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THE EFFECT OF DERIVATIVES OF 2-MERCAPTOBENZOTHIAZOLE ON THE PYROLYSIS OF POLYSTYRENES

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ABSTRACT

High yields of monomeric styrene and α-methylstyrene were obtained when polystyrene or poly(α-methylstyrene) was heated at temperatures above 350 °C. Other pyrolytic products obtained from polystyrene were benzene, toluene, ethylbenzene and traces of cumene and α-methylstyrene. Similar pyrolytic products were obtained from poly(α-methylstyrene) but toluene and ethylbenzene were present only as traces. Analysis by gas chromatography showed the thermal decomposition products to be similar when three different pyrolytic techniques were used, *viz.*, a hot platinum wire, heated open tubes and closed tubes.

No change in the composition of the products was noted when mixtures of these polymers and derivatives of 2-mercaptobenzothiazole were decomposed on the hot platinum wire or in heated open tubes. However, the ratio of monomer to the corresponding unsaturated alkylbenzene in the products obtained from the closed tubes decreased linearly as the concentration of 2-mercaptobenzothiazole derivative was increased.

INTRODUCTION

Over a billion pounds of polymers are being discarded annually and the volume of disposable plastics is expected to exceed 10 billion pounds in the 1970's. Since polymeric hydrocarbons are not readily degraded biologically, other techniques, such as incineration must be considered for the disposal of these solid wastes. That polystyrene and poly(α-methylstyrene) may be pyrolyzed to produce high yields of monomers has been demonstrated previously by several investigators[5-7]. However, little information is available on the effect of additives on the composition of these pyrolytic products.

In this investigation, the effect of selected additives on these thermal decompositions was studied and the pyrolytic products were characterized by gas chromatography using techniques comparable to those described by other investigators[1,3,4,8].

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EXPERIMENTAL

Polystyrene[a] and poly(α-methylstyrene)[b] films with and without additives were pyrolyzed on a hot platinum wire[c] and in a porcelain boat for 15 seconds at 525 °C using the technique described previously by Ettre and Vardi for open tube pyrolysis[2]. The products of pyrolysis were characterized in a gas chromatograph[d] equipped with a copper column containing acid washed chromosorb W with 20% SE 52[e] using helium as the carrier gas. The pyrolytic effluents were characterized by comparison of retention times of known hydrocarbons.

Samples (1g) in glass tubes were evacuated for 5 min at 1 torr before being sealed. These closed tubes were heated at 370 ± 5 °C for 30 min, cooled to room temperature and broken. The solutions obtained by extracting the contents with isopropyl ether were injected into the gas chromatograph and the pyrograms were characterized.

RESULTS

The principal products obtained by the hot wire or hot open tube pyrolytic techniques were monomeric styrene from polystyrene and monomeric α-methylstyrene from poly(α-methylstyrene). Minor quantities of benzene and alkylbenzenes were also obtained. Similar pyrograms were obtained with pure polymers and with films containing up to 10% by weight of 2-mercaptobenzothiazole and its derivatives.

In contrast, the composition of products obtained by heating pure polymers and mixtures of the polymers and mercaptobenzothiazole were different and related to the amount of additive present. Thus, as shown in Fig. 1 the pyrolytic products from polystyrene (PS) were styrene (A), ethylbenzene (B), benzene (C), toluene (D), α-methylstyrene (E) and a trace of cumene (F). As shown by the other pyrograms in Fig. 1, the relative amounts of benzene (C) and an unidentified high boiling product, not noted in the pyrolytic products from polystyrene, increased as the relative amount of 2-mercaptobenzothiazole (MBT)[f] was increased from 1 to 10%. More significant was the increase in the ratios of saturated to unsaturated hydrocarbons, *viz.*, ethylbenzene (B)/styrene (A) and cumene (F) /α-methylstyrene (E).

Comparable changes in the ratios of saturated to unsaturated hydrocarbons were observed in the pyrograms from the closed tube thermal decomposition of polystyrene in the presence of increasing amounts of 2-bis-benzothiazyl disulfide [$(MBT)_2$], *N*-t-butylbenzothiazole-2-sulfenamide (TBBTS) and *N*-cyclohexylbenzothiazole-2-sulfenamide (CHBTS).

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[a] Cosden Oil and Chemical Co., Big Spring, Texas, 79720, U.S.A.
[b] Dow Chemical Company, Midland, Michigan, 48640, U.S.A.
[c] Aerograph Pyrolyzer Model A425, Varian Aerograph, Walnut Creek, California 94598, U.S.A.
[d] Model A100C Varian Aerograph, Walnut Creek, California, 94598, U.S.A.
[e] General Electric Company, Waterford, New York, 12188, U.S.A.
[f] 2-Mercaptobenzothiazole and its derivatives were supplied by the Goodyear Tire and Rubber Company, Akron, Ohio 44316, U.S.A.

