

Research Article

Synergistic Fire Retardancy of Bis(1-methoxy-2,2,6,6-tetramethylpiperidin-4-yl)sebacate and Tris(2,4,6-tribromophenoxy)-1,3,5-triazine/Sb₂O₃ in HIPS

Hongzhi Wu, Junhong Liu, Qi Zhang, Mingmei Sun, Jingwei Yang , and Linsheng Tang 

State Key Laboratory Base of Eco-chemical Engineering, College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

Correspondence should be addressed to Jingwei Yang; jingwei0701@163.com and Linsheng Tang; linshengt2@163.com

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Bis(1-methoxy-2,2,6,6-tetramethylpiperidin-4-yl)sebacate (NORMS) was found to perform an exceptional synergistic effect with tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBPC)/Sb₂O₃ in HIPS. The LOI of fire retardant HIPS (FR-HIPS) with 16 wt% of TTBPC/Sb₂O₃ increased from 23.8% to 25.2%, the flame retardant rating of FR-HIPS was improved from UL 94 V-2 to UL 94 V-0, and various heat release parameters such as peak heat release rate, total heat release, and mean effective heat of combustion were greatly lowered by combining NORMS of 0.50 wt%. The Py-GC/MS results revealed that NORMS induced the role of synergistic effect; the main mechanisms were as follows: the active radicals such as methoxy radicals and aminyl radicals produced by the pyrolysis of NORMS promote the release of bromine radicals from TTBPC and the formation of HBr and CO₂, which improves the flame retardancy of TTBPC/Sb₂O₃; the above active radicals, together with HBr, quench active free radicals, such as the hydroxyl radical (OH), and decompose the free radical source, which interrupts the chain reaction during combustion and results in a more efficient flame retardant effect in gaseous phase.

1. Introduction

High impact polystyrene (HIPS) is widely used in decoration of automobiles, buildings, electronic and electrical parts, and so forth due to its good dimensional stability, excellent physical properties, low price, and so forth. However, HIPS are flammable, thus underlining the importance of flame retardant treatments. The fire retardants used in HIPS are mainly phosphorus fire retardants, including red phosphorus [1–4], ammonium polyphosphate [5, 6], and organophosphorous compounds [6–9]; brominated flame retardant, metal hydroxide [1–3, 9, 10]; and inorganic nanoparticles, such as multiwalled carbon nanotube [6, 11], graphene and molybdenum disulfide [12], silica nanoparticle [7], and montmorillonite [8, 12, 13].

Although there are many reported flame retardants that can be used in HIPS, the primarily used flame retardants are brominated flame retardants, as they have better

comprehensive performance. The most common brominated flame retardants are decabromodiphenyl ether (decaBDE) [14], tetrabromobisphenol A (TBBA) and its derivatives [15], decabromodiphenyl ethane (DBDPE) [14, 16, 17], and so forth. decaBDE was gradually restricted in use due to its environmental impact [18]. Besides, TBBA also involves environmental and safe impact [19]. Tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBPC) is a novel brominated flame retardant containing nitrogen, which exhibits good melt fluidity, flame retardancy, thermal stability, antistatic ability, UV light stability, and so forth [20, 21]. It is suitable for TTBPC in HIPS and other polymers. Nevertheless, it also needs to be used at a higher concentration (usually about 20 wt%) as compared to other brominated flame retardants. How to effectively improve the flame retardancy of brominated flame retardants, especially TTBPC in HIPS, is important to promote the development and application of HIPS.

In the last few years, it has been found that 1-alkoxy-2,2,6,6-tetramethylpiperidine-based compounds (NORs) not only exhibited UV stabilization but also contributed to the flame retardancy and synergistic flame retardant effect in polyolefin, especially polypropylene [22, 23]. NOR116, the first commercial NORs product introduced by Ciba (now BASF) in 2000, primarily exhibits the following characteristics: (1) adequate performance as a flame retardant in polypropylene fiber and thin films [24]; (2) adequate performance as a synergist in traditional flame retardants such as brominated flame retardants [25, 26], phosphorus flame retardants [25], melamine and its derivatives [27, 28], intumescent flame retardants (IFR) [29, 30], and inorganic flame retardants [31]; (3) lower smoke production and toxic gases release by replacing or decreasing the quantity of the commonly used synergist, Sb_2O_3 , in halogen flame retardants; (4) being environment-friendly and safe in use because of its halogen-free nature and lower additive dosage; and (5) appreciable thermal stabilization as well as UV stabilization. Regardless of these properties, NOR116 exhibited some shortcomings: (1) adequate performance as a flame retardant only in thin polyolefin products; (2) discolored or yellowed the polyolefin when it was in use; (3) occurrence of dripping during burning; and (4) being exceedingly complex in structure and synthesis method [32], leading to increased cost of production and large three-waste emissions during synthesis.

To overcome the shortcomings of NOR116, some new NORs, with better performance and simpler molecular structure and synthesis process, have been developed domestically and abroad. One of these, a series of NORs containing AZO structure (AZONORs), was designed and synthesized by Aubert et al. in Åbo Akademi University in Finland [33, 34]. The DIN4102 B2 flammability test showed that AZONORs had appreciable flame retardancy and self-extinguishing effect in polypropylene films and templates. Moreover, they proved capable of preventing dripping while burning. Besides, AZONOR compounds showed an exceptional performance and exhibited a significant synergistic effect with different brominated flame retardants and mineral fillers such as aluminum hydroxide (ATH).

Series of bis(1-alkoxy-2,2,6,6-tetramethylpiperidin-4-yl)sebacate (NORSs) and 1-n-alkoxy-4-(dodecyl-2-enyl)-2,2,6,6-tetramethylpiperidine were designed and synthesized by Wilén and Pfaendner [23]. Results showed that the structure of the alkoxy group resulted in a great impact on the thermal stability and the flame retardancy of above NORs. Some of the above NORs had a flame retardancy equivalent to or better than that of the NOR116, and 1-methoxy-4-(dodecyl-2-enyl)-2,2,6,6-tetramethylpiperidine (NOMe) did the best. What is more, NOMe exhibited a very significant synergistic effect with brominated flame retardants.

Cao et al. [35], Zhejiang University, China, also designed and synthesized a silicon-containing NOR, which not only exhibits good synergistic effect with IFR but also can improve the UV stability and mechanical properties of the composite. Some other types of NORs had also better flame retardant effect in polypropylene than that of NOR116 [23, 36, 37].

