

# Bromostyrene Crosslinked Polyesters. IV. The Effects of the C—Br Bond Strength and of Synergists on Fire Retardancy

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## Synopsis

The present study compares the effect of ortho-bromostyrene to that of para-bromostyrene on fire retardancy of polyesters at low and high flame temperatures. It is shown that the first isomer is more effective at the lower temperature and vice versa at the higher temperature. Thermoanalysis results partly explain this difference as well as the effect of additives such as  $\text{Sb}_2\text{O}_3$  and *bis*(2-chloroethyl) vinylphosphate.

## INTRODUCTION

Flame formation requires the presence of free radicals, and involves free-radical reactions in the volatile phase, which forms the fuel supply. It is commonly accepted that flame retardancy in halogen-containing polymeric materials is governed by the concentration of the halogen free radicals in the volatile phase. This results from the situation where Cl or Br radicals, and HCl or HBr formed, react with active radicals existing in the flame, and terminate the chain reactions.<sup>1</sup> It is clear that the stability of the carbon-halogen bond and the temperature of the flame, both factors determining the availability of the halogen radicals, are therefore the significant factors which control the fire retardancy of halogen containing polymers.

The effect of the carbon-halogen bond strength on the efficiency of the flame retardancy can be demonstrated by a few examples of published results. In a very extensive paper by Jolles<sup>2</sup> questions such as a maximum effectiveness of a flame retardant within a narrow range of carbon-halogen bond strength are discussed. Examples such as the greater effectiveness of hexachlorocyclohexane compared with hexachlorobenzene, and of organic bromine compounds compared with the corresponding chlorine compounds are thoroughly discussed. Similar problems are examined in relation to fire retardant unsaturated polyesters.<sup>3</sup> Another work deals with the effect of the C—H bond energy on the HBr formation, which is an essential step in the flame extinguishing process.<sup>4</sup>

The present work was initiated by a few observations in our previous work,<sup>5</sup> which studied the flammability of an unsaturated polyester crosslinked by various styrene/bromostyrene proportions within a constant crosslinking monomer/alkyd molar ratio. Polyester specimens which underwent weathering treatment exhibited improved flame retardancy properties when tested according to ASTM 635 and ASTM 2863, whereas such specimens tested according to ASTM 757 exhibited deteriorated flame retardancy properties. The explanation given was that weathering treatment might result in additional crosslinking of

the resin with a more rigid structure, and hence, lower decomposition and oxygen penetration rates. The first two flammability tests, which used a low-temperature ignition source, were sensitive to the new structure, while the later test, which used a much higher ignition temperature, was not. However, we now think that a more prominent reason for those observations is the formation during the weathering treatment of more labile bromine, which is more effective in the low-temperature flammability tests. This point is strengthened even further by the observation that for identical Br concentrations the low-temperature ASTM 635 yields better results (lower rates of burning) than the high temperature ASTM 757. Also, the slope of the rate-of-burning vs. % Br line for the ASTM 635 results is steeper than that for the ASTM 757, indicating that at a lower burning temperature more active Br radicals are available in the flame as the bromine percentage in the resin increases.

In view of the above observations, and in view of the fact that the commercial bromostyrene used in our studies was a mixture of the ortho and para isomers (OPBS) in a ratio of 1:2.5, it was decided to examine the effects of the C—Br bond strength and of synergists on the fire retardancy at two temperatures. The present work compares results obtained with ortho bromostyrene to those obtained with the commercial ortho/para mixture. Although the difference between the C—Br bond strength of the two isomers is only about 0.6 kcal/mol it is expected to be more significant in the polymer due to greater sterical hindrance. Synergists were added to see how they act with the different isomers.

