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Instantaneous, Facile and Selective Synthesis of Tetrabromobisphenol A using Potassium Tribromide: An Efficient and Renewable Brominating Agent

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Abstract:

An instantaneous method for the bromination of bisphenol A has been reported using potassium tribromide for the first time as an efficient brominating agent affording the corresponding tetrabromobisphenol A in a reaction time of only 5−10 min at ambient temperature in high yields (99%) and purity (>99%), free from reaction byproduct and having very low ionic impurities. Mild reaction conditions and simple workup provide a practical and commercially viable route for the synthesis of the largest selling flame retardant. The generated HBr during the bromination reaction is used either in the preparation of value-added brominated products or is disposed of as waste, causing serious environmental problems. An environmentally acceptable method for an inbuilt recycling of HBr by its neutralisation, thereby generating additional amounts of metal bromide and recovering the solvent from the liquid mixture has been designed and developed. The KBr used for the preparation of potassium tribromide can be recovered, regenerated in additional amounts, and reused without any significant loss.

Introduction

Flame retardants are substances that can be chemically inserted or be physically blended into polymers to reduce, delay, or modify the propagation of a flame. There are several classes of flame retardants:[1] halogenated hydrocarbons (chlorine- and bromine-containing compounds and reactive flame retardants), inorganic flame retardants (boron compounds, antimony oxides, aluminium hydroxide, molybdenum compounds, zinc and magnesium oxides), phosphorous-containing compounds (organic phosphate esters, phosphates, halogenated phosphorus compounds and inorganic phosphorus containing salts).

Tetrabromobisphenol A (TBBPA), chemical name 4,4′-isopropylidine-bis-(2,6-dibromophenol) is a specialty chemical with a wide range of applications in industries. It is used as a reactive flame retardant in epoxy, vinyl esters, polystyrenes, phenolic resins, and polycarbonate resins. Tetrabromobisphenol A may also be used as a parent compound for the production of other commercial flame retardants, such as tetrabromobisphenol A bis (2-hydroxyethyl ether), tetrabromobisphenol A dibromopropylether, tetrabromobisphenol A bis (allylether), tetrabromobisphenol A carbonate oligomers, and tetrabromobisphenol A brominated epoxy oligomer.

Scientific Studies of TBBPA.[2,3] TBBPA is fully recyclable and complies with all legislation for recycling and recovery. According to an article in Dataweek 2009, 18 February, the European Commission is unlikely to add tetrabromobisphenol A (TBBPA) to the list of substances monitored or banned under RoHS (Restriction of Hazardous Substances). Recent studies revealed that processes used for the production of TBBPA fall into the following categories.

The first category[4] includes processes in which bromination of bisphenol A was carried out at 20−30 °C with bromine in aq acetic acid reaction medium. The main disadvantages were that the process requires postheating of the reaction mass at 80−120 °C and the process suffered from the problem of relatively low yield (81.5%) which makes the process cumbersome and unsuitable for manufacturing-scale operations.

The second category[5] involves the process in which bisphenol was reacted with bromine in the presence of alkali metal chlorate as oxidant in methanol. Disadvantages of the process lie in its low economics as the process requires mineral acid to increase the reaction rate and a strong oxidant such as $NaClO_3$ which are the major drawbacks.

The third category[6,7] includes processes reacting bisphenol and bromine in methanol solvent. The HBr produced during reaction reacts with the methanol to produce methyl bromide coproduct. Generally, up to 40−50 kg of methyl bromide can be expected per 100 kg of tetrabromobisphenol A produced. After the bisphenol A and bromine feed are finished, the reactor contents are cooked for 1−2 h to complete the reaction. The drawbacks in the above process are the formation of methyl bromide,[7] which is going to be a banned chemical[9,11] and that the recovery and reuse of hydrogen bromide is cumbersome.