NORSs is a kind of NORs with comparatively simpler chemical structure and synthesis process [38–40], the long chain in its structure leads to its good thermal stability and good dispersion in matrix [41], and its moderate molecular weight results in its somehow mobility resistance. Tinuvin NOR123, the trade name of bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl)sebacate, is a commercial product of Ciba, and it exhibits strong UV stabilization along with an appreciable synergistic flame retardancy. Charla, et al. found that Tinuvin NOR123 exhibited a good synergistic flame retardant effect with brominated phosphate in PP fiber, which could pass the FMVSS 302 test when the concentrations of Tinuvin NOR123 and brominated phosphate were 1 wt% and 2 wt%, respectively [42]. Except what is mentioned above, very few relative studies on the flame retardancy and the flame retardant synergistic effect of NORSs were reported, and no report on those performances in HIPS was found either. Therefore, in this paper, more attention will be paid to the studies of the synthesis and synergistic flame retardancy of bis(1-methoxy-2,2,6,6-tetramethylpiperidin-4-yl)sebacate (NORSM) with TTBPC/ Sb_2O_3 in HIPS.

2. Experimental

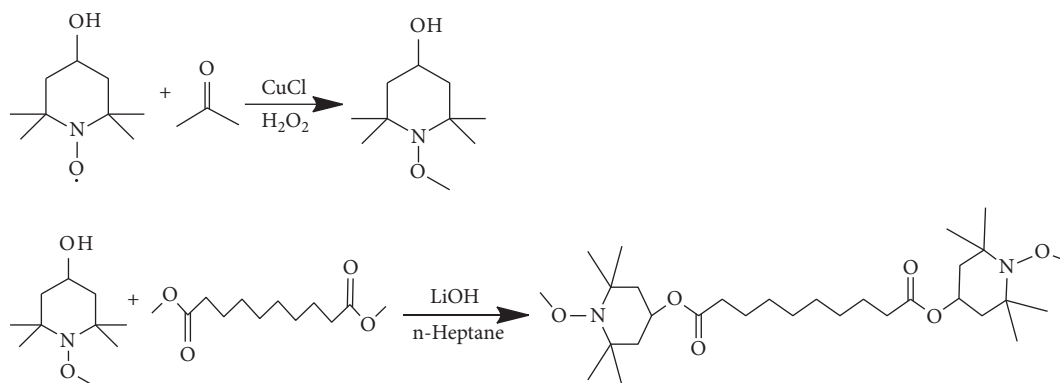
2.1. Chemical Reagents and Materials. Chemical grade acetone, CuCl, 30% hydrogen peroxide (H_2O_2), triethylamine, and so forth were purchased from Sinopharm Chemical Reagent Co., Ltd. Commercial grade HIPS/4440(AS) and HIPS/4241(AS) were purchased from Total (France); 4-hydroxy-2,2,6,6-tetramethylpiperidinoxy (ZJ-701), dimethyl sebacate (MSDS), Sb_2O_3 , and TTBPC were purchased from Beijing Jiacheng Additives Institute, Shanghai Nuotai Chemical Co., Ltd., Jinan Taixing Fine Chemical Co., Ltd., and Shouguang Weidong Chemical Co., Ltd., respectively, and were also of commercial grade. All chemical reagents and materials were used as received.

2.2. Preparation of NORSM. The synthesis methods of NORs were reported in related literature [38–40], and one of the most effective methods was transesterification. In this paper, NORSM were synthesized by an improved catalyst transesterification with a novel methanol separation process.

In the synthesis principle, using ZJ-701 and acetone as the raw materials, 30% H_2O_2 as the oxidant, and cuprous chloride (CuCl) as the catalyst, 1-methoxy-2,2,6,6-tetramethylpiperidin-4-ol was synthesized through O-alkylation [43]. Following this, the obtained product transesterified dimethyl sebacate to synthesize NORSM using LiOH as the catalyst. The synthesis principle is shown in Scheme 1.

Regarding synthesis process of NORSM, it is divided into two steps, synthesis of 1-methoxy-2,2,6,6-tetramethylpiperidin-4-ol and synthesis of NORSM.

- (1) Synthesis of 1-methoxy-2,2,6,6-tetramethylpiperidin-4-ol: the synthesis was carried out in a three-necked 250 ml flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser, and the stirring rate was kept constant at 150 rpm. The



SCHEME 1: Synthesis principle of NORSM.

reaction temperature was controlled by a thermostated water bath. First, ZJ-701 (0.10 mol; 17.2 g) and acetone (1.5 mol; 87.2 g) were added to the 250 ml three-necked flask first; H_2O_2 (0.3 mol; 30 ml) was then slowly dripped into at $5\text{--}10^\circ\text{C}$ while stirring. With that temperature being unchanged, CuCl (6.36 mmol; 0.63 g) was added to the flask, and then the contents were heated up to 30°C and maintained for 24 h. Thereafter, the unreacted acetone was removed by vacuum distillation, the residue was extracted with 60 ml dichloromethane, and the organic phase was washed thrice with deionized water (3×40 ml). The dichloromethane was removed from the organic phase by distillation, and the residue was dissolved with 60 ml methanol/water (volume ratio = 1 : 1) by heating; the contents were then cooled down to 0°C and maintained for 24 h. The crystallized product was filtered and washed thrice with deionized water (20×3 ml). The product was then dried to constant weight at 60°C , and about 8.75 g white powder product was obtained (theoretical 18.73 g). 46.7% yield of the product was obtained with purity of 99.1% and melting point of $86\text{--}89^\circ\text{C}$.

- (2) Synthesis of NORSM: 0.11 mol 1-methoxy-2,2,6,6-tetramethylpiperidin-4-ol (20.6 g), 0.09 mol finely ground LiOH (2.2 g), n-heptane (100 g), 0.05 mol dimethyl sebacate (11.5 g), and 0.003 mol tetrabutylammonium bromide (about 1 g) were added to a dried 250 ml flask equipped with a mechanical stirrer, a thermometer, a water separator, and a reflux condenser, and the contents were then heated up to reflux (about 98°C), with methanol being continuously separated; stop the reaction till there was no methanol remained (about 6–8 h). After the reaction, the contents were cooled to room temperature, the organic phase was washed thrice with deionized water (40 ml \times 3) first and then washed twice with $35\text{ g} \times 2$ mixed solvent of methanol and water with the weight ratio of 1 : 1, the solvent and unreacted 1-alkoxy-2,2,6,6-tetramethylpiperidin-4-ol were separated from the organic phase by vacuum distillation, and the distillation residue was washed thrice with 35 g of the above mixed solvent. Finally,

21.6 g (theoretical 27.02 g) NORSM was obtained by removing residual mixed solvent through vacuum distillation. The yield of NORSM was 79.9% with purity of 96.3%.

For structural characterization, the Fourier transform infrared (FT-IR) spectra measurement of the product was performed by KBr tablet method in a wavelength range of 400 to 4000 cm^{-1} using TENSOR-27 Infrared Spectrometer from Bruker Inc., Germany. The ^1H NMR and ^{13}C NMR spectra were recorded by an AVANCE-500M NMR Instrument from Bruker Inc., Germany, with deuterated chloroform as solvent. The elemental analysis of H, C, O, and N was performed with vario MACRO cube Element Analyzer made by Elementar Company (Germany). Melting points were determined with an XT4B Melting Point Meter made by Beijing Scientific Instruments Electro-optic Instrument Factory.

