

Bromostyrene-Crosslinked Polyesters. I. Thermal Stability and Flame Retardancy

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Synopsis

Bromostyrene was used as partial replacement of styrene for crosslinking polyester resins. The oxidative stability of the polymer was studied and the performance in standard flammability tests was tested. It was shown that flame retardation increased linearly with the Br content. Under certain conditions, self-extinguishing polyesters were obtained.

INTRODUCTION

The flammability of polyesters was studied extensively by Anderson et al.¹ and Learmonth et al.^{2,3,4} They consider a few stages in the oxidation of polyesters. These stages include hydroperoxidation and cleavage, bond rupture and decarboxylation, and finally solid-phase oxidation of residual carbon. Flammability can be controlled by various methods, the most common being the introduction of species to inhibit the free-radical reactions involved in the flame formation. Chlorine and bromine containing additives are effective flame retardants because the carbon-halogen bond is weak and is easily cleaved. The Cl and Br radicals, and the HCl and HBr formed, react with the active radicals formed in the flame and terminate the chain reactions. Low molecular weight additives have some disadvantages, and one would prefer the halogen to be part of the polymer chain. The recent work on an industrial process for synthesis of bromostyrene by Daren et al.⁵ has raised considerable interest concerning the possibilities of using bromostyrene to replace styrene in polyesters, as well as in other products requiring flame resistance. This paper presents a study of the thermal and oxidative stability of polyesters crosslinked by bromostyrene as well as the results of some standard flammability tests. The succeeding paper⁶ deals with the mechanical properties and weathering stability of these polyesters.

EXPERIMENTAL

Materials

Bromostyrene was supplied from the pilot plant of Makhteshim Ltd., Beer-sheva, Israel. It was produced by catalytic cracking of 2-bromoethylbromo-

benzene and consists of a 2.5/1 mixture of the para and ortho isomers.⁵ The polyester is alkyd Crystic 196 produced by Makhteshim Ltd. and consisting of propylene glycol esterified with phthalic and fumaric acids. The optimal given ratio of styrene to alkyd was 0.5 g styrene to 1 g alkyd. The same molar ratio was kept throughout the experiments so that the weight of monomers used was increased during the gradual change from styrene to bromostyrene. The catalysts consisted of 2% methyl ethyl ketone peroxide and 0.2% cobalt naphthanate. Unidirectional glass fiber composites were prepared as follows. The fibers (E-glass from Fiberglass Inc.) were wound on a winding machine drum and were stuck by strips of adhesive tape to form unidirectional square layers. These were impregnated by the resin mixture and laid up in a mold which was evacuated to remove voids. Curing was carried out in a press at 80°C under 500 psi for 3 hr. The resulting GRP sheet was postcured at 80°C for 48 hr.

The sample PF contained commercial fire retardant Prefil-F based on Sb_2O_3 and chlorinated organic compound.

Weathering treatment consisted of alternating humidity and UV irradiation cycles as described in part II.⁶

Testing

Three standard flammability tests have been performed in the present study as follows: (i) Flammability of self-supporting plastics—ASTM D635-63. In this test, the external heat source is a 25-mm-high blue flame, produced by a 10-mm-diameter Bunsen burner. The specimen (127 × 12.7 × 3.2 mm) is supported with its longitudinal axis horizontal and its transverse axis inclined at 45° to the horizontal. In this test, the burning rate is measured. (ii) Flammability of plastics, self-extinguishing type—ASTM D-757-65. The external heat source is a silicon carbide incandescent rod at $950 \pm 10^\circ C$. The specimen of the above geometry is supported with its longitudinal axis horizontal and its transverse axis perpendicular. In this test, the time for ignition and the burning rate are measured. (iii) Flammability of plastics using the oxygen index

