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THERMAL DEGRADATION OF 2,4,6-TRI[(BROMO)$_x$ ANILINO]-1,3,5-TRIAZINES

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The need for more efficient and ‘greener’ flame retardants for polymeric materials is ever present and of increasing intensity as regulatory agencies continue to display concern about the environmental impact of traditional materials. Compounds capable of multiple modes of action would be particularly desirable. Compounds containing both bromine (for good gas-phase activity) and nitrogen (to promote solid-phase activity) should be good candidates for development as flame retardant agents. A series of 2,4,6-tri[(bromo)$_x$anilino]-1,3,5-triazines have been synthesized and characterized spectroscopically. The degradation characteristics of these compounds have been examined using thermogravimetry. They undergo step-wise decomposition beginning at about 400°C.

Keywords: *dual-action flame retardants, nitrogen-containing flame, retardants, thermal decomposition, triazine-based flame retardants*

Introduction

The rapid introduction of polymeric materials derived from synthesis has had a far-reaching impact on the development of society as we know it. The high standard of living that the people of the West are accustomed would simply not possible without the widespread availability of polymers and items formulated from polymers. Polymers are, in the main, hydrocarbons or hydrocarbon-like and as a consequence combustible. For many consumer applications, agents to control or suppress this combustibility must be incorporated into the polymeric formulation [1]. Organohalogen compounds, particularly brominated aromatics, continue to be among the most widely used [2]. They function by liberating, upon thermal decomposition, hydrogen halide or halogen atoms which interrupt gas phase flame propagating reactions. Other agents act in the solid phase to promote the formation of a char layer at the surface of the polymer which protects it from the heat of the flame. This prevents polymer degradation and the generation of the volatile fragments which fuel the flame. Organonitrogen compounds are often included in flame retardant formulations to enhance this latter effect. Compounds which contain high levels of both bromine and nitrogen offer the potential to display both types of activity simultaneously. In fact, synergy might be observed such that each effect is enhanced in the presence of the other [3, 4].

Experimental

Methods

Additives and polymers were characterized by spectroscopic, thermal, and chromatographic methods. Nuclear magnetic resonance spectra (^{1}H and ^{13}C) were obtained using a General Electric QE-300 NMR spectrometer and dilute solutions in deuterochloroform, perdeuterodimethyl sulfoxide, or perdeuterotetrahydrofuran. Chemical shifts are reported in δ units with respect to internal tetramethysilane. Infrared spectra (IR) were obtained using solid solutions (1%) in anhydrous potassium bromide (as pellets), dilute solutions (5–10%) in carbon tetrachloride or thin films between sodium chloride discs and a model 1600 Perkin-Elmer FTIR instrument. Absorption intensities were classified as weak (*w*), medium (*m*), strong (*s*), very strong (*vs*), relative to the most intense spectral band. Differential scanning calorimetry (DSC) was carried out at a heating rate of 5°C min^{-1}, using a TA Instruments Inc. model 2100 thermal analysis system equipped with a model 2910 DSC cell. The sample compartment was exposed to a constant purge of dry nitrogen at 50 mL min^{-1}. Thermal degradation characteristics were obtained by using a TA Instruments Inc. model 2950 TG unit interfaced with the TA Instruments Thermal Analyst 2100 control unit. The TG cell was swept with nitrogen at 50 mL min^{-1} during degradation runs. The temperature was ramped at a rate of 2–10°C min^{-1}. Mass spectra were obtained using a Hewlett-Packard 5995A GC/MS with programmed temperature inlet

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(90–200°C) or direct sample insertion with an ionizing potential of 70 electron volts. UV spectra were recorded using a Hewlett Packard 8453 UV spectrometer. Samples were dissolved in a suitable solvent at a concentration of 10^{-5} M.