## EXPERIMENTAL

The materials and the polymerization and casting techniques were mostly as described in the previous parts.<sup>5-7</sup> The ortho-bromostyrene (OBS) used in the present work was prepared according to Halpren and Meidar,<sup>8</sup> and the synergists employed were  $Sb_2O_3$  and *bis*(2-chloroethyl) vinylphosphate (BVP). The alkyd was crosslinked as before by a monomer mixture (including the BVP) with a constant ratio of 4.8 mmols of total monomer per 1 g alkyd. The ASTM 635 and 757 flammability tests and the thermal analysis apparatus are described in Paper 1.<sup>5</sup>

## RESULTS AND DISCUSSION

### Flammability Experiments

Table I summarizes the results of the flammability experiments. Normally the rate of burning is indicated, except for specimens which did not burn to the mark in the ASTM 635, and for specimens which did not burn for 3 min in the ASTM 757. Those specimens are marked self-extinguishing and denoted in Table I by SE (for example,  $SE_5^{35}$ , indicating self-extinguishing, burning time 35 sec, extent of burning 5 mm). Examination of the data in Table I shows that the ASTM 757 test exhibits higher rate-of-burning values than the ASTM 635. However, the important observation with regard to the present study is that polyesters crosslinked by OBS always exhibit lower rate-of-burning values compared with polyesters crosslinked by OPBS when tested in ASTM 635, and vice versa in the ASTM 757, except in one case. Also, in the ASTM 757 more OPBS-crosslinked polyesters are SE compared with the OBS-crosslinked

TABLE I  
Results of the Flammability Experiments of OBS and OPBS—Crosslinked Polyesters<sup>a</sup>

Additives in resin, wt. %			Rate of burning, mm/min			
			ASTM D 635-72		ASTM D 757-71	
Br	BVP	Sb <sub>2</sub> O <sub>3</sub>	OPBS	OBS	OPBS	OBS
0	—	—	24.6	24.6	28.3	28.3
5	—	—	16.2	15.9	23.8	24.2
5	3.8	—	8.5	8.4	21.6	21.6
5	11.2	—	SE <sub>5</sub> <sup>35</sup>	SE <sub>5</sub> <sup>35</sup>	15.8	16.2
5	18.8 <sup>b</sup>	—	SE <sub>5</sub> <sup>35</sup>	SE <sub>5</sub> <sup>35</sup>	SE <sub>40</sub> <sup>160</sup>	SE <sub>42</sub> <sup>160</sup>
5	—	0.5	13.2	13.1	24.7	24.9
5	—	1.5	12.1	11.9	23.7	24.3
5	—	2.5	SE <sub>15</sub> <sup>100</sup>	SE <sub>10</sub> <sup>255</sup>	21.0	23.2
12.8	—	—	9.2	8.4	19.0	20.5
12.8	3.8	—	SE <sub>5</sub> <sup>40</sup>	SE <sub>5</sub> <sup>35</sup>	16.2	17.5
12.8	11.2	—	SE <sub>5</sub> <sup>35</sup>	SE <sub>5</sub> <sup>35</sup>	SE <sub>28</sub> <sup>130</sup>	14.0
12.8	18.8	—	SE <sub>5</sub> <sup>35</sup>	SE <sub>5</sub> <sup>35</sup>	NB	SE <sub>32</sub> <sup>150</sup>
12.8	—	0.5	SE <sub>5</sub> <sup>45</sup>	SE <sub>5</sub> <sup>40</sup>	17.5	19.0
12.8	—	1.5	SE <sub>5</sub> <sup>35</sup>	SE <sub>5</sub> <sup>35</sup>	SE <sub>45</sub> <sup>148</sup>	16.3
12.8	—	2.5	SE <sub>5</sub> <sup>35</sup>	SE <sub>5</sub> <sup>35</sup>	SE <sub>26</sub> <sup>100</sup>	SE <sub>37</sub> <sup>110</sup>

<sup>a</sup> SE<sub>10</sub><sup>255</sup> denotes self-extinguishing, burning time 255 sec, extent of burning 10 mm. NB denotes nonburning. Each value is an average of at least three results.