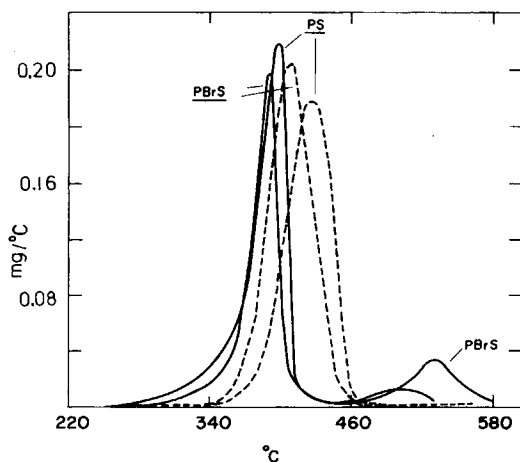


Fig. 1. Differential TGA of polystyrene and polybromostyrene in argon and in oxygen: rate of heating, 6°/min; (---) argon; (—) O_2 .

method—ASTM D2863-70. By this method, the minimum concentration of oxygen in a mixture of N_2/O_2 which sustains combustion for 3 min is measured. The flame is ignited by a Bunsen burner and the specimen size is $127 \times 6.35 \times 3.2$ mm.

Thermogravimetric analyses (TGA) with simultaneous differential thermal analysis (DTA) were carried out on a Mettler No. 194 thermoanalyzer, in a Pt crucible of diameter and height of 5 and 10 mm, respectively. Samples consisted of ground material weighing 9 mg with a reference of 4.7 mg Al_2O_3 . The rates of heating used were 4° , 6° , and $25^\circ/\text{min}$, and in all three cases similar results were obtained. Indium (mp 156.3°C and heat of fusion of 781 cal/mole) was used for calibration of the DTA curves in the various scale sensitivities used (i.e., 50, 100, and $200 \mu\text{V}$) so that the ratio of the amount of heat to the chart area was established. From this ratio, the heat of reactions were calculated.

RESULTS AND DISCUSSION

Thermal and Oxidative Stability

We first compared PS and PBrS in TGA, TGA/MS, and DTA. From the differential TGA curves shown in Figure 1, it can be seen that in argon the thermal decompositions of PBrS and PS are quite similar. The former decomposes at a temperature about 10°C lower than the PS itself. In the combined TGA/MS analysis, we observed that the main reaction is depolymerization and the monomers bromostyrene and styrene are the main products. In an oxygen atmosphere, the major decomposition is at the same temperature, however, a larger fraction remains as a residue in the PBrS sample, and it is oxidized at temperatures above 500°C . The TGA/MS results showed considerable CO_2 and H_2O , but also major peaks of monomers styrene and bromostyrene. Other bromine-containing compounds were not detected. This shows that the thermal degradation is still the major reaction under these conditions of partial combustion.

The DTA measurements in argon (Fig. 2) show endothermic peaks for both polymers at the same temperatures of decomposition as in the TGA. The heats of reaction calculated are 23 and 25 kcal/mole, respectively. These are very close to the reported values of depolymerization of PS.⁷

In an oxygen atmosphere, however, the situation is completely changed. The PS gives a large exothermic peak at a temperature 20°C lower than the main endothermic peak ($340\text{--}380^\circ\text{C}$) and a much smaller peak at about 500°C . The heat of reaction measured is 65 kcal/mole, while the heat of combustion for PS should amount to over 1000 kcal/mole.⁷ It is clear therefore that under these conditions complete combustion does not take place. This is also in agreement with the TGA/MS results showing considerable degradation to monomer in the oxidative decomposition. Another reason for the low value of the heat of combustion measured is probably due to the fact that most of the oxidation occurs in the gas phase outside the Pt crucible and therefore will not be registered. The heat of combustion at 500°C is probably closer to reality as it involves the oxidation of the solid carbon residue.

