SYNTHESIS AND CHARACTERIZATION OF DI (2, 4, 6–TRIBROMOPHENOXY) TRIPHENYL–ANTIMONY①

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ABSTRACT

The synthetic method and characterization of di (2, 4, 6–tribromophenoxy) triphenyl antimony are reported in this paper. This compound is prepared by reacting dihalotriphenyl-antimony with tribromophenol under definite conditions and its yield is 70–80 %. Below 250 ℃, the product has good thermal stability. It makes a favorable flame resisting effect on polyethylene, while the addition is only 10 Phr without using antimony trioxide, the oxygen index of the polymer increases from 18. 5 to 26. 5, and there are no adverse effects on the mechanical properties of polyethylene.

Key words: antimony organoantimony compounds flame retardant

1 INTRODUCT10N

With the development of processing antimony products and polymer industry, some inorganic compounds of antimony have been used as additive-type flame retardants, among which the amount of Sb_2O_3 is the largest. It is widely used in the departments of plastic, chemical fibre, coating and paint. But Sb_2O_3 has no flame resistance itself; only when reacting with the compounds containing halogen and phosphorus, can it resist flame for the polymers. To achieve flame resisting effect, a large quantity of Sb_2O_3 is needed, and there is a lot of smoking for flame resisting materials, the transparency and the mechanical performance of materials are affected. Therefore, in recent years organo-antimony compounds have been used as flame retardants, such as derivatives of dibromine triphenyl antimony and antimony ester for polymers[1–4]. They have overcome some weekness of antimony inorganic flame retardants.

In this paper, the synthesis and properties of di(2, 4, 6–tribromophenoxy) triphenyl antimony were studied. The flame resisting effect of this product on polyethylene was tested. The influence of the amount of the additive agent on the mechanical properties of the polymer was discussed.

2 EXPERIMENTAL

2. 1 *Synthetic Principle*

Dihalotriphenyl antimony reacts with tribromophenol in benzene solution of triethyl amine or dihalotriphenylantimony reacts with

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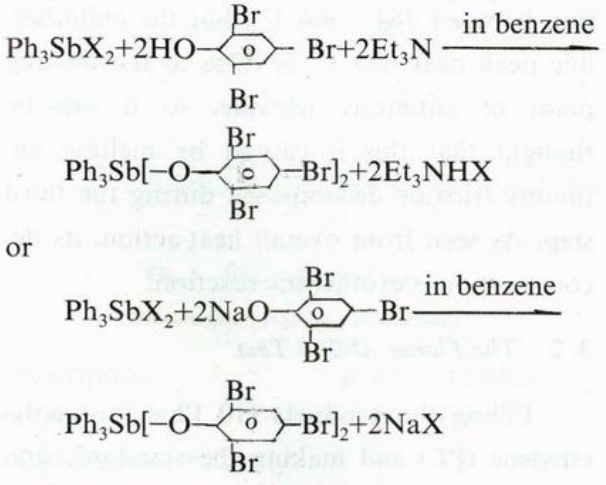
tribromophenol sodium in benzene solvent directly, there will be di (2, 4, 6–tribromophenoxy) triphenylantimony under definite condition. Its chemical reactions are listed as follows



where X = Cl or Br, Ph = C_6H_5

2.2 *Synthetic Method*

1 A definite amount of Ph_3SbBr_2, tribromophenol, triethylamine and benzene was put in a flask, stirred and reacting for a few hours at room temperature; and then refluxing the solution for a few hours. Triethylamine hydrobromide was filtered off, the filtrate was concentrated and addition of petroleum ether afforded the precipitate. The white powder was obtained by washing with organic solvent, and then drying in a vacuum-desicator. The yield was 80 %;

2 Using dichlortriphenylantimony as a substitute for dibrominetriphenylatimony to react with tribrophenol under the above conditions, then prolonging two hours for refluxing. The white powder was obtained after washing with the organic solvent. The yield was 70.5 %;

3 Substituting the sodium salt of tribromophenol for tribromophenol to react directly with dibrominetriphenylantimony in benzene solvent, heating and refluxing for a few hours. The sodium bromide in the solution was filtered off and the filtrate was concentrated. The resulting compound was precipitated by adding petroleum ether, then filterring, washing, and drying under a constant temperature, getting white powder products. The yield was 62.2%.