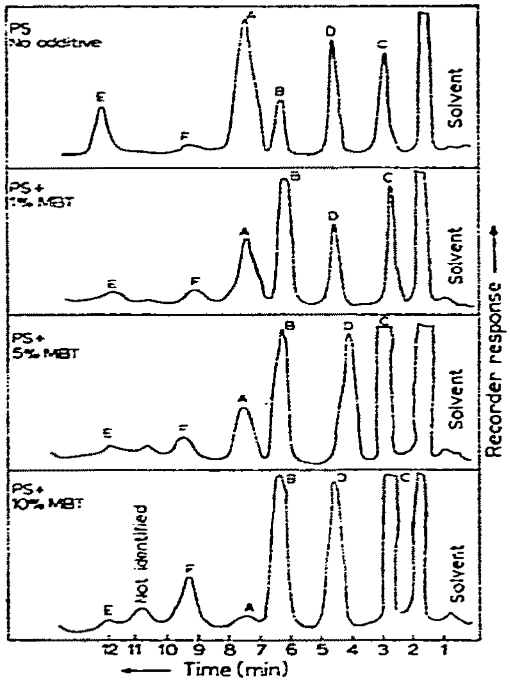

Fig. 1. Pyrograms of the pyrolytic products from polystyrene (PS) in the presence of increasing amounts of 2-mercaptobenzothiazole (MBT).

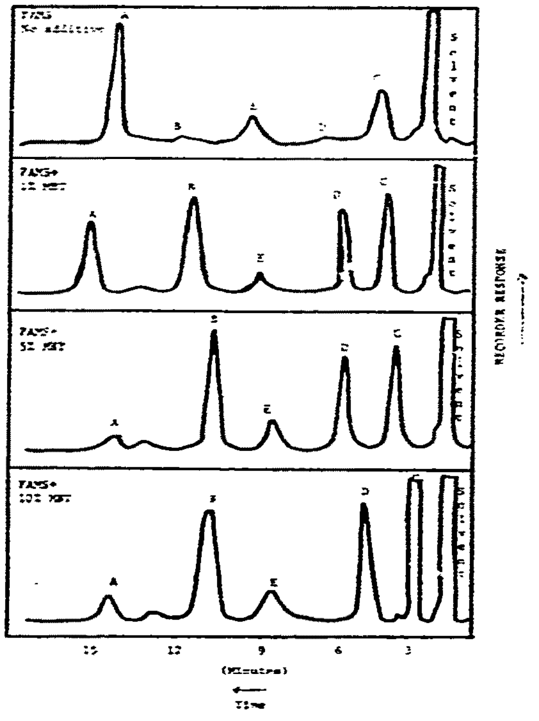

Fig. 2. Pyrograms of the pyrolytic products from poly(α-methylstyrene) (PAMS) in the presence of increasing amounts of 2-mercaptobenzothiazole (MBT).

As shown in Fig. 2, the pyrolytic products from poly(α-methylstyrene) (PAMS) were α-methylstyrene (A), cumene (B), benzene (C), toluene (D), and ethylbenzene (E). Similar products were observed in the pyrograms when PAMS was pyrolyzed in closed tubes in the presence of 2-mercaptobenzothiazole and its derivatives. As shown by the other pyrograms in Fig. 2, the relative amounts of benzene (C) and an unidentified high boiling product not noted in the pyrolytic products from poly(α-methylstyrene) increased as the relative amount of 2-mercaptobenzothiazole (MBT) was increased from 1 to 10%. More significant was the increase in the ratio of saturated to unsaturated hydrocarbons, *viz.*, cumene (B)/α-methylstyrene (A). There was also a significant increase in the relative amounts of toluene (D) and ethylbenzene (E) obtained as the per cent of 2-mercaptobenzothiazole (MBT) was increased.

Comparable changes in the ratios of saturated to unsaturated hydrocarbons were observed in the pyrograms from the closed tube thermal decomposition of poly(α-methylstyrene) in the presence of increasing amounts of 2-bis-benzothiazyl disulfide [$(MBT)_2$], *N*-t-butylbenzothiazole-2-sulfenamide (TBBTS) and *N*-cyclohexylbenzothiazole-2-sulfenamide (CHBTS).

