Synthesis of Novel Brominated Bis-tetrahydrophthalimides and Bis-nadimides and Their Possible Application as Flame-Retardant Additives for Polystyrene Composites

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SYNOPSIS

Ten tetrabrominated bisimides of which eight were novel were tested as flame-retardant additives. They were prepared from corresponding bisimides by the addition of bromine. Structural properties and related thermal characteristics of these brominated compounds were determined. Flame-retardant properties of tetrabrominated bisimides were tested on high-impact polystyrene, containing various amounts of brominated bisimides, according to ASTM-D-3801, "Standard Test Method for Measuring the Comparative Extinguishing Characteristics of Solid Plastics in a Vertical Position," and DIN-51960, "Testing of Organic Floor Coverings Assessment of Flammability." It was observed that tetrabrominated bisimides had improved flame resistance of high-impact polystyrene. In addition, thermoxidative stability of novel three bisimides, 04, 14, and 05, were compared with the others. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Most of the commercial polymers have limited usage for certain applications because of their flammability as well as their low thermoxidative stability.[1] However, their composites can attain a self-extinguishing property if they contain additives such as phosphorous or halogen-containing compounds. Organic compounds to be used as flame-retardant additives should have various characteristics.[1,2] They must form compatible mixtures with polymers and should not change their ultimate physical and mechanical properties unfavorably. It is well known that imide and phenyl groups are resistant to thermoxidative degradation. Therefore, compounds containing halogen and an alicyclic structure besides the above-mentioned groups can also be good candidates as flame retardants.[3]

New synthesis methods for various chlorinated and brominated N-phenylimides and bisimides and their structural and thermoxidative properties are reported in the literature.[4,5] Although it is well known that polyhalogenated compounds provide flame retardancy to various plastics, intensive research and development work still continues on more efficient and environmentally acceptable flame retardants as such.[6,7] Therefore, introduction of new environmentally acceptable polyhalogenated flame-retardant additives have a great interest in this area.

Brominated alicyclic (N-aryl) imide structures may be shown to be more suitable additives than are polybrominated aromatics. Since tetrabrominated alicyclic bisimides decompose at lower temperatures than do brominated aromatic bisimides, they do not form harmful polybrominated dioxines during decomposition.[6-8] However, they show good thermoxidative and flame resistance due to aromatic amine and brominated alicyclic structures, respectively. In this work, in the light of all above-mentioned information, 10 different bisimides were prepared by the reaction of endo-bicyclo [2,2,1]-hept-

5-en-1,2-dicarboxylic acid anhydride (endo-NBDA) and cis-cyclohex-4-ene-1,2-dicarboxylic acid anhydride (cis-THPA) with five different diamines. Flame-retardant additives were obtained with high yield after the addition of bromine to the double bonds of the bisimides (Scheme 1). Eight of them, **02-B, 12-B, 03-B, 13-B, 04-B, 14-B, 05-B,** and **15-B,** are new and cannot be found in the literature (Table I).

EXPERIMENTAL

Materials

Diamines, such as 4,4'-diaminodiphenylmethane (4,4'-DADPM) and 3,3'-diaminodiphenyl sulfone (3,3'-DADPS) were obtained from Aldrich as commercial products and purified by sublimation before use. Other diamines, 4,4'-bis(3-aminophenoxy)diphenyl sulfone (4,4'-BADS),[9] 1,4-bis[4-(3-aminophenoxy)benzoyl]benzene (1,4-BABB),[10] and 2,5-bis-(4-aminophenyl)-3,4-diphenyl thiophene (BADT)[11] were prepared by us in the laboratory. All the diamines were further characterized by IR, ^{1}H-NMR, and mass spectra. cis-THPA (Fluka) and bromine (Merck) were used as received. endo-NBDA was prepared from cyclopentadiene and maleic anhydride as described elsewhere.[12]

Characterization

Melting points were determined in Buchi.510 melting-point apparatus. ^{1}H-NMR and IR spectra were recorded by a Bruker AC 200, 200 MHz, NMR spectrometer and a Nicolet-510P FTIR spectrometer, respectively. MS studies were performed at 70 eV with a Fisons VG ZabSpec GC-MS. The thermal behavior of the products were evaluated using a DuPont 910 differential scanning calorimeter and a DuPont 951 thermogravimetric analyzer. All measurements were carried out in air and with a heating rate of 10°C/min. Bromine contents were determined by a Dionex 4000I model ion chromatograph as water-soluble bromine salts, obtained by burning the samples in a closed aqueous system.

