Thermal Degradation Products Evolved in the DP-MS Analysis of the Blends

Product	Structure	Molecular Weight
Methyl methacrylate	 $CH_2{=}C(CH_3)COOCH_3$	100
Sulfur	S_2	64
Styrene		104
Styrene sulfide		136
Cyclic styrene disulfide		168
Cyclic styrene trisulfide		200
Cyclic Styrene tetrasulfide		232

ing the carbon centered radicals[13] [Scheme 1, eq. (1)]. The thiyl radical formed from PSD further undergoes radical recombination reactions with the PMMA macroradicals, forming a block copolymer [Scheme 2, eq. (5)]. The reaction of thiyl radicals with the carbon-centered radicals is well known[6]; hence, further unzipping of the PMMA chain to the MMA monomer is prevented. Although the possibility of the reaction of thiyl radicals with the unsaturated chain ends of PMMA cannot be neglected, it can be ruled out based on the fact that the polymeric disulfides are known to be better chain-transfer agents than chain initiators in radical polymerization.[8] Since PSD is an excellent chain-transfer agent in radical polymerization reactions,[8] it terminates the unzipping of PMMA macroradicals by the reaction with the S—S bond, forming the block copolymer of

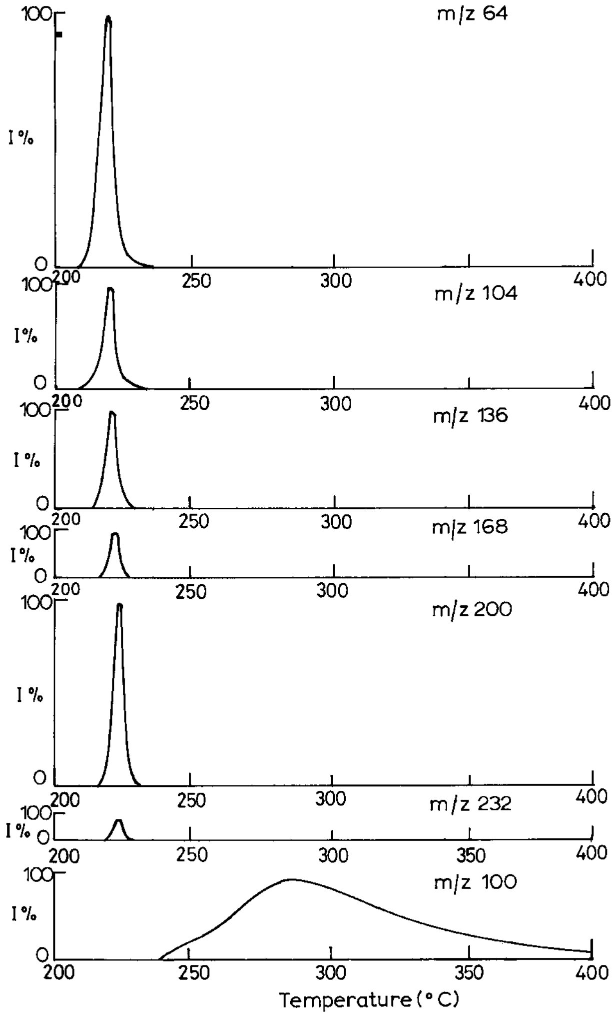


Figure 7 SIC curves of thermal degradation products of PMMA/PSD (90/10 w/w) blend.

PMMA–PSD [Scheme 2, eq. (6)]. A similar stabilization reaction involving diphenyl disulfide with PMMA was already reported by Chandrasiri et al.[11]; it showed acceleration of the degradation at lower temperature and stabilization at higher temperature. But PSD does not show any acceleration; only suppression of degradation of PMMA is observed. In the case of diphenyl disulfide, the accelerated degradation at lower temperature may be due to the volatilization of the additive as it has very low melting point (58–61°C).[16]