The ratio of styrene to ethylbenzene in the products of pyrolysis from polystyrene was approximately 70:1. However, as shown by the plots in Fig. 3, the ratio was decreased to less than 3:1 in the presence of 1% of derivatives of 2-mercaptobenzothiazole. The ratio was decreased in approximately a linear manner as the percent of these additives increased. 2-Mercaptobenzothiazole (MBT) and its disulfide [$(MBT)_2$] were more effective than the sulfenamides.

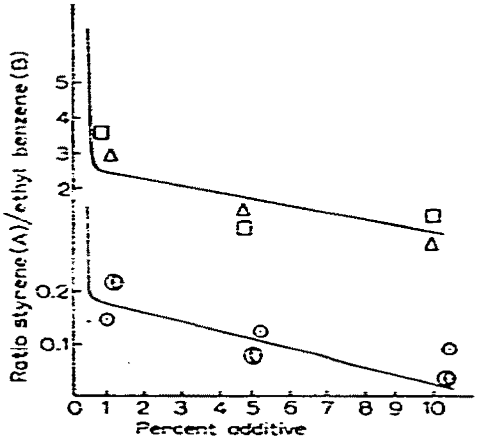

Fig. 3. Ratio of relative concentration of styrene (A) to ethylbenzene (B) in the presence of stabilizers; ◐ MBT, ⊙ $(MBT)_2$, △ TBBTS, □ CHBTS.

The ratio of α-methylstyrene to cumene in the products of pyrolysis from poly(α-methylstyrene) was approximately 150:1. However, as shown by the plots in Fig. 4, the ratio was reduced to less than 0.7 to 1 in the presence of 1 percent of derivatives of 2-mercaptobenzothiazole. The ratio was decreased in approximately a linear manner as the percent of these additives increased. The difference in effect among additives was not as great as than noted for polystyrene. Also, 2-bis-benzothiazyl disulfide [$(MBT)_2$] and *N*-t-butylbenzothiazole-2-sulfenamide (TBBTS) were slightly more effective than the other additives used.

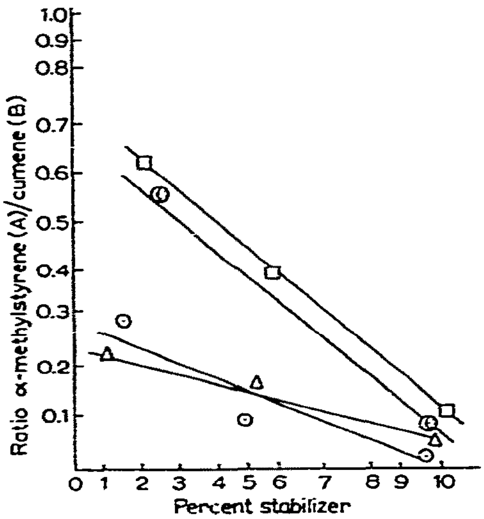

Fig. 4. Ratio of relative concentrations of α-methylstyrene (A) to cumene (B) in the presence of stabilizers; ◑ MBT, ⊙ $(MBT)_2$, △ TBBTS, □ CHBTS.

Because of the high volability of the products of pyrolysis of polypropylene and polyisobutylene, there was a high frequency of breakage of the sealed tubes. However, a definite reduction in the relative amounts of unsaturated and saturated products of pyrolysis from these polymers was noted in the presence of derivatives 2-mercaptobenzothiazole.

The composition of the products of thermal decomposition of poly(methyl methacrylate) could be altered when the pyrolysis took place at atmospheric pressure. The yield of monomeric methyl methacrylate and other volatile products decreased from 80% to zero percent when the polymer was heated at atmospheric pressure in the presence of 10% of derivatives of 2-mercaptobenzothiazole. Attempts to identify the non-volatile residues have not been successful.

CONCLUSIONS

The relative amounts of saturated and unsaturated hydrocarbons obtained in the pyrolysis of polystyrene and poly(α-methylstyrene) can be altered when these polymers are heated at 370±5°C in the presence of 2-mercaptobenzothiazole or its derivatives. These results could not be duplicated when these polymers were decomposed on a hot platinum wire or in a hot open tube. It is suggested that the free radicals resulting from the thermal decomposition of these polymers in closed tubes coupled with the free radicals produced by the thermal decomposition of the derivatives of 2-mercaptobenzothiazole. Thus, it is possible to decrease the yield of unsaturated hydrocarbons and increase the yield of related saturated hydrocarbons by the pyrolysis of polystyrenes in the presence of additives such as 2-mercaptobenzothiazole.

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