The fourth category[8−11] of processes features the production of tetrabromobisphenol A without the coproduction of substantial amounts of methyl bromide and without the use of oxidants to convert the HBr to Br_2. Generally, these processes brominate

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the bisphenol at a low temperature, e.g., 0−20 °C, in the presence of a methanol solvent and a specified amount of water.

In the fifth category,[12−16] the bisphenol A is brominated in a biphasic system comprising water, water immiscible halogenated organic compound, and an oxidant, e.g., H_2O_2, Cl_2, etc. The oxidant oxidizes the HBr to Br_2, which in turn is then available to brominate more bisphenol A and its underbrominated species. The disadvantages of these processes are longer reaction times and the high expense of handling. Also the process[12,13] involves the use of sulphuric acid (added for acidification of 50% H_2O_2).

The sixth category[14−18] involves the bromination of bisphenol using methanol[14−16] and ethanol[17,18] solvents in a water mixture and H_2O_2 as oxidant. Again the drawbacks are high temperature, long reaction times, formation of small amounts of methyl bromide, and the use of a strong oxidising agent such as H_2O_2 which is dangerous to handle.

The seventh category[19,20] relates to bromination using bromine in the presence of H_2O_2 and a heterogeneous catalyst in a biphasic system. Disadvantages are the use of a strong oxidising agent and catalyst, and the use of high temperature (75 °C).

The next category[21−23] involves a mixture of NaBr and $NaBrO_3$ as the brominating agent. The disadvantages of the process are low yields (<92.3%), the use of mineral acid (HCl), low temperature (10−15 °C), long reaction time (4 h), and use of surfactant which increases the cost of the product.

A recent U.S. Patent 6,613,947 has reported the bromination of bisphenol A with bromine in a water-immiscible polar solvent in the presence of H_2O_2.[24] The process involves the use of hazardous oxidant and surfactant, reaction time of 2−3 h, and elevated temperature of 45−50 °C. Also, the complex workup of the product involves first chilling the product layer at 5 °C and then boiling the crude product at 75−90 °C.

The above literature shows that several processes are available for TBBPA manufacturing, yet it has not been possible to develop a process that is instantaneous, gives tetrabromobisphenol A in high yields and good color (white crystalline powder) with an ease to recover the solvent from the reaction mixture, and does not involve formation of the byproduct HBr. The recovered solvent and alkali metal halide can be reused in the subsequent bromination reactions. The process does not require complex workup procedure and recrystallization of the product.

This report presents a study of the instantaneous bromination of bisphenol A using aqueous KBr and elemental bromine in nearly equimolar amounts forming KBr_3[25,26] as the active brominating agent.

Results and Discussion

It is well-known that halogens do not readily go into solution, and thus one must utilise a significant excess of these materials in order to provide a sufficient amount of them to achieve the results instantaneously. A number of organic ammonium tribromides such as tetrabutyl,[27] tetramethyl,[28] cetyl,[29] benzyltrimethyl,[29,30] pentyl pyridinium,[31] pyridinium,[32] DBU,[33] [Bmim],[34] hexamethylene tetramine,[35] and DPTBE[36] have been used previously in the bromination of organic compounds. The chief drawbacks of these reagents are the use of expensive organic ammonium cations and the use of 1/3 of its total bromine for an aromatic electrophilic substitution-type reaction and 2/3 of its bromine toward addition to C−C multiple bonds. Some of the organic ammonium tribromides have phase transfer proper-

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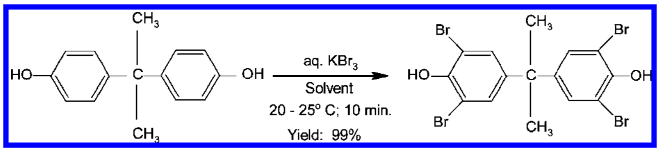
Scheme 1. **Bromination of bisphenol A**