Figures 1–3 correspond to the infrared spectrum (IR), ^1H NMR, and ^{13}C NMR of NORSM, respectively.

In Figure 1, the absorption peaks at 2975 cm^{-1} correspond to $\nu\text{C-H}$ of methyl; those at 2930 cm^{-1} correspond to $\nu\text{C-H}$ of methylene; those at 1735 cm^{-1} can be attributed to $\nu\text{C=O}$; those at 1217 cm^{-1} can be assigned to hydrogen-free $\nu\text{C-N}$; those at 1175 cm^{-1} can be attributed to hydrogen-free $\nu\text{N-O}$; those at 1049 cm^{-1} correspond to $\nu\text{C-O-C}$ linking with carbonyl; and those at 719 cm^{-1} can be attributed to $\nu\text{C-N}$ of long-chain methylene [43].

The ^1H NMR spectra of NORSM (500 MHz, CDCl_3) are as follows: $\delta = 4.99$ (qd, $J = 11.1, 5.5$ Hz, 2H), 3.59 (dd, $J = 8.7, 5.3$ Hz, 6H), 2.23 (dd, $J = 7.1, 2.8$ Hz, 4H), 1.79 (s, 4H), 1.54 (dd, $J = 24.0, 12.0$ Hz, 8H), 1.27 (d, $J = 5.8$ Hz, 8H), 1.22–1.10 (m, 24H) [44].

The ^{13}C NMR spectra of NORSM (125 MHz, CDCl_3) are as follows: $\delta = 173.39, 66.41, 65.45, 59.95, 44.13, 34.54, 33.02, 29.05, 24.93, 20.71$ [44].

Anal. Calcd for $\text{C}_{30}\text{H}_{56}\text{N}_2\text{O}_6$: C, 66.63; H, 10.44; N, 5.18; O, 17.75. Found: C, 66.57; H, 10.53; N, 5.20; O, 17.64.

It is shown from the above results that the synthesized product is NORSM.

2.3. Preparation of Flame Retarded Samples. HIPS and all the additives were dried beforehand in a vacuum oven at 80°C overnight. NORSM, Sb_2O_3 , and TTBPC were mixed

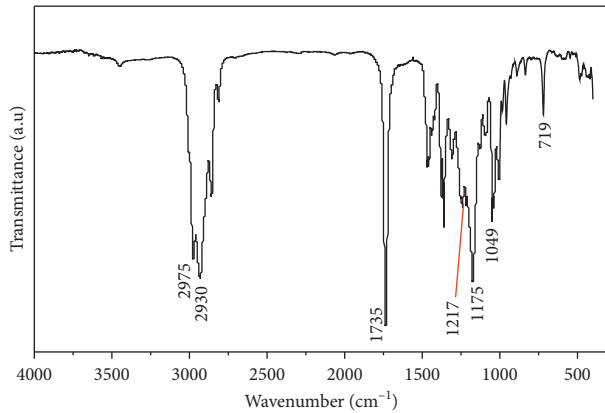
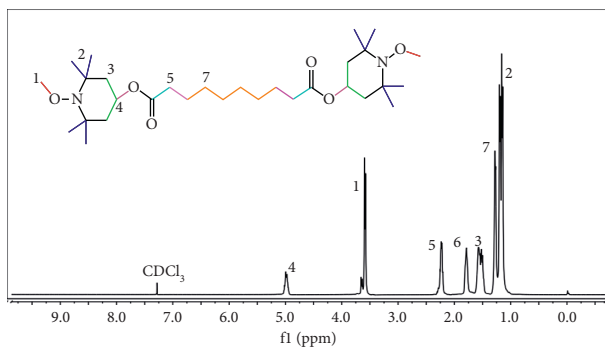
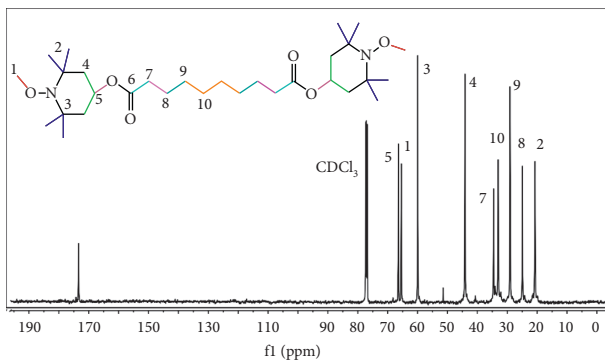


FIGURE 1: IR of NORSM.

FIGURE 2: ¹H NMR of NORSM.FIGURE 3: ¹³C NMR of NORSM.

proportionally, followed by the addition of a certain amount of the HIPS mixture of HIPS/4440 and HIPS/4241 (made in Total, France) with the weight ratio of 1 : 1. The mixed materials were added to a JS30 A twin-screw extruder (made by Yantai Qitong Powder Machinery Co., Ltd., China) and were extruded at 200–210°C at 20–30 r/min for granulation. The dried particles were mould-pressed into 100 × 100 × 1.6 mm³ sheets at 200–210°C under 5 MPa by 2G-10T Automation Pressure Precise Machine (Dongguan Zhenggong Mechanical and Electrical Equipment Technology Co., Ltd., China). The sheets were then cut into standard samples for flame retardant performance test.

2.4. Flame Retardant Performance Test. The limiting oxygen index (LOI) value was measured on the specimens of 100 × 6.5 × 1.6 mm³ according to the standard oxygen index test ISO4589-1984 using a JF-3 oxygen index meter (made by Jiangning Analytical Instrument Company, Nanjing, China); each sample was retested twice; vertical burning test was conducted on sheets of 100 × 13 × 1.6 mm³ according to the standard UL-94 test ASTM D635-77 using a CZF-3 horizontal vertical burning tester (made by Jiangning Analytical Instrument Company, Nanjing, China), and each sample was retested twice; the cone calorimeter test (CCT) was carried out at an incident heat flux of 50 kW/m² with specimens of 100 × 100 × 1.6 mm³ according to ISO5660 standard procedures by using an FTT Standard Cone Calorimeter (made by FTT Company, UK). All measured data were processed by relative software such as Origin.

2.5. Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was carried out using TA-SDTQ600 Thermogravimetric Analyzer (made by TA Company, USA) under nitrogen flow rate of 50 ml/min and the heating rate of 10°C/min from ambient temperature to 700°C. The used sample weight was 5–10 mg consistently. The samples were dried for 2 h at 150°C before testing.

2.6. Py-GC/MS Analysis. The pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) was carried out using Pyrolyzer EGA/PY-3030D (made by Frontier Laboratories Ltd., Japan) and Gas Chromatograph Mass Spectrometer GCMS-QP2010 Ultra (made by Shimadzu, Japan). The samples were cracked at 400°C under helium atmosphere.