Synthesis of Bisimides

Ten bisimides, which are the starting materials of tetrabrominated flame retardants, were synthesized in an NMP–toluene (3 : 1, v : v) mixture from reported anhydrides and diamines by solution imidization.[13] In the first step, amic acid was formed at room temperature and then was cyclized to the corresponding imide by the elimination of water at 180°C. The overall yields were 80–90%. Characterization results of four bisimides, of which three are novel, **04, 14, 05,** and **15,** are given below:

1,4-Bis[4-(3-N-trans-3a,4,7,7a-tetrahydrophthalimidophenoxy)benzoyl]benzene (04)

Mp 228–229°C. IR(KBr): 1784, 1716 (C=O imide), 1655 (C=O, ketone), 1648 (cyclic C=C), 1587, 1489, 1383, 1246 (phenyl ether), 1170 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 2.28 (dt; 4H; J = 11 Hz, J = 1 Hz), 2.5 (dt; 4H; J = 11 Hz, J = 1 Hz), 3.3(m; 4H), 5.9 (t; 4H; J = 1.5 Hz), 7.1–7.85 (m; 20H; arom). MS (70 eV): m/z 768 (M$^+$), 714 (M$^+$ —C$_4$H$_5$), 631 (M$^+$ —C$_4$H$_5$ —C$_4$H$_2$O$_2$).

1,4-Bis[4-(3-N-endo-norbornanedicarboxyimidophenoxy)benzoyl] benzene (14)

Mp 198–201°C. IR(KBr): 1774, 1713 (C=O imide), 1655 (C=O, ketone), 1645 (cyclic C=C), 1587, 1487, 1377, 1244 (phenyl ether), 1170 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 1.8 (d; 2H; J = 9 Hz), 2.07 (d; 2H; J = 9 Hz), 2.86 (s-like; 4H), 3.2 (s-like; 4H), 6.2 (s; 4H), 7.1–7.8 (m; 20H; arom). MS (70 eV): m/z 792 (M$^+$), 660 (M$^+$ —2C$_5$H$_6$), 578 (M$^+$ —2C$_5$H$_6$ —C$_4$H$_2$O$_2$).

2,5-Bis(4-N-trans-3a,4,7,7a-tetrahydrophthalimidophenyl)-3,4-diphenylthiophene (05)

Mp 288–290°C. IR(KBr): 1786, 1716 (C=O imide), 1650 (cyclic C=C), 1508 (C=C, arom), 1379, 1180 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 2.3 (dt; 4H, J = 11 Hz, J = 1 Hz), 2.5 (dt; 4H; J = 11 Hz, J = 1 Hz), 3.4 (m; 4H), 5.95 (s; 4H), 7.09 (d; 4H; arom), 7.16 (m; 10H; arom), 7.3 (d; 4H; arom). MS (70 eV): m/z 686 (M$^+$), 580 (M$^+$ —2C$_4$H$_5$), 498 (M$^+$ —2C$_4$H$_5$ —C$_4$H$_2$O$_2$).

2,5-Bis(4-N-endo-norbornanedicarboxyimidophenyl)-3,4-diphenylthiophene (15)[14]