ties; hence, a substantial amount gets extracted along with the organic products in the organic solvent during workup, thereby making the purification tedious and the method expensive for large-scale preparation. Recovery and recycling of expensive organic ammonium cations is also poor after the reaction. Some of these reagents are also not so stable, and deterioration of the reagents occurs during long periods of storage.[37] Recently, an organic ammonium tribromide has been prepared using V_2O_5, H_2O_2, and KBr.[29] The method was expensive, uses a strong oxidising agent, and also generates some heavy metal as toxic waste.[29] To overcome the problems of phase transfer properties, poor stability, regio- and stereoselectivity, and recovery and recycling of the spent reagent associated with organic ammonium tribromides, an alkali metal tribromide has been employed for the first time for the instantaneous bromination of bisphenol A (BPA), affording TBBPA in excellent yields (99%). The reagent can be readily prepared by mixing equimolar amounts of KBr and elemental Br_2, has high bromine content, better brominating efficiency and selectivity and is devoid of phase transfer properties, and can be recovered and regenerated easily. The bisphenol A was reacted with potassium tribromide in the presence of water and a water-miscible solvent (Scheme 1). The process is advantageous in a number of other respects. In the first place, potassium tribromide is readily formed by combining near equimolar proportions of elemental bromine and KBr in an aqueous medium. When the KBr is mixed in water at room temperature (30 ± 1.0 °C), the temperature of the solution decreases by 5 °C, suggesting that it is endothermic. When bromine is added to the above solution, there is a small increase in temperature (5 °C), indicating that this step is slightly exothermic, but there was no net rise in temperature, and the process can be conducted at ambient temperatures. Further, an additional amount of KBr can be generated by the addition of potassium carbonate to the byproduct hydrogen-bromide solution.

The filtrate which contains the solvent, KBr of the reagent (KBr_3), HBr evolved from the bromination of substrate, and water was neutralized by adding powdered potassium carbonate. The aromatic bromination of bisphenol A is an electrophilic substitution; thus, for the production of TBBPA, 4 mol of HBr is generated per mole of TBBPA produced. The pH of the reaction medium was adjusted using K_2CO_3 subsequent to removal of the TBBPA product; the liquid mixture thus formed was subjected to distillation to remove and recover the solvent from the aqueous liquid mixture for recycling back to the process. The aqueous liquid mixture after distillation of the solvent was concentrated to get the KBr and the additional KBr generated by the neutralization of HBr by potassium carbonate [eqs 1 and 2].

$$\mathrm{BPA} + \mathrm{aq\ KBr_3} \rightarrow \mathrm{TBBPA} + \mathrm{HBr} + \mathrm{KBr} \qquad (1)$$

$$2\mathrm{HBr} + \mathrm{K_2CO_3} \leftrightarrow 2\mathrm{KBr} + \mathrm{H_2O} + \mathrm{CO_2} \qquad (2)$$

To optimize the yields and purity, the main parameters of the reaction have been studied and determined as herein discussed.

Brominating Agent. If the reaction is carried out using liquid Br_2 as the only brominating agent, the product formation starts within 15−20 min of stirring, and yields are in the range of 89−90%, less than that obtained in the presence of aq KBr (99%) when potassium tribromide is used as the brominating agent. The resulting TBBPA products are slightly colored, and the melting points are in the range of 173 and 178 °C which are commercially unacceptable today. When the reaction is carried out using potassium tribromide as the brominating agent, instantaneous bromination of bisphenol A is observed in polar protic and aprotic solvents.

Effect of Mole Ratio of Bromine on Yield and Melting Point of TBBPA. It is quite obvious from Figure 1 that the quality of the product is strongly dependent on the mole ratio of Br_2/BPA. It has been observed that the optimum yield of TBBPA and the desired melting point of 182 °C (the melting point should be >180 °C as per international standards) are obtained at the mole ratio of Br_2/BPA = 5.0/1 in the bromination of BPA with potassium tribromide. The yield of the product becomes static when we further increase the mole ratio from Br_2/BPA = 5.0 to 5.5. With the decrease of mole ratio of Br_2/BPA from 5.0 to 4.5, the yield of the product drops to 98% with an HPLC purity of 97%, and the melting point also lowers to 180 °C (not within the required standards). It is noticed that the HPLC analysis of final product obtained at optimum mole ratio of Br_2/BPA = 5.0 shows 99.38% pure TBBPA, 0.39% of tribromobisphenol A, and 0.1% of dibromobisphenol A.

