2,2',6,6'-Tetrabromo-3,3',5,5'-tetramethyl-4,4'-biphenol (TTB)–Flame Retardant Copolycarbonates and Copolyesters*

P. L. KINSON and C. M. ORLANDO, *General Electric Company, Corporate Research and Development, Schenectady, New York 12301*

Synopsis

2,2',6,6'-Tetrabromo-3,3',5,5'-tetramethyl-4,4'-biphenol (TTB) is a new flame retardant monomer possessing a high degree of chemical and thermal stability. This brominated biphenol can be directly incorporated as a comonomer in condensation polymerizations. An example is the preparation of copolycarbonates of TTB and 2,2-(4-hydroxyphenyl)propane (BPA) via the aqueous caustic phosgenation method. The reaction of TTB with either ethylene oxide or ethylene chlorohydrin affords 4,4'-bis(2-hydroxyethoxy)-2,2',6,6'-tetrabromo-3,3',5,5'-tetramethylbiphenyl (TTB-Diol). This diol is melt polymerized into a series of terephthalate copolymers with 1,4 butanediol. The above copolymers possess flame retardancy, thermal stability, and good mechanical properties. These high-bromine-content copolymers are blended with nonhalogen-containing polymers to afford blends with specific degrees of flame resistance.

INTRODUCTION

TTB is a new flame retardant monomer[1] which offers an unusually high degree of thermal and chemical stability[†] (<10% weight loss at 300°C in air, vida infra). Examination of the thermal stability of a number of ortho-, meta-, and para-brominated phenols has associated the thermal stability of TTB to the higher stability of meta bromophenols over those having bromine either ortho or para to the hydroxyl group.[2] In addition, the sterically imposed orthogonality of its aromatic rings further enhances its stability relative to other brominated biphenols.

Since the stability of many flame retardant polymer systems, especially those utilizing a reactive monomer approach, is limited by the stability of the flame retardant monomer, the use of TTB as a stable flame retardant monomer presents a number of interesting possibilities. In particular, TTB has potential utility in many of the applications where 2,2-(3,5-dibromo-4-hydroxyphenyl)-propane (TBBPA) is currently employed. (The use of tetrabromobisphenol A is predicted to be 100 MM lbs. by 1980.[3]) The present paper describes the preparation of two systems incorporating TTB (I), namely, copolycarbonates of TTB and BPA and also terephthalate copolyesters of TTB-diol (II) and 1,4-butanediol.

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† This biphenol is surprisingly stable. For example, it is thermally stable at greater than 315°C, whereas tetrabromobisphenol A decomposes at 260°C. It is more stable than tetrabromobisphenol A to acid and base, to oxidation (Ag_2O, PbO_2), and also to reduction. Cyclic voltammetry shows that reduction potentials of the bis acetates of TTB and tetrabromobisphenol A are −1.50 and −1.25 V, respectively (CH_3CN solvent, Hg electrode, Ag/AgBr reference electrode with anthracene at −1.45 V).

The high-bromine-content copolymers of these systems have been blended with homopolymers to produce blends with specific degrees of flame retardancy. The physical properties of the materials and their blends are described.

EXPERIMENTAL

Preparation of Monomers

2,2',6,6'-Tetrabromo-3,3',5,5'-tetramethyl-4,4'-biphenol (TTB, I)

TTB is produced in two steps: 2,6-xylenol is first oxidized to 3,3',5,5'-tetramethyldiphenoquinone (TMDQ) in 80% yield via a modification[4] of a previously described procedure.[5] The TMDQ is then converted by reaction with bromine in carbon tetrachloride as described below.

A suspension of 3200 g (13.3 moles), TMDQ in 8 liters carbon tetrachloride in a jacketed 5-gallon glass-lined Pfaudler reactor equipped with stirring, dis-