Mp 281–284°C. IR(KBr): 1780, 1716 (C=O imide), 1646 (C=C, cyclic), 1506 (C=C, arom), 1375, 1176 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 1.56 (d; 2H, J = 9 Hz), 1.77 (d; 2H, J = 9 Hz), 3.41 (s-like; 4H), 3.49 (s-like; 4H), 6.28 (s; 4H), 7.1 (d; 4H; arom), 7.2 (m; 10H; arom), 7.35 (d; 4H; arom). MS (70 eV): m/z 10
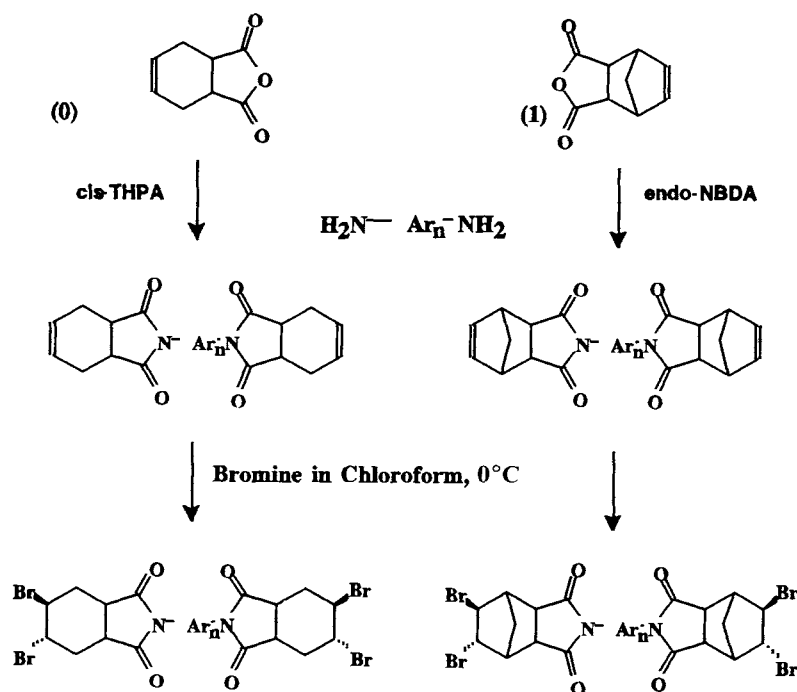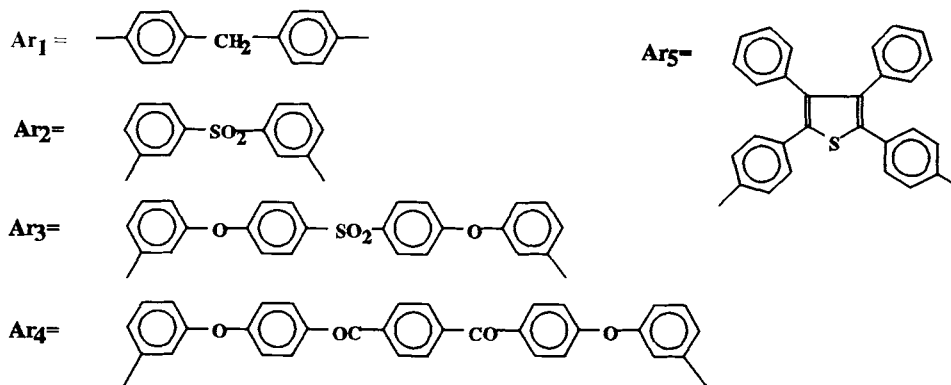
Scheme 1.

(M^+), 644 $(M^+ - C_5H_6)$, 590 $(M^+ - 2C_5H_6)$, 508 $(M^+ - 2C_5H_6 - C_4H_2O_2)$.

Synthesis of Tetrabrominated Bisimides

Initially, brominations were carried out by two different methods: one by bromine in chloroform solution and the other by HBr—H$_2$O$_2$ solution in chloroform. The second method was dropped since it gave unfavorable aromatic electrophilic bromination products.

Bromination with Bromine in Chloroform

In a 250 mL three-necked flask placed in an ice bath and equipped with a thermometer and a pressure-equilized dropping funnel, 20 mL chloroform solution of 0.02 mol bromine was added dropwise into 0.01 mol of bisimide in 100 mL of chloroform at 0°C. After the completion of bromine addition, the reaction mixture was stirred a further 2 h at 0°C. Two-thirds of the original solvent was evaporated and product was precipitated by the addition of di-

Table I Characteristics of Tetrabrominated Compounds

Comp. No.	Compound	% Br by Wt	Mp (°C)	Br Loss Temp (°C)
01-B	X—Ar$_1$—X^a	40.72	218–220	265
11-B	Y—Ar$_1$—Y	39.56	183–185	440^b
02-B	X—Ar$_2$—X	38.28	150–154	285
12-B	Y—Ar$_2$—Y	37.21	228–230	275^b
03-B	X—Ar$_3$—X	31.37	154–156	255
13-B	Y—Ar$_3$—Y	30.65	207–208	250^b
04-B	X—Ar$_4$—X	29.41	195–198	350
14-B	Y—Ar$_4$—Y	28.77	226–228	500^b
05-B	X—Ar$_5$—X	31.80	191–193	290
15-B	Y—Ar$_5$—Y	31.06	256–257	410^b
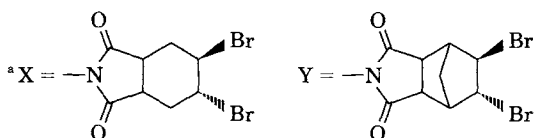
^{b} Bromine loss temperature together with reverse Diels–Alder reaction.