<sup>b</sup> For BVP concentration of 18.8 wt. % the resin contains 5% Cl and 2.5% P.

polyesters, and the extent of burning for SE specimens is always greater for the OBS specimens. Although occasionally the scatter of the results exceeded the differences between the average rate-of-burning values of OBS and OPBS-crosslinked polyesters, the general picture is one of a consistent difference between the OBS- and OPBS-crosslinked polyesters. Thus, it is maintained that the ortho-bromostyrene is more efficient in the low-temperature ASTM 635 test, while the para-bromostyrene is more efficient in the high temperature ASTM 757 test. It seems that the presence of either the BVP or the Sb<sub>2</sub>O<sub>3</sub> does not deepen the gap between the action of the two isomers in any of the flammability tests.

Another interesting issue—although slightly diverted from the main issue of this study—is the effect on the fire retardancy of the combination of BVP or Sb<sub>2</sub>O<sub>3</sub> with the bromine. If the rate-of-burning values in Table I are drawn as a function of the wt.% of BVP, they will generally result in parallel lines for the two Br concentrations suggesting an additive effect of bromine and phosphorous. However, when the relevant data are drawn as a function of the Sb<sub>2</sub>O<sub>3</sub> wt. %, the negative slope of the curve will generally be greater for the higher Br concentration. This might indicate a synergistic effect of Br and Sb<sub>2</sub>O<sub>3</sub>. This issue is demonstrated for the case of Sb<sub>2</sub>O<sub>3</sub> in Figure 1.

### Thermal Analysis Experiments

Thermal analysis experiments were carried out either under nitrogen or under oxygen atmospheres, and with a wide range of polymer compositions. The results reported here are mostly those directly related to the issue of the difference between the ortho and para isomers. Figures 2 and 3 present results of thermogravimetric analyses (TGA), and Figures 4 and 5 present results of dif-

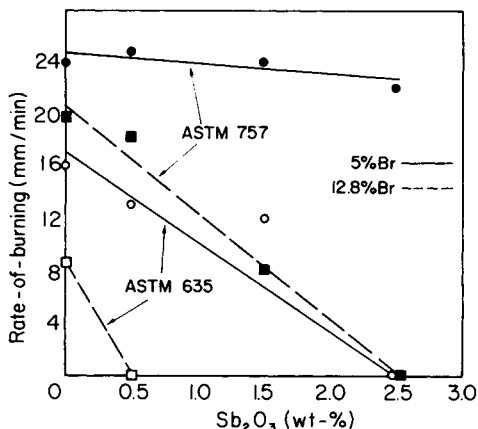


Fig. 1. Rate-of-burning values as a function of the  $\text{Sb}_2\text{O}_3$  wt. %, showing steeper lines for higher Br concentrations in each of the flammability tests. Every point is an average of the OPBS and OBS results.

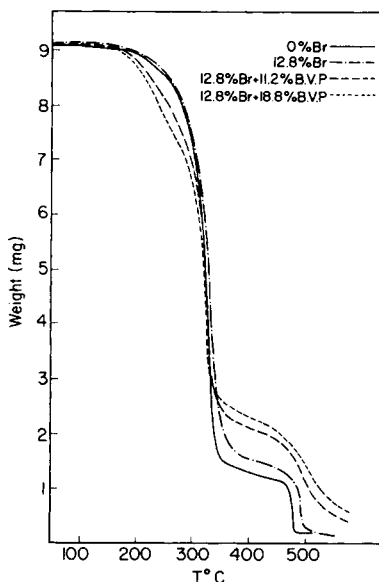


Fig. 2. Traces of thermogravimetric analyses under oxygen of OPBS-crosslinked polyesters containing various BVP concentrations.

ferential thermal analyses (DTA) under oxygen of polyesters crosslinked by OPBS and by OBS, respectively, and containing BVP.