I,   R = R' = H
II,   R = R' = —CH$_2$CH$_2$OH
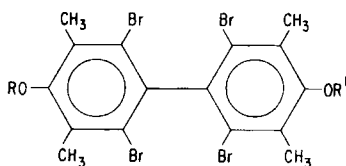
III, R = H, R' = —CH$_2$CH$_2$OH
IV,   R = —CH$_2$CH$_2$OH, R' = —CH$_2$CH$_2$O CH$_2$CH$_2$OH

tilling tower, and condenser was precooled to −10°C (internal reactor temperature) using a Dry Ice/glycol/water coolant mixture. The internal reactor temperature was monitored with a conventional thermocouple–recorder system. A total of 3200 ml (9600 g, 60 moles) bromine was then added to the cooled reaction mixture over a 20-min period and the internal temperature rose to −8°C. A further increase in this temperature to +3°C was observed during the next 20 min of stirring and the temperature then decreased to +1°C after an additional 5 min. The cooling system was shut off to the jacket and water was slowly added to the jacket to gradually increase the internal temperature. During the next 87 min the temperature rose to +27°C, whereupon a gradual evolution of hydrogen bromide occurred accompanied by a drop in internal temperature to +22°C. At this point 4800 ml (14,400 g, 90 moles) bromine was added rapidly over a 15-min period and steam heat was applied to the jacket to heat the reaction mixture. Within 46 min the reaction mixture was at reflux and held there for 1 hr. After this heating cycle the bromine–carbon tetrachloride mixture was distilled from the reactor. A total of 7 liters distillate was taken, and beginning with the next liter of distillate, each liter removed was replaced by addition of 1 liter carbon tetrachloride to the reactor. After a total of 28 liters distillate was replaced with 28 liters carbon tetrachloride, the distillate contained very little bromine, and the contents of the reactor were drained, cooled, and filtered to give a tan solid. The entire wet cake was recharged to the reactor, 8 liters acetone was added, and the mixture refluxed for 1 hr. The reaction mixture was cooled,

drained, filtered, and dried to give 5405 g (72%) TTB, mp 245°–246°C (recrystallization from acetone).

Spectral data: NMR (^{1}H, δ, CDCl$_3$), 2.34 (s, 6), 4.85 (s, 1); (^{13}C, δ, DMSO-d$_6$); 153.26 (C–OH), 135.74 (C—C), 125.25 (C—CH$_3$), 124.36 (C—Br), 17.44 (CH$_3$); mass spec [m/e (relative intensity)], M$^+$: 562 (18), 560 (65), 588 (100), 556 (70), 554 (19); M-Br: 481 (5), 479 (13), 477 (13), 475 (5); M-Br$_2$: 400 (13), 398 (26), 396 (13); M-Br$_3$: 319 (11), 317 (11); λ_{max} 95% EtOH, nm (ϵ): 296 (2500), 283 (2290).

4,4'-Bis(2-hydroxyethoxy)-2,2',6,6'-tetrabromo-3,3',5,5'-tetramethyl-biphenyl (TTB-Diol, II)

Ethylene Oxide Method. A 4-liter stainless steel vessel equipped with a sealed stirrer was charged with 360 g (0.645 mole) TTB, 2 liters xylene, and a catalyst consisting of 2 g sodium hydroxide pellets and 1 g dibenzo-18-crown-6 ether (Aldrich). The mixture was heated to 150°C and the air vented from the reactor. Ethylene oxide (75 g, 1.67 mol) which had been premeasured into a valved 100-ml stainless addition vessel was then introduced slowly, keeping the reactor pressure between 25 and 35 psig. Upon completion of the addition, the reaction mixture was heated and stirred for 6 hr and then cooled. The precipitate (360 g) was filtered and recrystallized from methanol (500 ml) to afford 240 g of the TTB-diol, mp 169°–171°C. A second crop (70 g) was obtained by concentrating the filtrate. The remaining filtrate wasdiluted with methanol and passed through a column of alumina. This removed some deeply colored material. The methanol was removed and the residue recrystallized from chloroform, affording an additional 30 g. Examination of the recovered solids by gas chromatography did not show detectable amounts of other materials. The total yield of combined solids after recrystallization is 81%.