In the case of PBrS only a minute exothermic peak appeared at 400°C and a major peak at about 500°C . This shows conclusively that under the conditions

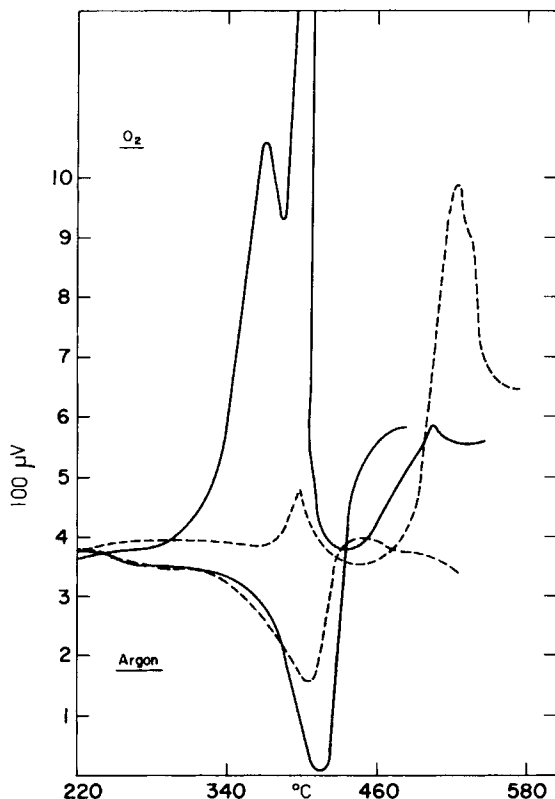


Fig. 2. DTA of polystyrene and polybromostyrene in argon and in oxygen: rate of heating, 6°/min; (—) PS; (---) PBrS.

of the experiment, the bromine present does inhibit most of the oxidative chain reactions. The polymer continues to degrade to the monomer, but combustion is not maintained. At higher temperatures, the carbonaceous deposit that remains is oxidized as seen from the large exothermic peak. The same general behavior is also seen in air, although the effect is less pronounced (Fig. 3). We can conclude, therefore, that the DTA analysis in oxygen demonstrates clearly the effect of the bromine inhibition on the chain reactions taking place during the burning of PBrS.

We can now compare the results in the polyester combinations. The results are shown in Figure 4 for two samples: one containing only styrene and another containing 0.8 mole fraction bromostyrene and 0.2 mole fraction styrene. The endotherms in argon are more complex. It seems that the polyester starts to degrade at a lower temperature than PS or PBrS as shown by Learmonth et al.² In an atmosphere of oxygen, however, the resin containing only styrene burns to give a large exotherm, while that containing bromostyrene shows a much smaller exotherm at 300°C and a larger one at about 500°C. The same experiments were also run with the intermediate compositions namely, 0.2, 0.4, and 0.6 mole fraction of bromostyrene. The calculated values of the heat evolved per gram of resin are shown in Table I.

It is interesting to note that in this test, 5% Br is enough for reducing the heat evolved by a factor of 5. This, apparently, stops the chain reactions produced

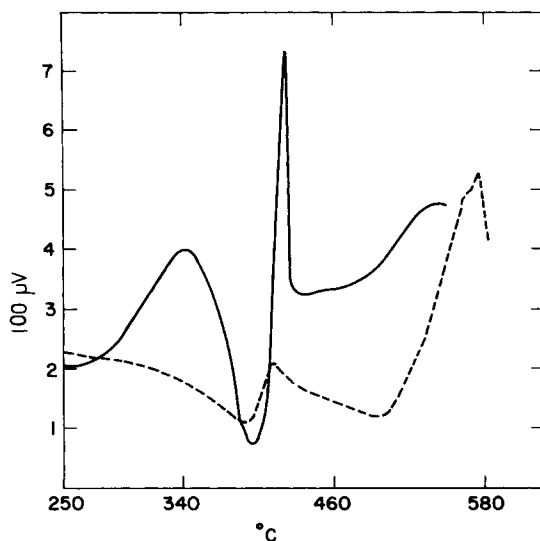


Fig. 3. DTA of polystyrene and polybromostyrene in air: rate of heating, 6°/min; (—) PS; (- - -) PBrS.