The data derived from TGA and DTA measurements provide a few possible explanations for the higher efficiency of OBS as a fire retardant in the ASTM 635 test. Resins crosslinked by OBS compared with those crosslinked by OPBS release less heat during the major step of oxidative decomposition (the results are summarized in Table II). This fact agrees with the theory of fire retardancy,<sup>9</sup> which suggests that the effectiveness of a fire retardant increases as the heat evolved decreases (the heat evolved being the arithmetic sum of the endothermal heat of decomposition and the exothermal heat of combustion). Since the bromine inhibits oxidation reactions in the gas phases the value of the heat

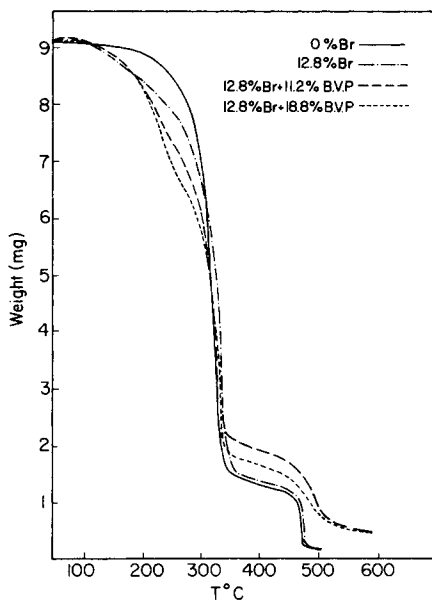


Fig. 3. Traces of thermogravimetric analyses under oxygen of OBS-crosslinked polyesters containing various BVP concentrations.

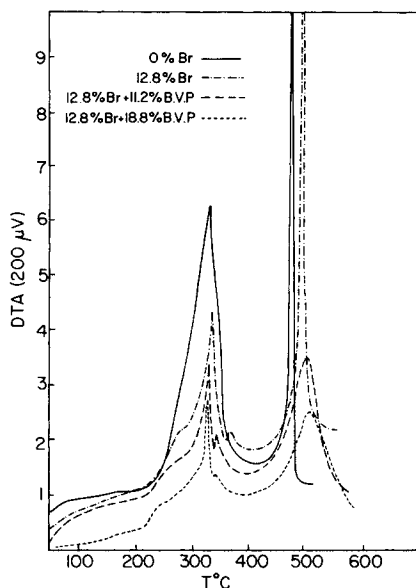


Fig. 4. Traces of differential thermal analyses under oxygen of OPBS-crosslinked polyesters containing various BVP concentrations.

evolved is expected to reduce as the bromine concentration increases, and as the C—Br bond strength decreases. This is seen clearly in Table II.

A further support to the conclusions drawn from the flammability experiments is the observation that polyesters crosslinked by OBS start to decompose at a lower temperature relative to polyesters crosslinked by OPBS. The rate of weight loss as measured by differential TGA (DTG) does not depend on the type of crosslinking monomer. The earlier decomposition of the OBS crosslinked

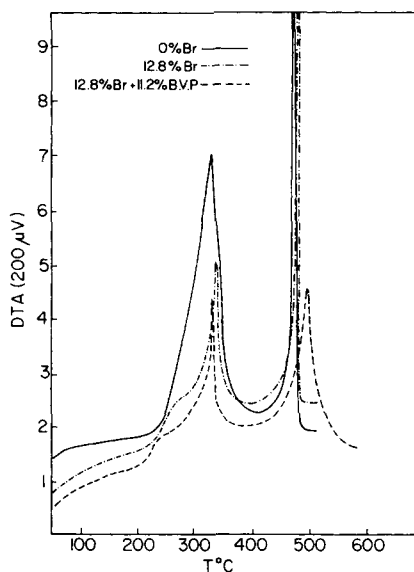


Fig. 5. Traces of differential thermal analyses under oxygen of OBS-crosslinked polyesters containing various BVP concentrations.