ethyl ether. The precipitate was filtered and washed with 3 × 50 mL of diethyl ether. Light yellow powdered products were obtained with nearly 100% yields. Melting points and bromine loss temperatures recorded from TGA are shown in Table I. Characteristics of the novel brominated bisimides are given below:

3,3'-Bis(N-trans-5,6-dibromohexahydrophthalimido)diphenylsulfone (02-B)

IR(KBr): 1788, 1716 (C=O imide), 1479, 1377 (arom amine), 1377, 1322 (SO2; asym), 1178, 1150 cm^{-1} (SO2; sym). ^{1}H-NMR (acetone-d_6): δ = 2.3 (d; 4H; J = 11 Hz), 2.72 (d; 4H; J = 11 Hz), 3.2 (m; 4H), 4.4 (m; 4H; CHBr), 7.5 (d; 2H; arom), 7.75 (t; 2H; arom), 7.85 (s; 2H; arom), 7.90 (d; 2H; arom). MS (70 eV): m/z 836 (M$^+$), 756 (M$^+$ — Br), 676 (M$^+$ —2Br), 516 (M$^+$ —4 Br).

3,3'-Bis(N-endo-5,6-dibromonorbornanedicarboxyimido) diphenylsulfone (12-B)

IR(KBr): 1782, 1716 (C=O imide), 1479, 1373 (arom amine), 1320 (SO2, asym), 1176, 1153 cm^{-1} (SO2, sym). ^{1}H-NMR (acetone-d_6): δ = 1.7 (s; 2H), 2.02 (s-like; 2H), 3.55 (m; 4H), 4.5 (m; 4H; CHBr), 7.5 (d; 2H; arom), 7.7 (t; 2H; arom), 7.84 (s; 2H; arom), 7.91 (d; 2H; arom). MS (70 eV): m/z 861 (M$^+$), 715 (M$^+$ — Br—C$_5$H$_6$), 635 (M$^+$ —2Br— C$_5$H$_6$), 475 (M$^+$ —4Br—2C$_5$H$_6$).

4,4'-Bis(3-N-trans-5,6-dibromohexahydrophthalimidophenoxy) diphenylsulfone (03-B)

IR(KBr): 1788, 1716 (C=O imide), 1583, 1487, 1381, 1319–1294 (SO2; asym), 1248 (phenyl ether), 1180, 1151 cm^{-1} (SO2; sym). ^{1}H-NMR (DMSO-d_6): δ = 2.34 (d; 4H; J = 11 Hz), 2.68 (d; 4H, J = 11 Hz), 3.3 (m; 4H), 4,6 (m; 4H; CHBr), 6.9 (s; 2H), 7.0 (d; 2H; arom), 7.18 (d; 6H, arom), 7.5 (t; 2H; arom), 7.9 (d; 4H; arom). MS (70 eV): m/z 1021 (M$^+$), 861 (M$^+$ —2Br), 808 (M$^+$ —2Br—C$_4$H$_5$), 701 (M$^+$ —4Br), 648 (M$^+$ —4Br —2C$_4$H$_5$).

4,4'-Bis(3-N-endo-5,6-dibromonorbornanedicarboxyimidophenoxy) diphenylsulfone (13-B)

IR(KBr): 1782, 1714 (C=O imide), 1583, 1487, 1379, 1300 (SO2; asym), 1246 cm^{-1} (phenyl ether), 1180, 1151 cm^{-1} (SO2, sym). ^{1}H-NMR (DMSO-d_6): δ = 1,28 (s; 2H), 1.43 (s; 2H), 3.33 (m; 4H), 3.47 (m; 4H), 4.8 (m; 4H; CHBr), 6.9 (s; 2H), 7.0 (d; 2H; arom), 7.18 (d; 6H; arom), 7.5 (t; 2H, arom), 7.9 (d; 4H, arom). MS (70 eV): m/z 044 (M$^+$), 898 (M$^+$ —Br—C$_5$H$_6$), 884 (M$^+$ —2Br), 818 (M$^+$ —2Br—C$_5$H$_6$), 658 (M$^+$—4Br—C$_5$H$_6$).