Scheme 3 refers to the mechanism of stabilization of PMMA by PST which is almost similar [Scheme 2, eqs. (3)–(6)] to that of PSD. Since the central S—S bond in the PST is the weakest,[12] it breaks to form thiyl radicals and neutral products such as styrene, sulfur, and cyclic sulfides[12] [Scheme 3, eqs. (7) and (8)]. The thiyl radicals further undergo radical recombination reactions with the carbon-centered PMMA radicals, forming the neutral block copolymer of PMMA–PST [Scheme 3, eq. (9)]. The PMMA macroradicals undergo a chain-transfer reaction with the central S—S bond of PST to form the PMMA–PST block copolymer [Scheme 3, eq. (10)]; hence, further unzipping of the PMMA radical to the MMA monomer is prevented as discussed for PSD. As reported elsewhere, the temperature of onset of the degradation of PSD and PST is around 220°C.[12] From the DP-MS analysis of the blends, we found that not only is PSD (or PST) involved in the stabilization reaction with the PMMA macroradical, but it also degrades to form the volatile products. Hence, with increase in temperature, on account of the loss of PSD or PST from the blend

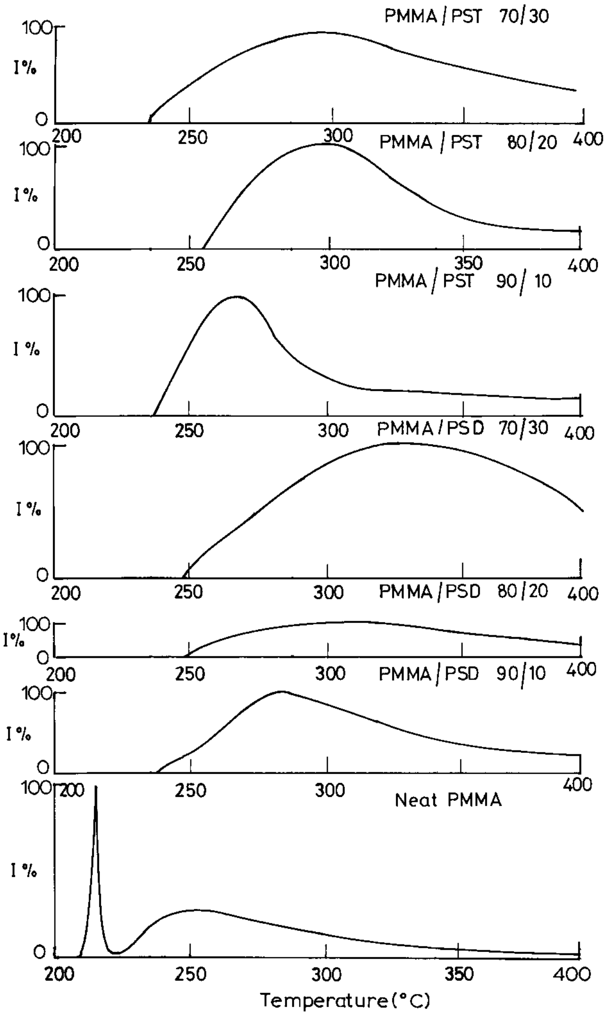
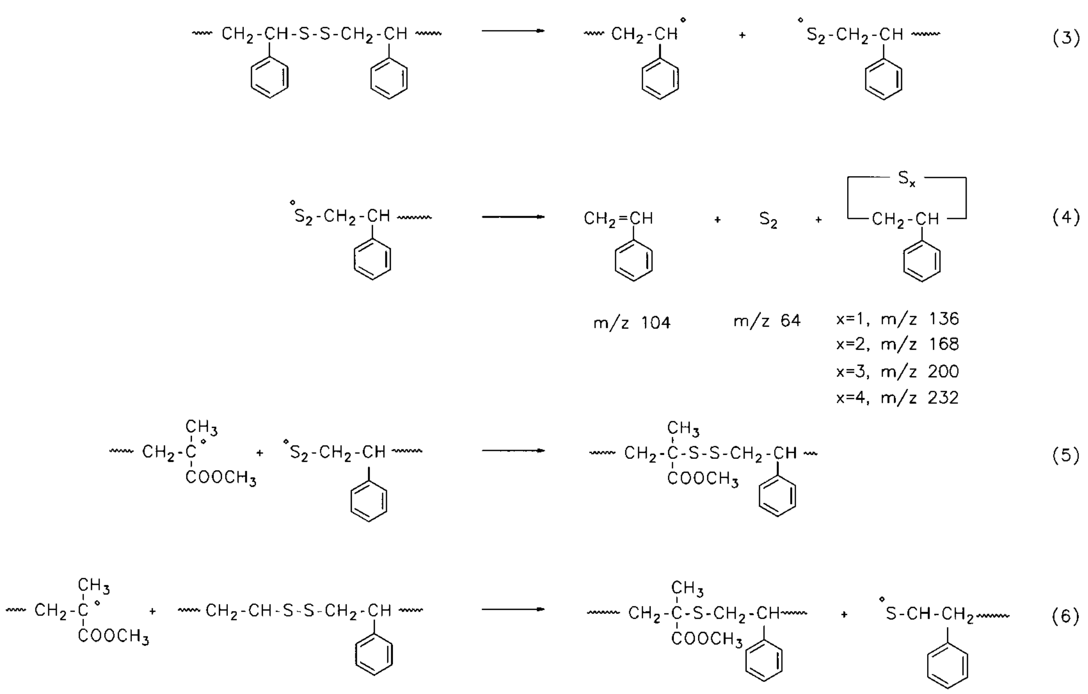