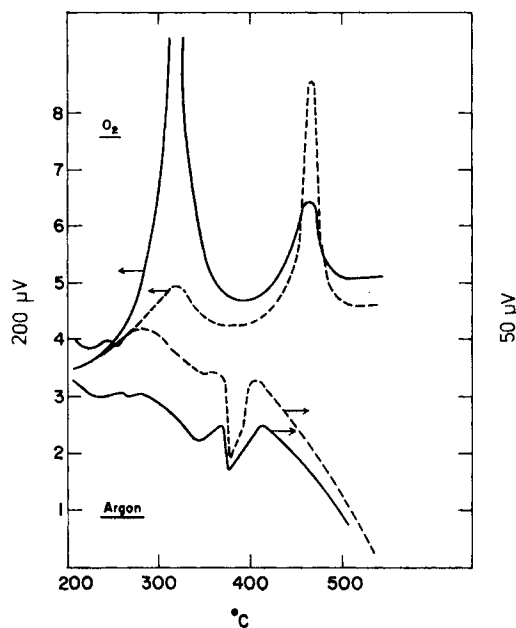


Fig. 4. DTA of polyesters crosslinked with styrene (—) and with 0.8 mole fraction bromostyrene and 0.2 mole fraction styrene (- - -). Rate of heating, 4°/min.

in the first stages of decomposition and only a minimal combustion takes place. Learmonth et al.² also showed that halogen-containing additives decrease somewhat the first endothermic peak. However, their experiments were carried out in air and apparently at a slower rate of heating, and therefore the effect is not as pronounced. In a few preliminary experiments, we have attempted to simulate realistic fire conditions by lowering the sample into a minioven pre-

TABLE I
Heat Evolved per gram of Resin

Mole fraction bromostyrene	% Br	Calculated heat evolved, cal/g
0	0	1460
0.2	4.9	320
0.4	9.3	250
0.6	13.4	220
0.8	17.1	280

TABLE II
Results of Flammability Tests for Polyester Resins^a

% Br	635-Rate of burning, mm/min		757-Rate of burning, mm/min		LOI, %	
	-W	+W	-W	+W	-W	+W
0	22.6	20.5	28.6	28.5	18.6	19.1
4.9	15.6	13.9	23.8	25.8	20.2	20.7
9.3	11.4	10.5	21.0	22.9	21.0	21.9
13.4	5.6	0	17.1	21.1	22.0	23.0
17.1	0	0	14.0	19.3	22.9	23.7
20.4	0	—	12.4	—	23.5	—
4.9 ^b	9.3	—	20.5	—	21.2	—
9.3 ^b	0	—	19.7	—	22.6	—
PF	0	—	15.5	—	24.5	—

^a Pf = Prefil-F; -W = before weathering; +W = after weathering.

^b 4% Phosphate-based synergist.

heated to temperatures between 400° and 700°C, with air or oxygen as the carrier gas. In most cases the PBrS did not burst into flames. However, in some cases two to three small explosions and flash bursts were observed. Similar observations were reported by Learmonth et al.² Their explanation is that there was enough fuel and oxygen for ignition, but the flame was snuffed out by the presence of volatile inhibitors that prevented the propagation of the flame. Further work is, however, necessary in order to explain this phenomenon.

ASTM Flammability Tests

The TGA and DTA experiments are important for understanding the process taking place in oxidative degradation. However, for actual performance of the materials under fire conditions, well-defined standard tests have to be used. We have chosen three ASTM tests: D635-63, D-757-65, and D-2863-70 (LOI).