3. Results and Discussion

3.1. Thermal Stability of NORSM. The thermal stability of NORSM was characterized by TGA. TGA and DTG curves of NORSM under nitrogen atmosphere are represented in Figure 4. As shown in Figure 4, the temperature at 2% weight loss ($T_{2wt\%}$), 5% weight loss ($T_{5wt\%}$), and 10% weight loss ($T_{10wt\%}$) and the maximum thermal degradation rate (T_{max}) of NORSM are 273.2°C, 281.9°C, and 293.2°C and 301.5°C, respectively, and the residual of NORSM at 700°C is 5.97%. The above results indicate that NORPM exhibits a good thermal stability.

3.2. Synergistic FR-Effect of NORSM and TTBPC/Sb₂O₃. To evaluate the synergistic effect of NORSM with TTBPC/Sb₂O₃ in HIPS, LOI was determined and UL-94 tests were conducted. The proportions of used samples and the results were presented in Table 1. As shown in Table 1, the flame retardant property and antidripping of HIPS are obviously improved by the combination of appropriate amounts of NORSM, rising first and then decreasing with the increase of the concentration of NORSM. When the loadings of TTBPC and Sb₂O₃ are 12.8 wt% and 3.2 wt%, respectively (sample-2), the LOI of FR-HIPS is 23.8%, the flaming time t_1 of the first ignition and the flaming time t_2 of the second ignition

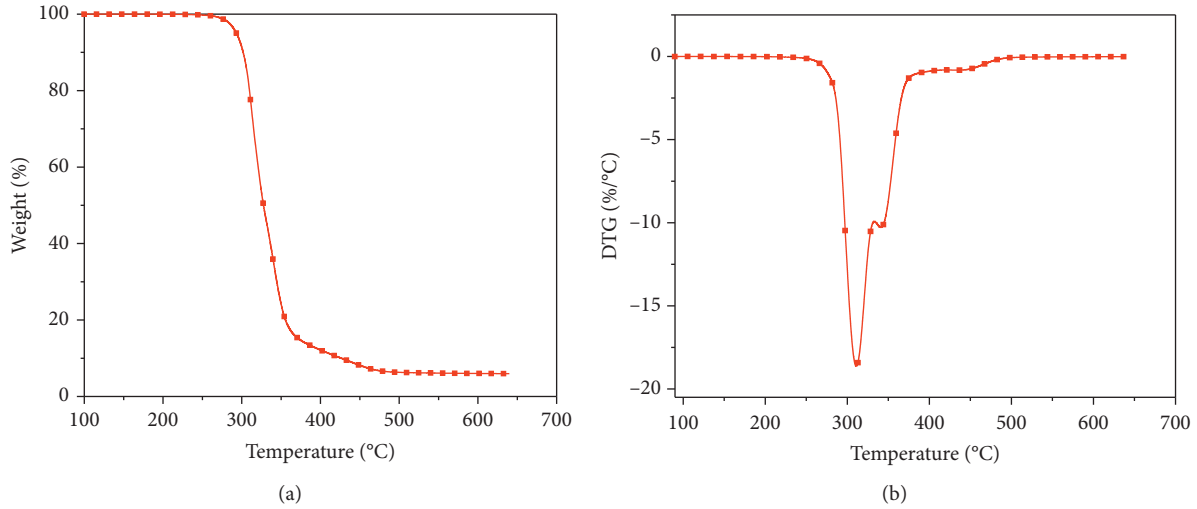


FIGURE 4: TGA (a) and DTG (b) curves of NORSM.

TABLE 1: Proportion and the flame retardant property of the samples.

Sample	Proportion (%)				UL94 test (1.6 mm)				LOI (%)
	HIPS	TTBPC	Sb ₂ O ₃	NORSM	<i>t</i> ₁ (s)	<i>t</i> ₂ (s)	Rating	Dripping	
Sample-1	100.0	0.0	0.0	0.0			No	Yes	18.4
Sample-2	84.0	12.8	3.2	0.0	16.2	6.5	V-2	Yes	23.8
Sample-3	82.0	14.4	3.6	0.0	7.0	3.7	V-2	Yes	24.0
Sample-4	80.0	16.0	4.0	0.0	1.8	2.0	V-0	Yes	25.8
Sample-5	83.75	12.8	3.2	0.25	3.3	3.2	V-0	No	24.7
Sample-6	83.50	12.8	3.2	0.50	2.4	1.5	V-0	No	25.2
Sample-7	83.25	12.8	3.2	0.75	2.4	1.5	V-0	No	24.5
Sample-8	83.00	12.8	3.2	1.00	2.8	1.4	V-0	No	24.4
Sample-9	82.75	12.8	3.2	1.25	2.4	1.6	V-0	No	24.8
Sample-10	82.50	12.8	3.2	1.50	3.7	1.8	V-2	Yes	24.1
Sample-11	82.75	12.8	3.2	1.75	4.1	2.9	V-2	Yes	24.0

are 16.2 s and 6.5 s, respectively, dripping happens during burning, and then FR-HIPS can only pass UL 94 V-2 test, but in the presence of 0.5 wt% NORSM, the LOI of FR-HIPS increases from 23.8% to 25.2%, *t*₁ is reduced from 16.2 s to 2.4 s, and *t*₂ is reduced from 6.5 s to 1.5 s, respectively, no dripping happens, and the FR-HIPS can pass UL 94 V-0 test, which demonstrates very close efficiency of sample-4; however, the addition of TTBPC/Sb₂O₃ decreases by 20% compared with sample-4, which indicates that NORSM shows an obvious synergistic effect with TTBPC/Sb₂O₃ in HIPS and can improve dripping resistance of HIPS.

3.3. Fire Performance of HIPS and FR-HIPS. The CCT based on the oxygen consumption principle has been widely conducted to evaluate the flammability of polymeric materials because CCT results have good correlation with real fire disaster and can be used to predict the combustion behavior. Various heat release and mass loss parameters of the neat HIPS and the FR-HIPS samples, such as heat release rate (HRR), total heat release (THR), mass loss rate (MLR), mass loss (ML), smoke production rate (SPR), total smoke production (TSP), and the CO production (COP) rate, were

measured by CCT and used to investigate the effect of the novel flame retardant system on the combustion behavior of the FR-HIPS composites in real fires. The above-mentioned parameters as a function of time are shown in Figure 5, and some typical parameters are listed in Table 2.