It is evident that the first method has the highest yield, and the second method is next to the first. But chloride was used to take the place of expensive bromine, in the first method.

2.3 *Product Analysis*

1 The melting point of product measured by the micro apparatus of melting point is 239～241℃;

2 The antimony content measured by $KBrO_3$ method in product is 12.5 % (its calculation value is 12.0 %);

3 The bromine content in the compound determined by oxygen cylinder combustion is 46.8 % (the calculation value is 47.3 %);

4 IR spectrum was recorded in KBr pellets in the range 4,000～400 cm^{-1}. As seen in Fig.1, the strong absorption peak at 1,428 cm^{-1} is the phene ring skelton. The absorpting peak at 1,284 cm^{-1} is the absorption of Ph-O stretching band, which is fairly higher than the wave number of Ph-O in phenol, indicating the oxygen of phenolic-OH group was bonded with the metal in the compound. The peak at 736 and 685 cm^{-1} is the vibration frequency of five contigent hydrogen in phene ring. In the low wave number region (below 600 cm^{-1}), there is a medium intensity band around 400 cm^{-1}, which may be assigned to v (Sb–O) stretching vibration[5–6]. A strong band at 450 cm^{-1}, may be assigned to asymetric C–Sb

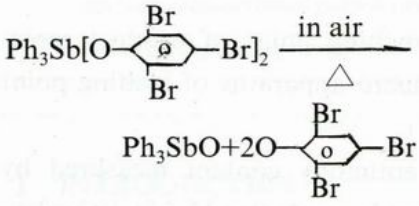
stretching band.

3 PROPERTY TESTS OF THE COMPOUND

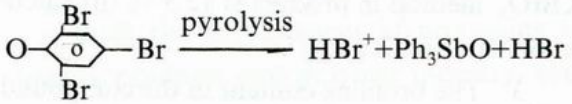
3.1 *Thermal Analysis*

The thermogravimetry curve of the product is presented in Fig. 2.

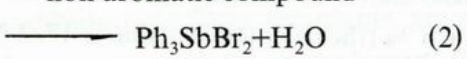
As known from Fig. 2, the product is thermally stable below 250 ℃; the largest losing-weight peak occurred while the temperature is 250～280 ℃, and a smaller one between 280～550 ℃, and then the third is between 550 ～ 610 ℃. The corresponding decomposition reaction may be



(1)



non-aromatic compound



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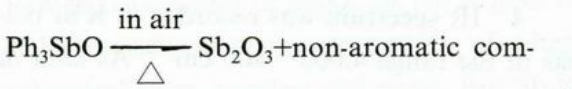

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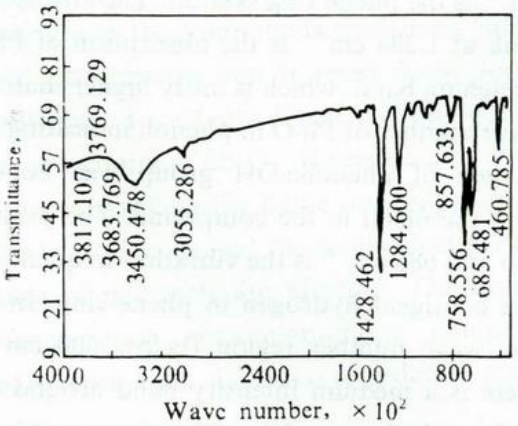

Fig. 1 IR spectrum of di (2, 4, 6–tribromophenoxy) triphenylantimony

The DSC curve of the product is shown in Fig. 3.