1,4-Bis[4-(3-N-trans-5,6-dibromohexahydrophthalimidophenoxy) benzoyl]benzene (04-B)

IR(KBr): 1784, 1716 (C=O imide), 1655 (C=O, ketone), 1587, 1489, 1383, 1246 (phenyl ether), 1170
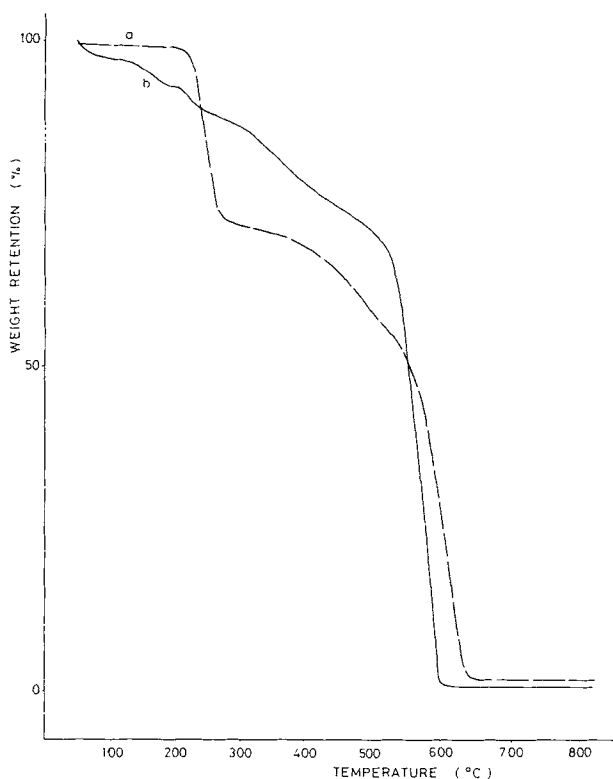
Figure 1 Thermogravimetric analysis of (a) **04-B** and (b) **14-B** in air.

cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 2.33 (d; 4H; J = 11 Hz), 2.57 (d; 4H; J = 11 Hz), 3.4 (m; 4H), 4.3 (m; 4H; CHBr), 7.1–7.85 (m; 20H; arom). MS (70 eV): m/z 1090 (M$^+$), 928 (M$^+$ — 2Br), 848 (M$^+$ — 3Br), 767 (M$^+$ — 4Br), 712 (M$^+$ — 4Br — C_4H_5), 659 (M$^+$ — 4Br — 2C_4H_5).

1,4-Bis[4-(3-N-endo-5,6-dibromonorbornanedicarboxyimidophenoxy) benzoyl]benzene (14-B)

IR(KBr): 1774, 1713 (C=O imide), 1655 (C=O, ketone), 1587, 1487, 1377, 1244 (phenyl ether), 1170

cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 1.85 (d; 2H; J = 9 Hz), 2.1 (d; 2H; J = 9 Hz), 2.80 (s-like; 4H), 3.25 (s-like; 4H), 4.45 (m; 4H; CHBr), 7.1–7.8 (m; 20H; arom). MS (70 eV): m/z 1114 (M$^+$), 968 (M$^+$ — Br — C_5H_6), 888 (M$^+$ — 2Br — C_5H_6), 728 (M$^+$ — 4Br — C_5H_6), 662 (M$^+$ — 4Br — 2C_5H_6).

2,5-Bis(4-N-trans-5,6-dibromohexahydrophthalimidophenyl)-3,4-diphenylthiophene (05-B)

IR(KBr): 1786, 1716 (C=O imide), 1508 (C=C, arom), 1379, 1180 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 2.35 (dt; 4H; J = 11 Hz, J = 1 Hz), 2.6 (dt; 4H; J = 11 Hz, J = 1 Hz), 3.3 (m; 4H), 4.1 (m; 4H; CHBr), 7.01 (d; 4H; arom), 7.15 (m; 10H; arom), 7.3 (d; 4H; arom). MS (70 eV): m/z 1007 (M$^+$), 851 (M$^+$ — 2C_5H_6), 683 (M$^+$ — 4Br), 575 (M$^+$ — 4Br — 2C_4H_5).