As shown in Figure 5 and Table 2, the THR and HRR of pure HIPS increase rapidly, its HRR curve displays a sharp peak, and it burns out within 280 s after ignition, but those of FR-HIPS increase slowly, and there is no sharp peak in their HRR curves. Compared with pure HIPS, the peak heat release rate (PHRR), the THR, and the mean heat release rate (MHRR) of sample-2 are reduced by 70.45, 61.70, and 59.89%, respectively, while the time required for complete burning (BT) is prolonged from 280 s to 285 s; those of sample-4 are reduced by 83.99, 72.34, and 74.27%, respectively, while the BT is prolonged from 280 s to 320 s; those of sample-6 are reduced by 76.85, 67.23, and 71.63%, respectively, while the BT is prolonged from 280 s to 310 s. Compared with sample-2, PHRR, THR, MHRR, PEHC, and MEHC are reduced by 21.64, 14.44, and 28.07, respectively. The decrease of various heat release parameters is beneficial to suppress the pyrolysis of materials and then to effectively inhibit combustion of materials. In addition, compared with

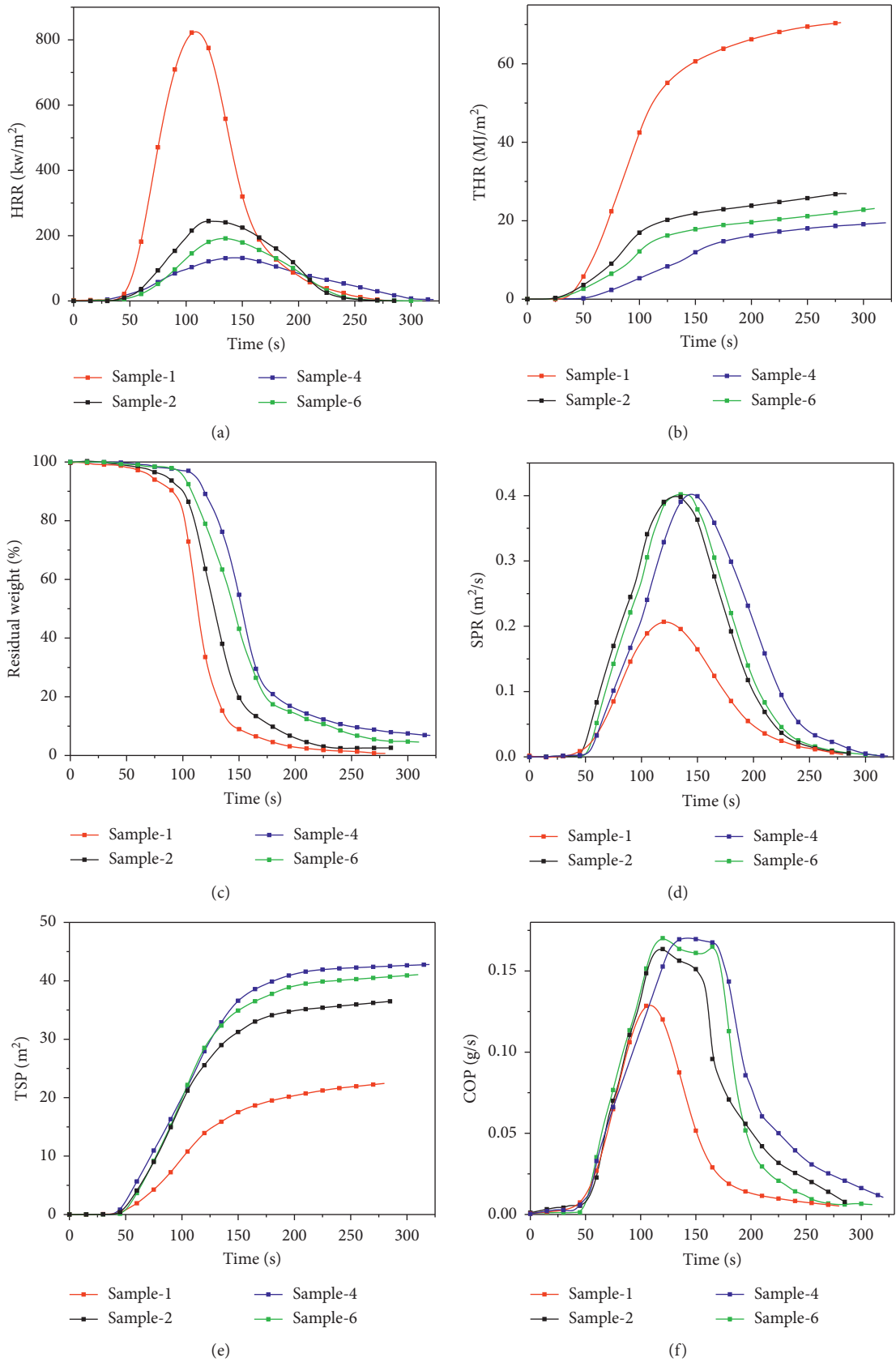


FIGURE 5: HRR (a), THR (b), ML (c), SPR (d), TSP (e), and COP (f) curves of HIPS and the FR-HIPS.

TABLE 2: Cone calorimeter test data of HIPS and FR-HIPS.

Sample	THR (MJ·m ⁻²)	MHRR (kW·m ⁻²)	PHRR (kW·m ⁻²)	MMLR (g·s ⁻¹)	PMLR (g·s ⁻¹)	TSP (m ³)	MSPR (m ³ ·s ⁻¹)	MCOP (g·s ⁻¹)	BT (s)
Sample-1	70.5	231.6	827.2	0.073	0.623	22.4	0.07	0.037	280
Sample-2	27.0	92.9	244.4	0.076	0.414	36.5	0.14	0.062	285
Sample-4	19.5	59.6	132.4	0.070	0.469	42.8	0.14	0.062	320
Sample-6	23.1	65.7	191.5	0.071	0.355	41.1	0.13	0.062	310

neat HIPS, the peak mass loss rate (PMLR) of FR-HIPS is obviously reduced, but the mean mass loss rate (MMLR) even increases somehow on the contrary, which may be due to the reduction of the stability of HIPS by the addition of the flame retardant.

The above results reveal that the flame retardant property of sample-4 is the best, that of sample-6 is slightly poorer than sample-4 but better than sample-2, which means that TTBPC/Sb₂O₃ has good flame retardancy, and combining NORSM can improve its flame retardancy.

The smoke production along with the HRR is also considered as another critical parameter in fire. As shown in Figure 2 and Table 2, total smoke production (TSP), smoke production rate (SPR), and CO production (COP) rate of all samples increase rapidly, but those of FR-HIPS do more rapidly. Compared with pure HIPS, TSP, MSPR, and MCOP of sample-2 increase by 62.94, 100.00, and 67.57%, respectively, those of sample-4 increase by 91.07, 100.00, and 67.57%, respectively, and those of sample-6 increase by 83.48, 85.71, and 67.57%, respectively. The results show that the addition of TTBPC/Sb₂O₃ brings about an increase of smoke and CO during burning and goes up with the concentration of TTBPC/Sb₂O₃. Brominated flame retardant/Sb₂O₃ induces the flame retardancy mainly through gaseous phase mechanism, making the pyrolysis produce incomplete combustion, so TSP, SPR, and COP of the FR-HIPS increase markedly. NORSM make the pyrolysis produce more incomplete combustion; then TSP further increases in the presence of NORSM.