As known from Fig.3, there is a endothermic peak between 240～ 254 ℃, and exothermic heat peak of decomposition reaction between 264～ 306 ℃; but the endothermic peak near 633 ℃ is close to the melting point of antimony trioxide, so it can be thought that this is caused by melting antimony trioxide decomposed during the third step. As seen from overall heat-action, its decomposition is exothermic reaction.

3.2 *The Flame Ability Test*

Filling the products (10 Phr) into polyethylene (PE) and making the standard samples of 120 mm× 6.5 mm× 4 mm (product-PE), limiting oxygen index (LOI) was measured on GB 2406～80, the test result is as follows

sample	LOI
pare PE	18. 5
product–PE	26. 5

In comparison di (2, 4, 6–tribromophenoxy) triphenylantimony with decabromodipheny ether, its prescription and oxygen index

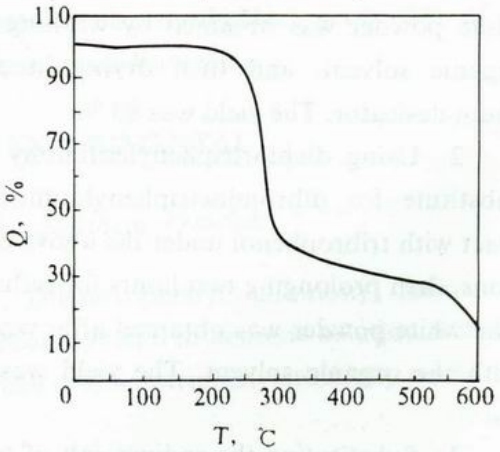

Fig. 2 TG curve of di (2, 4, 6–tribromophenoxy) triphenylantimony

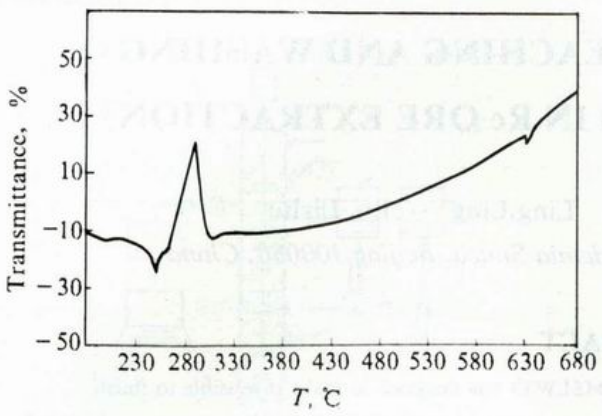

Fig. 3 DSC curve of di(2, 4, 6–tribromophenoxy) triphenlantimony

prescription	portion number
polyethylene	100
othylenetrimethoxysilyl	2
decabromodipheny ether	20
LOI	26

are as follows:

The test showed that the addition of 10 Phr of the product only, the LOI of polyethylene increased from 18. 5 to 26. 5 for polyethylene. With the same oxygen index, the amount of this product is only as half as that of decabromodiphenyl ether, moreover it needs not antimony trioxide and other auxiliaries.

3. 3 *The Influence on Mechanics Performance of Polyethylene*

Filling the products (10 Phr) into polyethylene, injecting the mixture to become standard samples (product-PE), then measuring their curving intensity according to GB1043–79 and getting the results of 4.12～15.87 MPa for pure PE and 9.30 MPa for product–PE.

4 CONCLUSION

(1) Dihalotriphenyl-antimony can reacts with tribromophenol or tribromophenol sodium to form di (2, 4, 6–tribromophenoxy) triphenyl antimony, with yield of 80% or 70% The product appears as white powder, and its mp. is 239～241 ℃;

(2) This product has favorable thermal stability below 25 ℃, and there is a heat decomposition between 250 ℃ and 610 ℃ which is a exothermic reaction;

(3) This product can be used as additive for flame retardant of polyethylene with very small amount of 10 Phr, and the oxygen index of polyethylene with this additive can be increased from 18. 5 to 26. 5 even if without antimony trioxide as auxiliary added;

(4) As a flame retardant for polyethylene, the compound has no bad effect on its curving and punching intensity, and the original mechanical performance of polyethylene can be maintained.

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