Effect of Mole Ratio of KBr on Yield and Melting Point of TBBPA. Figure 2 shows an identical pattern in the increase of mole ratio of KBr/BPA from 2.0 to 4.0 in the bromination of BPA using aq KBr_3 as brominating agent; the optimum yield and desired melting point are obtained at the mole ratio of KBr/BPA = 4/1. The melting point does not change considerably, but the yield of the product increases from 97 to 99% when we increase the mole ratio of KBr/BPA from 2.5 to 4.0. As we go down in the mole ratio of KBr/BPA from 2.5 to 2.0, underbrominated species were formed which melt at 160 °C.

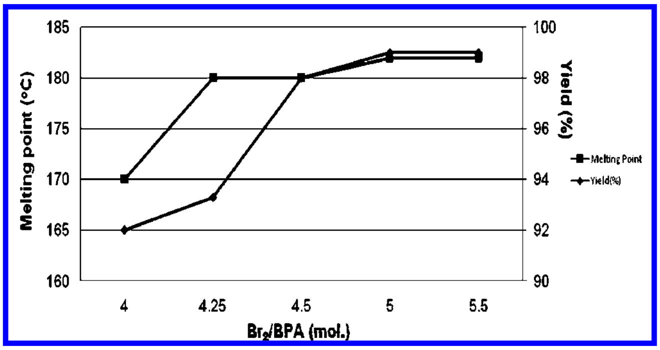


Figure 1. **Effect of mole ratio of Br_2/BPA on the yield and melting point in the bromination of BPA to TBBPA using aq KBr_3. Reaction conditions: substrate 10 mmol; KBr 40 mmol; acetonitrile 15 mL; water 10 mL; temp 25 °C, time 10 min.**

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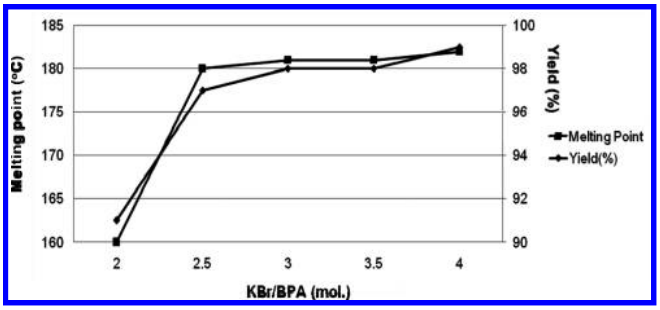


Figure 2. **Effect of mole ratio of KBr/BPA on the yield and melting point in the bromination of BPA to TBBPA using aq KBr_3. Reaction conditions: substrate 10 mmol; Br_2 50 mmol; acetonitrile 15 mL; water 10 mL; temp 25 °C, time 10 min.**

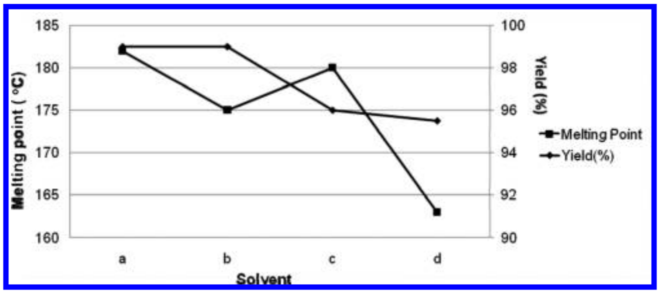


Figure 3. **Effect of solvent on the yield and melting point of TBBPA in the bromination of BPA using aq KBr_3. Reaction conditions: BPA:KBr:Br_2 mole ratio, 1:4.0:5.0; solvent 15 mL, water 10 mL; temp 25 °C, time 10 min (a = acetonitrile; b = methanol; c = ethanol; d = acetic acid).**