3.4. Action Mechanisms. The synergistic action mechanism of the NORSM with TTBPC/Sb₂O₃ in HIPS was discussed by the thermogravimetric analysis, the analysis of the residues obtained in CCT, and Py-GC/MS analysis of the samples.

The thermal stability of the HIPS samples was studied by TGA. The results of TGA are presented in Figure 6 and Table 3. As shown in Figure 6 and Table 3, $T_{2wt\%}$, $T_{5wt\%}$, $T_{10wt\%}$, and T_{max} of the FR-HIPS decrease obviously compared with pure HIPS, which means that the addition of flame retardants significantly reduces the thermal stability of HIPS but slightly increases the residual of the composites at 700°C from 1.3% to about 3.5%. There appear two T_{max} in FR-HIPS; T_{max1} might result from the decomposition of the flame retardants. In addition, $T_{2wt\%}$ of samples decreases markedly in the presence of NORSM, which is perhaps owing to the relative lower decomposition temperature of NORSM.

For the analysis of the residues obtained in CCT, images of the residues obtained in CCT are presented in Figure 7.

The results show that pure HIPS is almost completely burned out, while FR-HIPS has a small amount of unexpanded black residues, which is almost consistent with the TGA results. The residuals of sample-2, sample-4, and sample-6 are 2.58%, 5.76%, and 3.56%, respectively, and increase with the concentration of TTBPC/Sb₂O₃, but all no-intumescent layers are formed, which results in weak flame retardancy of TTBPC/Sb₂O₃ in condensed phase. Adding of NORSM slightly increases the residual, which revealed that NORSM has relatively a small effect in condensed phase.

Next, we discuss Py-GC/MS analysis of samples. In order to further investigate the action mechanism of the new flame retardant system, the pyrolytic products of HIPS samples were analyzed by GC/MS, and the pyrolysis reaction was deduced.

The GC of the pyrolytic products of NORSM, HIPS (sample-1), HIPS/TTBPC/Sb₂O₃ (sample-2), and HIPS/TTBPC/Sb₂O₃/NORSM (sample-6) is presented in Figure 8, and the chemical structure of the main products is shown in Table 4.

The MS analysis showed that the main cracking products of HIPS (sample-1) were styrene (**3**), styrene dimers (**9**, **10**, **12**, **14**, **16**), trimers (**13**), and a small amount of diphenylpropane (**8**). Styrene might result from the scission of a head-to-head bond, from random scission, or by both random scission and chain-end depolymerization, while styrene dimers and trimers might be formed due to β -scission reactions [45].

The main pyrolytic products of HIPS/TTBPC/Sb₂O₃ (sample-2) were also styrene (**3**), styrene dimers (**9**, **10**, **12**, **14**, **16**, **17**, **19**), trimers (**13**, **20**), and diphenylpropane (**8**). Besides, the pyrolysis products of TTBPC, such as tribromophenol (**7**; about 3.28 wt%), dibromophenol (**6**; about 1.41 wt%), and CO₂ (**1**; about 1.68 wt%), were observed. The production of dibromophenol indicated that TTBPC released bromine free radicals, which captured hydrogen from polymers and produced hydrogen bromide during thermal degradation, which is shown in Scheme 2. Besides, CO₂ might be due to the decomposition of the triazine ring in TTBPC (Scheme 2).

The analysis of the pyrolysis products shows that TTBPC/Sb₂O₃ mainly performs flame retardancy through the following mechanisms: the oxygen in the gas phase is diluted by HBr and CO₂; meanwhile, the active radicals such as the hydroxyl radical (\cdot OH) and hydrogen free radicals in the gas phase during combustion are captured by HBr, which interrupts the chain reaction during combustion [46], thus imparting a flame retardant effect in the gas phase. SbBr₃ produced through the reaction of HBr with Sb₂O₃

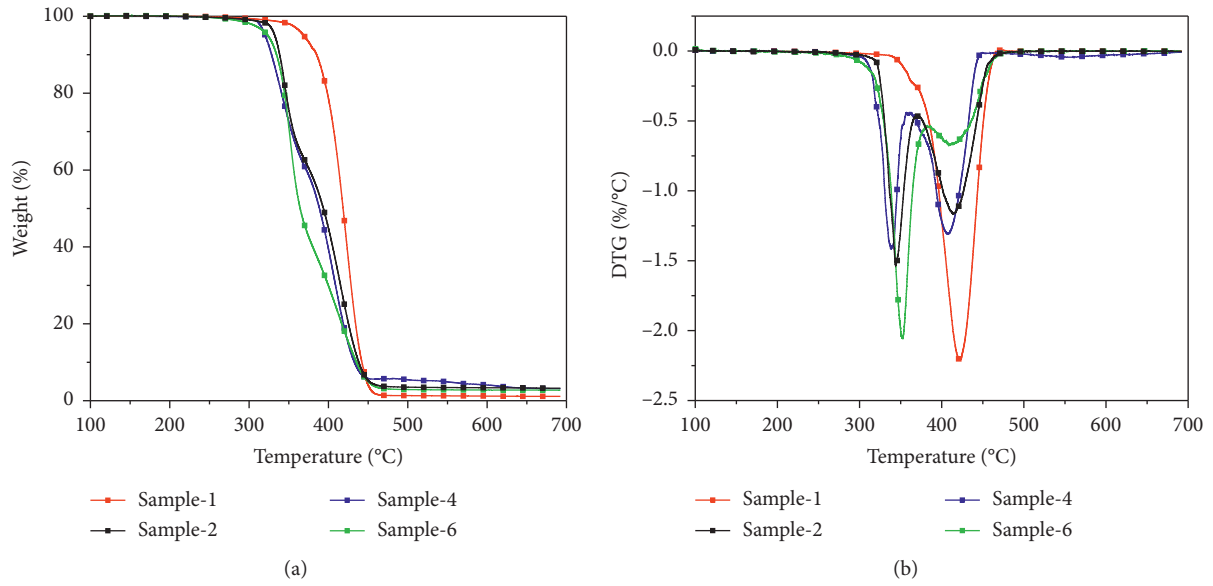


FIGURE 6: TGA (a) and DTG (b) curves of HIPS samples.

TABLE 3: TGA results of HIPS and the FR-HIPS.