TABLE II  
Heat Evolved During the Main Step of Oxidative Decomposition of OBS and OPBS-Crosslinked Polyesters

Additives in resin, wt. %			Heat evolved, cal/g	
Br	BVP	Sb <sub>2</sub> O <sub>3</sub>	OPBS	OBS
—	—	—	557.0	557.0
5	—	—	341.1	297.4
5	11.2	—	201.3	195.7
5	18.8	—	174.4	163.8
5	—	1.5	214.6	205.8
5	—	2.5	201.3	180.2
12.8	—	—	259.3	232.3
12.8	11.2	—	179.4	172.1
12.8	18.8	—	150.4	104.7
12.8	—	1.5	198.8	177.6
12.8	—	2.5	177.3	163.1

polyesters implies that more labile bromine might be available at a lower temperature. The examination of similar TGA and DTG data of the homopolymers of OBS and OPBS turns out to be somewhat confusing in view of an earlier decomposition exhibited by the later polymer, and a higher rate of decomposition at the main oxidation stage exhibited by the first. Since these results are highly dependent on structural factors such as molecular weight, to which the homopolymers are more sensitive than the crosslinked structures of the polyester resins, it is thought that the results of the polyesters are more applicable than results of the homopolymers to a comparison with the flammability data.

The thermoanalyses strengthen the conclusion reached earlier in view of the flammability results that neither of the additives employed deepens the gap between the two isomers. Figure 6 is an example of TGA traces of polyesters containing Sb<sub>2</sub>O<sub>3</sub> crosslinked by OPBS. It is seen that with Sb<sub>2</sub>O<sub>3</sub> present in-

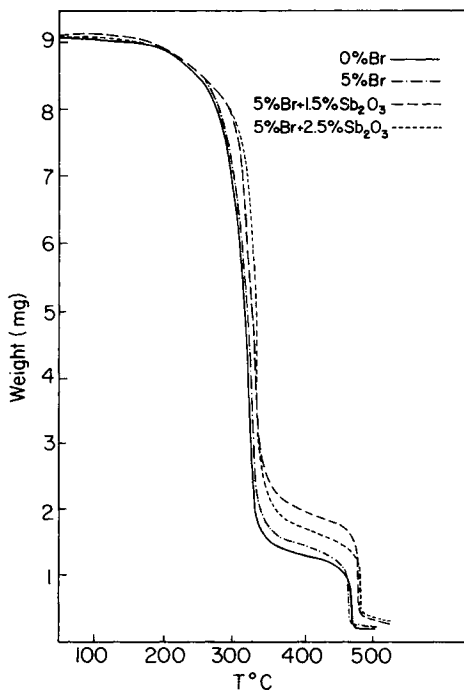


Fig. 6. Traces of thermogravimetric analyses under oxygen of OPBS-crosslinked polyesters containing various  $\text{Sb}_2\text{O}_3$  concentrations.

stead of BVP relatively much smaller weight losses occur in the range of  $125^\circ\text{--}160^\circ\text{C}$ . The greater weight loss recorded by BVP containing polyesters probably results from a condensation reaction of the BVP which results in additional crosslinking of the resin and release of dichloroethane.<sup>10</sup> Another prominent difference between the action of BVP and  $\text{Sb}_2\text{O}_3$  is the char percentage at temperatures of  $500^\circ\text{C}$  and higher. The higher char percentage exhibited by polyesters containing BVP strengthens the idea that phosphorus compounds are active as flame retardants in the solid phase.

## CONCLUSIONS

The observations that the effectiveness of bromostyrene as a fire retardant depends on the strength of the C—Br bond strength and on the temperature of the flame; and the requirement of a commercial material to be resistant to fire at a wide temperature range suggest, that an effective bromine containing fire retardant should include a range of C—Br bond strengths. This could be achieved by using a mixture of isomers, or alternatively by using a mixture of various aromatic and aliphatic bromine compounds.

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