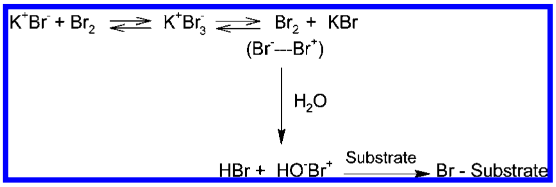
Although the KBr used in the preparation of brominating agent (aq KBr_3) is fully recyclable, its concentration does play a major role in the yield and melting point of the product.

An attempt was also made to brominate the bisphenol A using tetrabutylammonium tribromide (TBATB)[38] as the brominating agent. Being a mild brominating agent, TBATB fails to brominate the bisphenol A.

Effect of Solvent. The solvents acetonitrile, methanol, ethanol, and acetic acid were tried. Figure 3 indicates that acetonitrile has proved to be excellent in the bromination of bisphenol A to obtain TBBPA wrt yield (99%), melting point (182 °C), color (white crystalline solid), and texture of the product. A powdered product (yield: 99%) is obtained which melts at 175 °C when methanol is used as solvent, suggesting the presence of under-brominated product. Acetonitrile is resistant to bromination compared to methanol[14−16] and ethanol[17,18] which give alkyl bromide as byproduct. Acetic acid leads to low yield (96%) and low melting (170 °C) product.

Effect of Temperature. We have observed flexibility in terms of temperature that ranges from 15−40 °C. No change in the color of the product, no effect on yield, or on the crystallinity of the product was observed when the reaction was carried out at 15, 20, 25, 30, 35, and 40 °C, respectively, which is an additional advantage of the present method over previously known methods[15,18−20,24] which employed temperatures >55 °C and up to 70°−80 °C. Hence, ambient temperatures, or temperatures slightly above or below ambient, have been employed. The postheating time and temperature were not required for this reaction as is employed in various brominations[4,6,7] of bisphenol A and the pure product was obtained at the temperature of the reaction itself.

Scheme 2. **Generation of hypobromous acid and formation of organobromocompound**



Time. The bromination step was achieved in 10 min of reaction time, affording the product in high yields (99%). It has been discovered that it is advantageous to add the aq KBr_3 solution rapidly. The only limit was that addition should not be so rapid as to increase locally high concentrations of the active bromo species. Rapid addition has been found to produce products with significantly less color, reduced byproduct, and a product with a higher melting point.

Stirring. As the reaction was instantaneous, efficient stirring (725 rpm or higher) was essential for mixing the hydrophobic aromatic substrate with the aqueous inorganic medium and for preventing local high concentrations of the active bromo species.

Role of Water. The water used for the preparation of aq KBr_3 has been found to have a significant role in following ways. The presence of water was important to convert "free" hydrogen bromide to hydrobromic acid so as to allow thorough bromination of bisphenol A, which otherwise was inhibited by the presence of HBr. When the water-miscible solvent was methanol, the formation of methyl bromide (a substance having high toxicity)[11] was attenuated because HBr was diluted by the large amount of water in the reaction mass. Another key feature of this method is that, when water is contained in the solvent for reaction, hypobromous acid forms in the system (by the reaction identified in Scheme 2), which serves to be the active brominating species.