Spectral data: NMR (^{1}H, δ, acetone-d$_6$): 2.38 (12H, s), 3.92 (8H, broad s − A$_2$B$_2$ pattern), 4.18 (2H, broad s); (^{13}C, δ, acetone-d$_6$, partially decoupled multiplicity), 18.5 (q), 62.6 (t), 76.1 (t), 125.1 (s), 132.4 (s), 140.7 (s), 156.8 (s); ν_{CHCl_3}cm^{-1}: 3535, 3440, 2995, 2927, 2872, 1549, 1442, 1398, 1370, 1352, 1184, 1070, 1021; mass spec [m/e (realtive intensity)], M$^+$: 650 (9), 648 (37), 646 (53), 644 (36), 642 (9); M-C$_2$H$_4$O: 604 (6), 602 (10), 600 (7); M-C$_2$H$_4$O-C$_2$H$_4$O: 562 (10), 560 (31), 558 (40), 556 (32), 554 (9), 45 (100); λ_{max} 95% EtOH, nm (ϵ): 275 (7.25 × 10^2), 282 sh (5.31 × 10^2).

Ethylene Chlorohydrin Method. A solution of TTB (400 g, 0.718 mole) and sodium hydroxide (65.2 g, 1.63 mole, 2.27 molar equivalents) in 600 ml deaerated 50% aqueous ethanol was heated at reflux under nitrogen for 30 min. Deaerated distilled ethylene chlorohydrin (237 g, 2.94 moles) was added slowly to this hot solution and the resulting mixture was heated for 1 hr. About 30 min into this reflux period, an additional 200 ml deaerated 95% ethanol was added to partially redissolve a solid which had formed (some sodium chloride remains precipitated). After the 1-hr reflux period, an additional 65.2 g (1.63 moles) sodium hydroxide and 50 ml deaerated water were added and the mixture refluxed for 30 min. Ethylene chlorohydrin (237 g, 2.94 moles) was added and the mixture heated for 75 min. Sodium hydroxide (100 g, 2.5 moles), deaerated water (200 ml), and deaerated 95% ethanol (450 ml) were added, and this mixture refluxed for 45 minutes. A final portion of ethylene chlorohydrin (474 g, 5.88 moles) was added and this mixture refluxed for 75 min. Deaerated water (3 liters) was then added

to the vigorously stirred mixture and the mixture allowed to cool. After standing overnight, the crystals that formed were filtered and dried in vacuo for 4 hr at 100°C. The product was recrystallized from 500 ml methanol giving, after vacuum drying, 322.0 g TTB-diol, mp 170°–172°C. Additional product was obtained from the original reaction mixture, totaling 137.7 g. The total yield of combined product was 99.1%.

Gas-chromatographic analysis of the product shows it is contaminated with trace amounts of the mono- (III) and trishydroxyethylated (IV) materials.

Preparation of Polymers

Copolycarbonate of TTB (I) and BPA

Schnell[6] and co-workers have described a similar procedure for preparing the homopolycarbonate of BPA. A 1-liter, five-neck round-bottom flask was fitted with a mechanical stirrer, phosgene–nitrogen inlet, dropping funnel, pH meter, and Dry Ice condenser. This flask was charged with BPA (40.7 g, 0.179 mole), TTB (40.7 g, 0.073 mole), water (84 ml), methylene chloride (300 ml), triethylamine (1.4 ml), and phenol (0.826 g, 8.79 mmoles). Phosgene was added through a dip tube at the rate of 0.75 g/min concurrently with nitrogen at 1 SCFH for 30 min with the pH being maintained at 9 by means of addition of a 15% aqueous sodium hydroxide solution. The pH of the reaction mixture was raised to 12, and stirring was continued for 15 min. At this point the polymer was endcapped by addition of 0.5 g phenol to the reaction mixture. After stirring for 10 min, the reaction mixture was diluted to 1000 ml with methylene chloride, washed once with 10% sodium hydroxide, twice with 10% hydrochloric acid, and three times with water. The organic layer was then stirred with silica gel and pressure filtered, and the filtrate was precipitated into 2.5 liters methanol. The solid was filtered, washed with methanol, and dried in vacuo at 100°C for 8 hr to afford 85.20 g polymer having an intrinsic viscosity (dioxane, 30°C) of 0.43 dl/g. The material exhibits a glass transition temperature of 191°C as determined by DSC and an oxygen index of 51 and contains 25.9% bromine.

Copolycarbonate of TBBPA and BPA

This copolymer was an experimental material. The material contained 27% bromine prepared as above and provided by F. N. Liberti, Lexan Products Section, Mt. Vernon, IN.

BPA Polycarbonate

This polymer was commercial Lexan polycarbonate (140 grade).