2,5-Bis(4-N-endo-5,6-dibromonorbornanedicarboxyimidophenyl)-3,4-diphenylthiophene (15-B)

IR(KBr): 1780, 1716 (C=O imide), 1506 (C=C, arom), 1375, 1176 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 1.6 (d; 2H; J = 9 Hz), 1.8 (d; 2H; J = 9 Hz), 3.4 (s-like; 4H), 3.5 (s-like; 4H), 4.25 (m; 4H; CHBr), 7.1 (d; 4H, arom), 7.2 (m; 10H; arom), 7.4 (d; 4H; arom). MS (70 eV): m/z 1031 (M$^+$), 954 (M$^+$ — C_5H_6, 883 (M$^+$ — Br — C_5H_6 — 2H), 805 (M$^+$ — 2Br — C_5H_6 — 2H$^+$), 725 (M$^+$ — 3Br — C_5H_6 — 3H$^+$), 579 (M$^+$ — 3Br — 2C_5H_6 — 4H$^+$).

RESULTS AND DISCUSSION

In this study, commercially available anhydrides were selected for bisimide synthesis. Besides, their various conformations, such as cis–trans and endo–exo, they can also easily give Diels–Alder and reverse

Table II   Modified ASTM-D-3801 Test Results

% Comp.*	Compound 01			Compound 11			Compound 04			Compound 14		
	%Br	Ft	Dfp	%Br	Ft	Dfp	%Br	Ft	Dfp	%Br	Ft	Dft
a	1.628	+	+	1.58	+	+	1.17	+	+	1.15	+	+
b	3.256	+	+	3.16	+	+	2.35	+	+	2.3	+	+
c	6.512	1	+	6.32	1	+	4.70	2	+	4.6	2	+
d	13.0	0	—	12.6	0	—	9.4	0	—	9.2	0	—

Ft: Flaming time in seconds: Time interval after removal of burner flame and lasting until flaming combustion of the specimen ceases. (+) means burning continues. Dfp: Drips flaming particles. (+) means, material drips flaming particles.

* [a] 94% polystyrene, 4% Br–bisimide, 2% antimony oxide. [b] 90% polystyrene, 8% Br–bisimide, 2% antimony oxide. [c] 82% polystyrene, 16% Br–bisimide, 2% antimony oxide. [d] 66% polystyrene, 32% Br–bisimide, 2% antimony oxide.
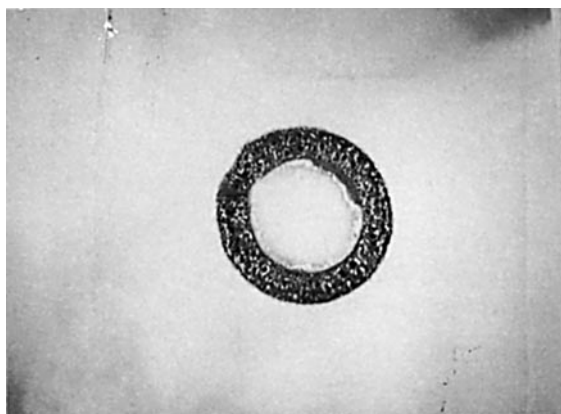
Figure 2 Photograph of a specimen containing 32% 01-B, after the test.

Diels–Alder reactions. Priority was given for the aromatic diamines since their bisimides exhibit high thermoxidative stability. Moreover, the regiospecificity of bromination reaction was examined by the use of different diamines. It is well known that *ortho* positions to ether linkages of aromatic rings may be brominated besides the bromination of double bonds at room temperature. This is also observed in the case of ether linkage-containing bisimides.[8,15,16] *N,N'-trans*-Tetrabromo-bisimides were obtained in high yield when diamines 4,4'-DADPM and 3,3'-DADPS were used. It is observed that in diamines such as 4,4'BADS, and 1,4-BABB, having aromatic ether linkages, bromination occurs on the aromatic ring as well as at the double bonds. Chemical analysis confirmed that the bromine consumption was above the theoretical amount necessary for the saturation of double bonds of bisimides. It was observed that even mild reaction conditions will give a small amount of undesirable bromine-substituted aromatic products. The appearance of 4.1–4.8 ppm peaks due to hydrogens at brominated carbon in ^{1}H-NMR spectra also confirmed that the bromination predominantly occurred at double bonds. MS fragmentations showed that desintegration started from the aliphatic ends by dehydrobromination and followed by reverse Diels–Alder reaction. Residual bis-maleimide continued to decompose to various fragments depending on the type of its diamine constituent. It was observed from thermal analysis that a reverse Diels–Alder reaction starts after the completion of debromination in THPA-derived brominated bisimides but debromination and reverse Diels–Alder reaction proceeds simultaneously in the NBDA-derived brominated bisimides. This situation is exemplified in the thermogravimetric analysis of brominated bisimides **04-B** and **14-B** as shown in

Figure 1. **04-B,** a THPA-derived derivative, has a sharp initial weight loss corresponding to the loss of bromine at around 200°C. A well-defined inflection point is observed after the loss of bromine. A second weight loss is observed above 350°C, corresponding to the decomposition of the remainder of the molecule. In the case of **14-B,** an NBDA-derived derivative, a gradual weight loss is observed starting at around 100°C and continuing up to 550°C, corresponding to the loss of bromine. A reverse Diels–Alder reaction proceeding simultaneously with debromination is believed to lead to crosslinked structures and thus decreases the rate of bromine weight loss.