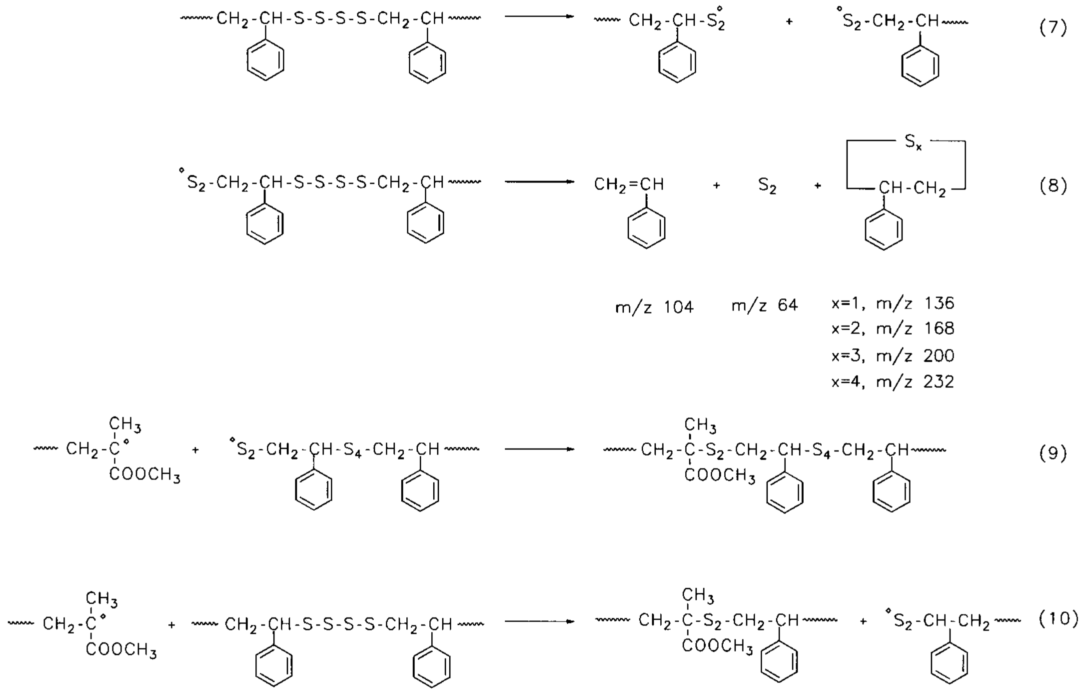
Figure 8 SIC curves of MMA formed from neat PMMA, PMMA/PSD, and PMMA/PST blends.

Mechanism of stabilization of PMMA by PSD



Scheme 2

Mechanism of stabilization of PMMA by PST



Scheme 3

due to degradation, its availability for the stabilization of PMMA in the blend decreases. Once all the PSD or PST completely degrades, which happens around 300°C, the PMMA degradation to MMA begins and that is why we observe MMA evolution only after 300°C.

CONCLUSION

The effect of PSD and PST on the thermal degradation of PMMA was studied by TG and DP-MS analysis. The study revealed that both PSD and PST show a stabilizing effect up to the temperature of 300°C. The mechanism of stabilization was explained by the chain-transfer reaction of PMMA macroradicals to the S—S bond as well as the radical recombination reaction of the PMMA macroradicals with the thiyl radicals formed from the PSD or PST.

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