Terephthalate Copolyesters of TTB-Diol (II) and Butanediol

The copolyesters were obtained by first preparing a low molecular weight (I.V. = 0.14 dl/g, 25°C, 60 phenol/40 tetrachloroethane) prepolymer from butanediol (GAF) and dimethyl terephthalate (Aldrich) using a tetra-n-butyl titanate catalyst at 150 ppm titanium metal as described by Smith, Kibler, and Sublett.[7] Appropriate quantities of the TTB-diol and prepolymer were then placed in a small resin kettle and polymerized as described by Smith et al.[7]

TABLE I
Preparative Conditions and Properties of TTB-Diol and 1,4-Butanediol Terephthalate
Homopolymers and Copolymers

No.	TTB-diol, mole-%[a]	% Br	Polymerization time, hr	Polymerization temp., °C	Polymerization pressure, mm Hg	I.V.[b]	T_g, °C	T_m, °C[c]
1	100	41.2	5.3	265	0.20	0.13	143	N.O.[d]
2	95	40.6	5.0	260	0.35	—	—	—
3	80	38.5	5.0	265	0.20	0.18	138	N.O.
4	50	32.1	5.5	270	0.20	0.29	109	N.O.
5	20	19.3	4.0	268	0.22	0.60	70	N.O.
6	8	9.6	6.2	240	0.25	0.80	N.O.	210
7	8	9.6	4.0	260	0.20	0.86	—	—
8	8	9.6	1.5	280	0.15	0.72	—	—
9	0	0	3.0	270	0.15	0.64	22[e]	225

[a] Based on mole-% TTB-diol + mole-% butanediol = 100% of the diols in the final polymer.
[b] Run in 60/40 phenol/tetrachloroethane.
[c] Determined by DSC.
[d] N.O. = Not observed.
[e] From Smith, Kibler and Sublett.[7]

Table I summarizes the composition, reaction conditions, and intrinsic viscosities for a series of the copolymers. Reaction conditions have not been optimized, thus improvement in molecular weight should be possible.

Poly(1,4-butylene Terephthalate) (PBT)

This material was commercial Valox 310 polyester resin.

Poly(ethylene Terephthalate) (PET)

This material was commercial Goodyear VFR-3599 resin.

RESULTS AND DISCUSSION

TTB-Diol/1,4-Butanediol Terephthalate Copolyesters

Preparation and Stability

A broad range of compositions of TTB-diol/1,4-butanediol terephthalate copolyesters were prepared by a melt polymerization procedure at temperatures up to 280°C (Table I). This temperature is the upper limit for the polymerization of poly(1,4-butylene terephthalate) (PBT),[7] since erratic molecular weights are obtained above 280°C. The thermal stability of the TTB-containing copolyesters is evident from TGA weight loss data shown in Table II. A comparison of the temperature at which 10% weight loss occurs for PBT and copolyesters containing 8% and 95% TTB-diol in both nitrogen and air shows that the latter exhibit thermal stability comparable to that of PBT.

TABLE II
TGA Weight Loss for PBT and TTB-Diol/1,4-Butanediol Terephthalate Copolyesters

Polyester	Temp.-10% wt. loss °C, air	Temp.-10% wt. loss °C, N_2
PBT	380	382
8 mole-% TTB-diol copolyester	390	390
95 mole-% TTB-diol copolyester	392	391

Properties of Glass-Reinforced Copolyester Systems

It was of interest to examine the flammability and physical properties (Table III) as well as the thermal aging (Table IV) of a glass-reinforced TTB-diol/1,4-butanediol terephthalate copolyester. Molded specimens were prepared and evaluated from the formulation (A) consisting of 100 parts copolyester (14 mole-% TTB-diol, I.V. 0.9), 37.5 phr (parts per hundred of resin) glass fibers, 3.7 phr antimony oxide, 1.87 phr fumed silica, and 0.57 phr of an antioxidant. The results show that TTB-diol/1,4-butanediol terephthalate copolyester formulation (A) is very similar in physical and flammability properties to the commercial glass-reinforced PBT, Valox 420-SEO.

The high-bromine-content copolyesters also lend themselves to the "concentrate" approach for producing flame retardant materials. A blend of 17 parts copolyester (95 mole-% TTB-diol; 40.6% bromine, cf. Table I), 83 parts PBT, 26 phr glass fibers, 3 phr fumed silica, and 3 phr antimony oxide was prepared by milling. This material upon compression molding crystallized rapidly and was similar in appearance and strength to both the 14 mole-% TTB-diol copolyester above and to PBT. This material was V-O by UL Bulletin 94 flame test.