Sample	$T_{2wt\%}$ (°C)	$T_{5wt\%}$ (°C)	$T_{10wt\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	700°C (%)
Sample-1	350.6	368.9	385.2	421.8	—	1.3
Sample-2	323.2	332.4	338.5	345.8	407.8	3.3
Sample-4	313.3	324.2	332.0	339.2	407.8	3.14
Sample-6	302.2	323.7	334.6	351.5	409.1	3.0
NORM	273.2	281.9	293.2	301.5	—	5.97

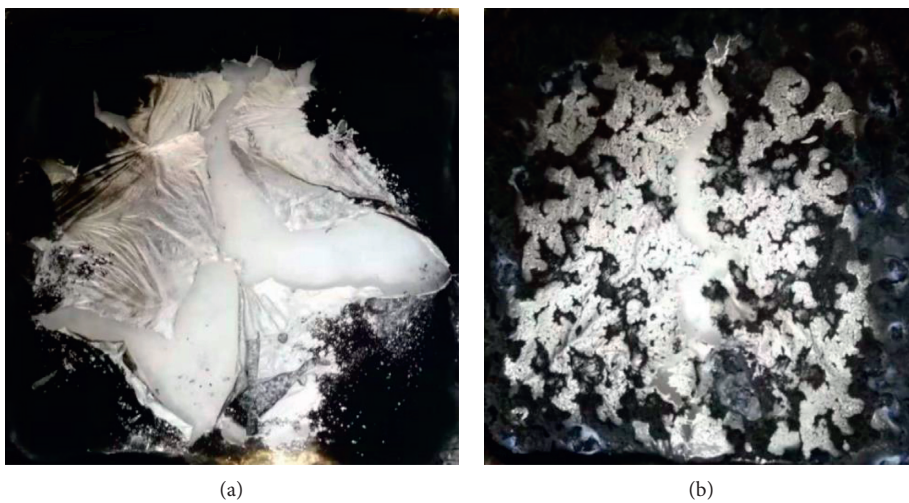


FIGURE 7: Continued.

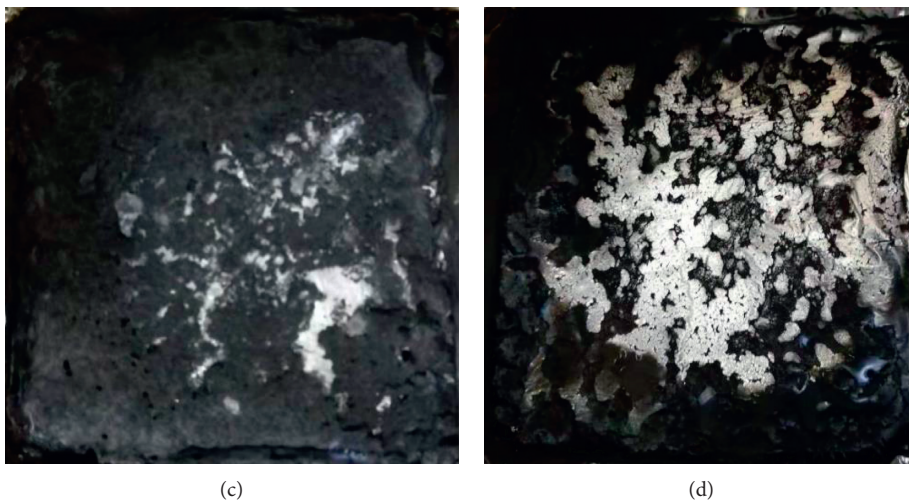


FIGURE 7: Photos of the residues obtained in CCT. (a) Sample-1. (b) Sample-2. (c) Sample-4. (d) Sample-6.

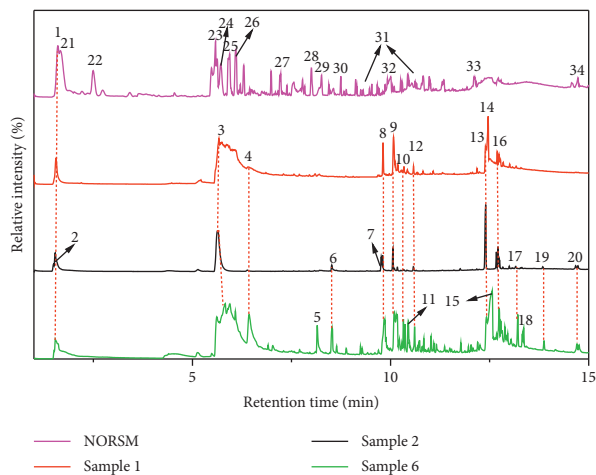


FIGURE 8: GC of pyrolytic products of the samples.

TABLE 4: Structure of pyrolytic products of the samples.

No.	R. time (min)	Mol weight (m/z)	Structure
1	1.527	44	CO ₂
2	1.538	18	H ₂ O
3	5.848	104	<chem>C=Cc1ccccc1</chem>
4	6.426	118	<chem>CC(=C)c1ccccc1</chem>
5	8.139	172	<chem>Oc1ccc(Br)cc1</chem>

TABLE 4: Continued.

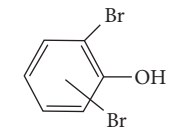
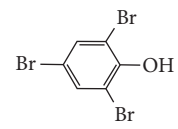
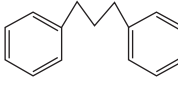
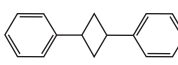
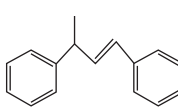
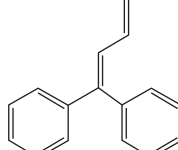
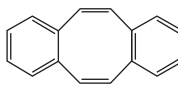
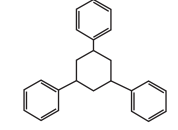
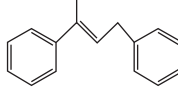
No.	R. time (min)	Mol weight (m/z)	Structure
6	8.500	250	
7	9.766	328	
8	9.819	196	
9	10.079	208	
10	10.350	208	
11	10.426	206	
12	10.582	204	
13	12.405	312	
14	12.459	208	

TABLE 4: Continued.

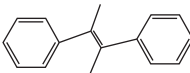
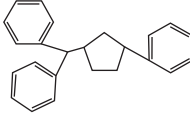
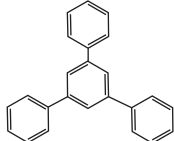
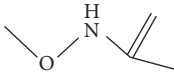
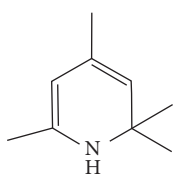
No.	R. time (min)	Mol weight (m/z)	Structure
15	12.543	312	
16	12.699	208	
17	13.179	312	
18	13.295	312	
19	13.840	306	
20	14.686	208	
21	1.700	32	CH ₃ OH
22	5.477	87	
23	5.477	107	
24	5.620	123	

TABLE 4: Continued.