Recycling and Reusability of KBr and Solvent. The Br^- of the HBr is found to have been transformed into the KBr in the filtrate by the neutralisation of HBr using potassium carbonate. The filtrate comprising the recycled KBr was used four times using Br_2/BPA = 5.0/1 (mole ratio) in each cycle without addition of the fresh KBr in the bromination of BPA to afford TBBPA with the identical yields, and purity. The products were obtained with excellent yields and purity, and all the international specifications were confirmed.[39] Results are presented in Table 1, and all the parameters were analysed by standard analytical procedures. After three or four cycles, when the KBr concentration became high enough in the filtrate, it was isolated from the filtrate, and an additional amount of KBr (11 mol) was recovered after four cycles: 1.8−2.0 mols of KBr generated additionally in each cycle by the neutralisation of HBr by adding potassium carbonate. The solvent was also distilled out from the filtrate and can be used in the subseqent brominations. In this way, starting with 4 mol of KBr wrt 1 mol of bisphenol in the fresh batch, we have isolated 11 mol of KBr in the end after four cycles. Thus, the present method

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Table 1. **Recyclability of the KBr vs product (TBBPA) purity in the bromination of BPA**[a]

entry	parameter	fresh batch	recycle 1	recycle 2	recycle 3	recycle 4	international standards
1	appearance	white powder	white powder	white powder	white powder	white powder	white powder
2	melting point (°C)	182	182	182	182	181	182
3	hydrolysable bromide (ppm)	24	25	24	24	25	50 maximum
4	ionisable bromide (ppm)	18	18	17	16	14	50 maximum
5	moisture (%)	0.05	0.08	0.06	0.07	0.08	0.1 maximum
6	turbidity (20% (w/w) in methanol NTU)	2.8	2.7	3.0	3.3	3.6	5.0 maximum
7	bromine content (%)	58.74	58.71	58.72	58.68	58.38	58.0 minimum
8	assay (HPLC) (%)	99.38	99.36	99.31	99.26	99.28	99.0 minimum
9	yield (%)	99.0	98.6	98.5	98.7	98.3	99 maximum

[a] Reaction conditions: BPA, 10 mmol; Br_2, 50 mmol (BPA and Br_2 moles charged in each cycle); KBr, 40 mmol (charged only in the fresh batch); temp 25 °C.

has solved the problems of conventional methods associated with discharge of HBr byproduct waste which is toxic, corrosive, and environmentally polluting. Thus, the byproduct hydrobromic acid can be utilized effectively, and the production cost of TBBPA can be minimised. The present work has been accomplished on the basis of this discovery.

Conclusion

Reported herein is a quick, mild, and simple method for the efficient and selective bromination of bisphenol A using KBr_3 as brominating agent. The method is suitable for industrial-scale synthesis.

Experimental Section

Materials and Instrumentation. Starting material, reagents, and solvents were obtained from commercial suppliers and were used without further purification. HPLC analyses were conducted using a Waters 2695 instrument with PDA detector, column C_{18} (250 mm × 4.6 mm × 5 μ), solvent system 70% CH_3CN + 30% H_2O, flow rate 1 mL/min. HPLC purity is reported by area %. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ solution on a Bruker Avance II 400 NMR spectrometer and are reported in ppm using TMS as an internal standard. Mass spectra were recorded on Micromass Quattro Micro API triple quadrupole MS equipped with a standard APCI ion source. The bromine content, percentage of moisture, and turbidity of the product were determined according to the literature.[40,41]

General Procedure for the Synthesis of TBBPA. Into a 100 mL round-bottom flask were charged bisphenol A (2.2829 g, 10 mmol) and acetonitrile (15 mL). Separately prepared was a solution of KBr (4.76 g, 40 mmol) in water (10 mL) to which was added bromine (8 g, 50 mmol), and the resulting mixture was stirred to form an aqueous solution of KBr_3 at 30 °C. This solution was added rapidly to the bisphenol A solution by utilising a pressure-equalising funnel within 2−3 min. The bromine color disappeared immediately, and white crystals of TBBPA were obtained within 5 min of reaction time at 30 °C. Hydrazine hydrate (80%) was added to destroy the residual bromine, and the mixture was poured into water to separate the precipitated TBBPA. The precipitated reaction mass was separated from the mother liquor by vacuum filtration, utilising a Buchner funnel, and then was washed twice with deionised water and dried in oven at 100 °C. The total isolated yield of TBBPA was 99%, and the purity of the crystals was found to be 99.38% with a bromine content of 58.74%. Further, the crystals were subjected to potentiometric titration[40] by means of an aq $AgNO_3$ solution, whereby they were found to contain 24 ppm of hydrolyzable bromide and 18 ppm of ionizable bromide. The moisture content of the product was found to be 0.05%. The characteristic data recorded for the isolated sample were mp, 182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.58 (s, 6H, CH_3), 5.79 (s, 2H, OH), 7.25 (s, 4H, Ph). MS *m*/*z* calculated for $C_{15}H_{12}{}^{79}Br^{81}BrO_2$ [M^+] 543.9, found 543.0.