TABLE III
Physical Properties of Valox-420-SEO and Copolyester Formulation A

Property	Copolyester formulation A	Valox-420-SEO, 30% glass
Tensile strength, psi	16,900	17,000
Flexural strength, psi	25,750	27,000
Flexural modulus, psi $\times 10^5$	1.02	1.2
Notched Izod impact, ft-lb/in.	1.7	1.8
Oxygen index	29.5	28.5
UL Bulletin 94 flame test	V-O	V-O

TABLE IV
Retention of Tensile Strength of Copolyester Formulation A After Thermal Aging

Time, hr	% Retention at 170°C	% Retention at 180°C
168	109	94
336	88	80
744	82	73
1080	70	56

TTB/BPA Copolycarbonate

Preparation

One TTB/BPA copolycarbonate (50/50 wt-%) was prepared in this study and evaluated as a flame retardant concentrate for BPA polycarbonate, and PET (cf. experimental section). Several attempts were made to prepare a TTB homopolycarbonate via different phosgenation methods; however, in each case low molecular weight oligomer was formed which precipitated from solution, precluding the formation of high molecular weight polymer.

Properties of TTB/BPA Copolycarbonate Blends

A blend of TTB/BPA copolycarbonate (25.9% bromine) was prepared with Lexan polycarbonate 140 to provide a composition containing 4.2% total bromine. This blend was extruded and injection molded, and flammability and physical properties were evaluated (Table V).

The thermal stability of TTB is strongly evidenced in the thermal molding behavior of the TTB/BPA copolycarbonate–Lexan 140 blend. The copolycarbonate discolored only above 740°F, the same temperature at which the BPA polycarbonate itself discolors.

Table VI shows a comparison of physical properties of a PET control and blends (6.25% bromine, 5% antimony oxide) of PET with the copolycarbonates of TTB/BPA and TBBPA/BPA. The physical properties of the blends are in general quite similar to those of the homopolymer. During processing, both

TABLE V
Properties of TTB/BPA Copolycarbonate/Lexan 140 Blend

Property	Copolycarbonate/Lexan-140 blend
Heat distortion temp., °F	281.3
Flexural modulus, psi	314,000
Flexural yield, psi	13,300
Tensile yield, psi	9,480
Tensile break, psi	7,760
Notched Izod impact, ft-lb/in.	14.11 (3)[a]
	2 (7)[a]
Oxygen index	37
UL Bulletin 94 flame test	V-O

[a] Ten notched specimens were tested; three had the higher impact number and seven, the lower value.

TABLE VI
Properties of Copolycarbonate Blends with PET

Property	PET	PET–TTB/BPA copolymer (6.25% Br, 5% Sb_2O_3)	PET–TBBPA/BPA copolymer (6.25% Br, 5% Sb_2O_3)
Yield Strength, psi	8940	9450	9680
Ultimate Strength, psi	5890	7020	5260
% Elongation	490	490	250
Flexural modulus, psi $\times 10^5$	3.61	3.46	3.61
UL Bulletin 94 flame test	burns and drips	V-O	V-O
Oxygen index	26.9	35.2	37.1

blends showed some discoloration relative to PET. However, the TTB/BPA blend with PET showed less discoloration than TBBPA/BPA blend with PET. This discoloration is believed due to the presence of antimony oxide, which has been shown to lower decomposition temperatures in tetrabromobisphenol A systems.

SUMMARY

TTB, a compound with unusual thermal and chemical stability, is easily incorporated as a comonomer into polycarbonates and polyesters as described above. The TTB-containing copolyesters and copolycarbonates can be blended with other polymers providing compositions with good physical and flammability properties. These blends exhibit thermal stability comparable to that of the base resin, except in those cases where antimony oxide is used as an additive. These blends containing antimony oxide when processed at higher temperatures are less thermally stable compared to the base resin in the absence of antimony oxide. However, in the latter case as well as in other examples studied, the TTB-containing blends still exhibit enhanced thermal stability compared to corresponding blends employing TBBPA.[8]

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