Testing of Tetrabrominated Bisimides as a Flame Retardant

Four of the tetrabrominated bisimides, **01-B, 11-B, 04-B,** and **14-B,** were tested as flame-retardant additives in high-impact polystyrene A-825 E of Petkim-Turkey. They were compared with each other. It was determined that the maximum permissible amount of additive is 35 wt %, without causing any adverse effect in the film-formation property. An ethyl acetate solution of 45/35 (w/w) % of high-impact polystyrene and brominated bisimides, respectively, were spread on a glass plate with a paint applicator to obtain 125 μm-thick wet films. In the first stage, films were dried slowly in an air-circulating oven at room temperature for approximately 1 h. Then, the temperature was raised to 80°C for further drying for 3 h to remove any residual ethyl acetate for 3 h. Dry films were easily removed from the glass plate by immersing in water and then redried in a vacuum oven at 80°C for another 3 h. Each formulation contained 2% antimony
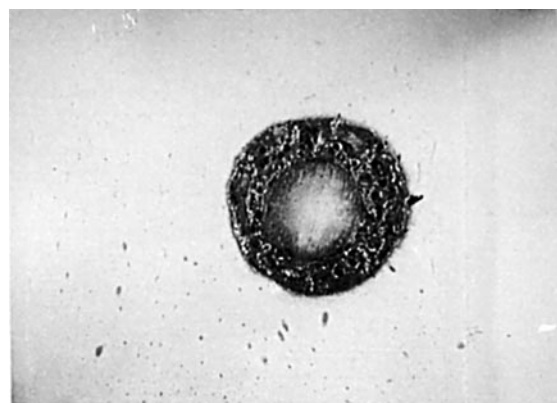

Figure 3 Photograph of a specimen containing 32% **04-B,** after the test.

oxide and 4, 8, 16, and 32% of tetrabrominated bisimides, respectively. Flame-retardant properties of formulations were tested according to ASTM-D-3801 with small modifications. Observations about the flaming time of the specimen and whether flaming material drips or not from the specimen are reported in Table II.

The test performed according to ASTM-D-3801 indicated that 32% brominated bisimide containing compositions were self-extinguishing with dripping flameless particles. Samples containing 16% brominated bisimides were also self-extinguishing, but with dripping flaming particles. Brominated bisimide, 4 and 8%, containing the specimen were not self-extinguishing with dripping flaming particles. The test was also applied to the other six **02-B, 12-B, 03-B, 13-B, 05-B,** and **15-B** brominated bisimides, and the high-impact polystyrene test specimen containing 32% brominated bisimide and 2% antimony oxide were also determined as self-extinguishing materials with dripping flameless particles.

DIN-51960 was also used to test flame retardancy. In this test, 32% brominated bisimides and 2% antimony oxide containing 10 polystyrene plates in the dimensions of $100 \times 100 \times 3$ mm were molded from the solution for each brominated bisimide to be tested: **01-B, 11-B, 04-B,** and **14-B.** In the test procedure, 0.8 g of superimposed thin disks of cellulose with a diameter of 25 mm were placed on the middle of the test specimen. They were saturated with 2.5 mL of ethyl alcohol and then ignited. The maximum length burned and the depth of the burnt spot at the cross-sectional areas of the specimen plates were measured and reported. A test specimen containing only 2% antimony oxide burned completely. According to the test DIN-51910, compositions which contained 32% of brominated bisimides, **01-B** and **11-B,** showed a maximum burning length of 5 mm with a depth of the burnt spot as 1 mm, as shown in Figure 2. But **04-B** and **14-B** containing the test specimen had a maximum burning length of 7 mm with a depth of the burnt spot as 1 mm, as shown in Figure 3. Finally, four compositions were classified as "difficulty flammable" according to DIN-51960.

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