Procedure for Regeneration and Reuse of KBr (Recycle 1). The filtrate originating from the above reaction was neutralised by adding K_2CO_3 to convert HBr to KBr. Acetonitrile was distilled off, and bromine (8 g, 50 mmol) was added to the aqueous solution. The resulting mixture was stirred to form an aqueous solution of KBr_3. In a 100 mL round-bottom flask, bisphenol A (2.2829 g, 10 mmol) and acetonitrile (15 mL; distilled off in the above experiment) were charged. The KBr_3 solution was added rapidly within 5 min to the bisphenol solution by utilising a pressure-equalising funnel. After 10 min of stirring, the bromine color disappeared, and white crystals of TBBPA were obtained within 20 min. Hydrazine hydrate (80%) was added to destroy the residual bromine, and the precipitated TBBPA was separated from the mother liquor by vacuum filtration, then washed twice with deionized water, and dried in oven at 100 °C. The total isolated yield of TBBPA was 98.6% with an HPLC purity of 99.36%. The solvent was distilled off, and the aqueous layer was reused in the next run with an additional amount of Br_2.

Procedure for Recycle 2, 3, and 4. Identical to the above procedure of recycle 1, bromine (8 g, 50 mmol) was added to the aqueous layer obtained after separation of TBBPA, and the reaction proceeded in a similar fashion with bisphenol A (2.2829 g, 10 mmol) in every cycle.

Scaled-Up Process for the Synthesis of TBBPA. A 10 L, three-necked, round-bottom flask equipped with a thermometer and pressure-equalising funnel was charged with bisphenol A (1 kg, 4.38 mol) and acetonitrile (4 L). Separately prepared was a solution of KBr (2.085 kg, 17.52 mol) in water (3.5 L) to

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(40) Mendham, J.; Denney, R. C.; Barnes, J. D.; Thomas, M. J. K. *Vogel's Textbook of Quantitative Chemical Analysis*, Revised 6th ed.; Pearson Education: Upper Saddle River, NJ, 2003; pp 401−402 and 458.

(41) Willard, H. H.; Merritt, L. L.; Dean, J. A.; Settle, F. A. *Instrumental Methods of Analysis*, 7th ed.; CBS Publishers & Distributors: Delhi, 1986; p 186.

which was added bromine (3.504 kg, 21.9 mol); the resulting mixture was stirred to form an aqueous solution of KBr_3 at 30 °C. This solution was added rapidly within 30 min to the stirring bisphenol A solution by utilising a pressure-equalising funnel. The white precipitate of TBBPA was obtained instantaneously following KBr_3 addition. The reaction mixture was stirred for another 15 min at 30 °C to complete the reaction. Hydrazine hydrate (80%; 400 mL) was added to destroy the residual bromine, and the reaction mass precipitated was separated from the mother liquor by vacuum filtration utilising a Buchner funnel and then washed twice with deionised water (3−4 L), and dried in an oven at 100 °C to obtain shining-white crystals of TBBPA. The filtrate containing HBr was neutralized by adding K_2CO_3. The solvent was distilled off, and the aqueous liquid mixture (4 L) was concentrated to get the solid KBr. The TBBPA was obtained in 98.4% yield with mp 182 °C. The characteristic data for the isolated product were found to be same as given in the above general procedure.

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