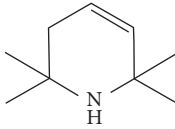
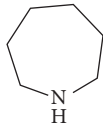
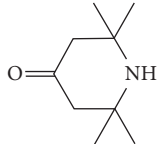
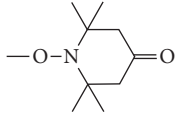
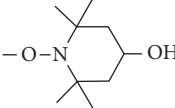
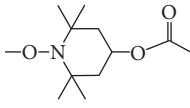
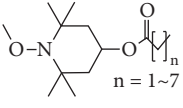
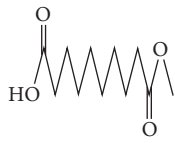
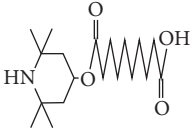
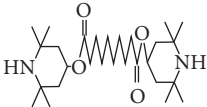
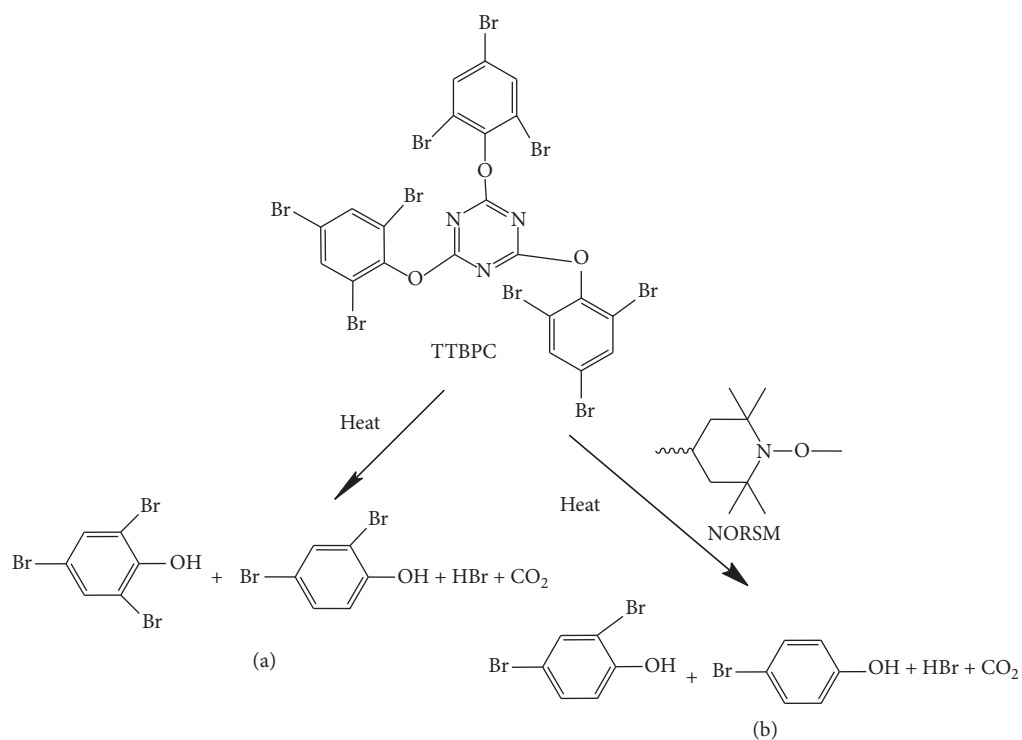
No.	R. time (min)	Mol weight (m/z)	Structure
25	5.934	139	
26	6.088	99	
27	7.224	155	
28	7.997	185	
29	8.253	187	
30	8.740	229	
31	9.114~11.993	243~285	
32	9.999	216	

TABLE 4: Continued.

No.	R. time (min)	Mol weight (m/z)	Structure
33	12.102	341	
34	14.726	480	



SCHEME 2: Pyrolysis pathways of TTBPC.

covers the surface of the material and isolates oxygen and heat, which results in flame retardant effect [46].

The pyrolysis products of HIPS/TTBPC/Sb₂O₃/NORSM (sample-6) mainly consisted of styrene (3), styrene dimers (9, 10, 11, 12, 14, 16, 17, 19), trimers (13, 15, 18, 20), and diphenylpropane (8). In addition, dibromophenol (6; about 1.55 wt%), bromophenol (5; about 1.28 wt%), and CO₂ (1; about 7.27 wt%) were produced through TTBPC pyrolysis. As the concentration of NORSM in sample-6 was only 0.50 wt%, no pyrolysis product of NORSM in sample-6 was detected. Compared with sample-2, no tribromophenol but bromophenol was found in the pyrolysis products of sample-

6, which indicated that NORSM could promote the decomposition of TTBPC and the release of bromine free radicals, which was similar to the phenomenon described in the literature [23, 47–49]. Although NORSM itself can pyrolyze to CO₂, its concentration is very small; therefore, the marked content increase of CO₂ from 1.68 wt% to 7.27 wt% indicated that NORSM could obviously promote the decomposition of the triazine ring in TTBPC. As a result, it could be inferred that TTBPC was decomposed as shown in Scheme 2 in the presence of NORSM.

The main pyrolysis products of NORSM were methanol (21), N-alkoxyamine (22, 28–31), amines (23–27), and

4. Conclusions

NORSM exhibits a good synergistic flame retardant effect in HIPS. When the concentration of NORPM is 0.5 wt%, the LOI of FR-HIPS with 16 wt% of TTBPC/Sb₂O₃ increased from 23.8% to 25.2%, t_1 was reduced from 16.2 s to 2.4 s and t_2 was reduced from 6.5 s to 1.5 s, respectively, dripping was prevented during burning, and the flame retardant rating of FR-HIPS could be improved from the UL 94 V-2 to the UL 94 V-0 rating. The PHRR, the THR, and the MHRR were reduced by 21.64, 14.44, and 28.07%, respectively. The TGA, analysis of the residues obtained in CCT, and Py-GC/MS analysis of FR-HIPS revealed that NORSM imparted the synergistic effect with TTBPC/Sb₂O₃ mainly through the following mechanism: active radicals such as methoxy radicals and aminyl radicals produced by NORSM pyrolysis promote the release of bromine radicals from TTBPC and the formation of HBr and CO₂, which improves flame retardant effect of TTBPC/Sb₂O₃. The methoxy radicals and aminyl radicals together with HBr quench active free radical such as hydroxyl radical (\cdot OH) and decompose the free radical source—peroxide. Thus, the chain reaction is interrupted during combustion and results in a more highly efficient flame retardant effect in the gaseous phase. [47–49].

Data Availability

The data (IR of NORSM, ¹H NMR of NORSM, ¹³C NMR of NORSM, TGA (a) and DTG (b) curves of NORSM, HRR (a), THR (b), ML (c), SPR (d), TSP (e), and COP (f) curves of HIPS and the FR-HIPS, TGA (a) and DTG (b) curves of HIPS samples, and GC of pyrolytic products of the samples) used to support the findings of this study have not been made available because the dissertation and patents related to this paper are still under further study.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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Supplementary Materials

Graphic abstract: Bis(1-methoxy-2,2,6,6-tetramethylpiperidin-4-yl)sebacate(NORSM) has good synergistic flame retardant effect with tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBPC)/Sb₂O₃ in HIPS due to its promotion of the release of bromine radicals from TTBPC and the formation of HBr and CO₂. (*Supplementary Materials*)

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