The results of the tests on nonreinforced samples are summarized in Table II and Figure 5. All three tests show a linear increase in flame retardation with increase in Br content. However, only one test, namely 635, arrives at conditions considered sufficient for self-extinguishing materials when the Br content reaches 17%. This is the test where a Bunsen burner is used, i.e., when the initial temperature of ignition is not too high, and therefore the Br is enough for quenching the propagation of the chain reaction. This is equivalent to 20% Prefil-F added in a control experiment. The 757 test uses a higher ignition temperature and

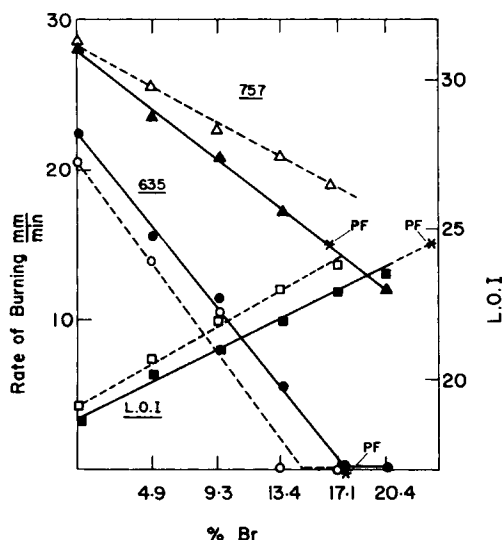


Fig. 5. Results of ASTM flammability tests on polyester containing increasing proportions of bromostyrene before (—) and after (---) weathering. PF-sample containing 20% Prefil-F.

the results show a considerable decrease in rate of burning, but self-extinguishing characteristics are not obtained. Prefil-F is not self-extinguishing either, in this test, and its rate of burning corresponds to 17% Br, as in the previous test. The LOI test also shows a linear increase with the Br content. For this test, however, Prefil-F seems more effective and corresponds to roughly 23% Br. The addition of 4% synergetic agent based on phosphate has only a small effect on the result. It seems that one has to find a synergetic agent that will be more specific for the bromostyrene system.

The effect of weathering was also studied as it was thought that UV light might decompose the bromo compound and deterioration of the properties may result. In fact, for the 635 and the LOI tests, improvement was observed even in the resin without any bromostyrene. This may be explained by additional curing that results in higher crosslinking. As the structure is more rigid, the rate of decomposition and penetration of oxygen will be slower. Apparently, this is not enough in the 757 test, which uses a higher ignition temperature and therefore can be expected to break up the rigid structure more readily. This then may release any smaller molecules that could have been formed during the weathering process and thus support the combustion more efficiently.

In practice, these polyester resins are usually used as composite materials, and therefore the tests were also carried out on glass-reinforced samples as shown in Table III. Here, one can see that the 757 test is more stringent than the 635 test. In the latter, even the resin without any bromine is self-extinguishing. In the 757 test and LOI tests, 13% Br in the resin are enough to make the samples self-extinguishing. In fact, it means that in the product as a whole, the sufficient Br content is less than 10%. The direction of the flame in relation to the fiber has an effect as this determines whether there is a constant supply of volatiles to the flame and also constant diffusion of oxygen. Furthermore, when the flame is parallel to the fibers, there is no accumulation of molten glass or ashes as they fall and produce a new surface.

TABLE III
Results of Flammability Tests for Glass-Reinforced Polyesters^a

% Br	635-Rate of burning, mm/min		757-Rate of burning, mm/min		LOI, %	
	L	T	L	T	L	T
0	0	11.9	19.9	21.1	22.8	21.0
4.9	0	8.4	15.5	19.6	24.2	22.0
9.3	0	0	12.2	16.5	24.9	23.0
13.4	0	0	2.8	6.4	26.2	24.5
17.1	0	0	2.5	2.1	28.5	25.7
20.4	0	0	2.6	2.1	33.5	27.1

^a L, T = Longitudinal and transverse reinforcement relative to the direction of flame propagation.

In conclusion, we can say that it was shown that bromine added as a ring-brominated monomer has a considerable effect on the general oxidative decomposition of the homopolymer and the polyester crosslinked with bromostyrene. The results show a linear decrease in rate of burning with increase in bromine content leading to self-extinguishing compositions. With glass-reinforced polyester, less than 10% Br content gives self-extinguishing materials.

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