Materials

2,4-6-Tri[(bromo)$_x$anilino]-1,3,5-triazines

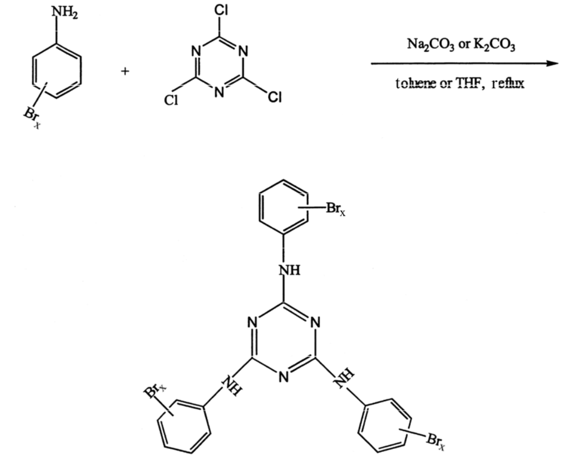
In general, brominated triazines were prepared by treating 2,4,6-trichloro-1,3,5-triazine with the appropriate bromoaniline in refluxing tetrahydrofuran (THF) or toluene in the presence of potassium carbonate. For illustration the synthesis of one of these is described below.

2,4,6-Tri(2,4-dibromoanilino)-1,3,5-triazine

Into a 100 mL, three-necked, round-bottomed flask fitted with a magnetic stirring bar, a dropping funnel and an Allihn condenser was placed 1.81 g (7.21 mmol) of 2,4-dibromoaniline, 1.08 g (7.83 mmol) of potassium carbonate and 20 ml of THF. The stirred solution was heated to solvent reflux and a solution of 0.47 g (2.55 mmol) of 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) in 10 mL of THF was added dropwise over a period of 0.25 h. The resulting mixture was stirred at solvent reflux. Progress of reaction was monitored by periodic removal of aliquots of the reaction mixture for analysis by TLC (silica gel plates; hexane/ethyl acetate, 2/1, as eluant). After the trichlorotriazine had been completely consumed the mixture was poured into 100 mL of cold water to provide a solution which was treated with 1.0 g of solid sodium bisulfite to remove residual bromine (yellow color). The precipitate which formed was collected by filtration at reduced pressure, washed thoroughly with cold water, and allowed to dry. The crude product was recrystallized from hexane/THF (4:1) to provide 1.77 g (95.8% yield) of 2,3,4,5,6-pentabromoaniline as colorless needles, mp 263.1°C (DSC): ^{1}H NMR (δ, DMSO-d_6) 6.02 (s, 2H, amino protons); ^{13}C NMR (δ, DMSO-d_6) 109.8 (aromatic carbon atom adjacent to nitrogen), 112.6 (aromatic carbon atoms ortho to nitrogen, adjacent to bromine), 127.8 (aromatic carbon atoms adjacent to bromine, meta to nitrogen), 145.4 (aromatic carbon atom adjacent to bromine, para to nitrogen); IR (cm^{-1}, KBr), 3471 (m) and 3373 (m) (H-N-H str of primary amine), 1588 (m) and 1340 (m) (C=C str of phenyl nucleus); mass spectrum (*m*/*e*, % of base), 483 (M^{+}, 11%), 485 ([M+2]$^{+}$, 49%), 487 ([M+4]$^{+}$, 91%), 489 ([M+6]$^{+}$, 100%), 491 ([M+8]$^{+}$, 49%), 493 ([M+10]$^{+}$, 9%), 408 (26%), 327 (27%), 248 (16%), 167 (37%), 141 (22%), 61 (34%).

Results and discussion

Aniline and aniline derivatives are quite reactive toward bromination and it is possible to prepare a series of variously brominated (both the number and positions of bromine atoms may be varied) anilines. These compounds are nucleophilic and interact with 2,4,6-trichloro-1,3,5-triazine to replace the chlorine atoms and generate adducts containing three halogenated amine groups per triazine nucleus. These compounds may be generated readily by stirring a solution of the aniline and the trichlorotriazine in THF containing suspended sodium carbonate at solvent reflux (Scheme 1).



Scheme 1 Synthesis of 2,4,6-tri[(bromo)$_x$anilino]-1,3,5-triazines

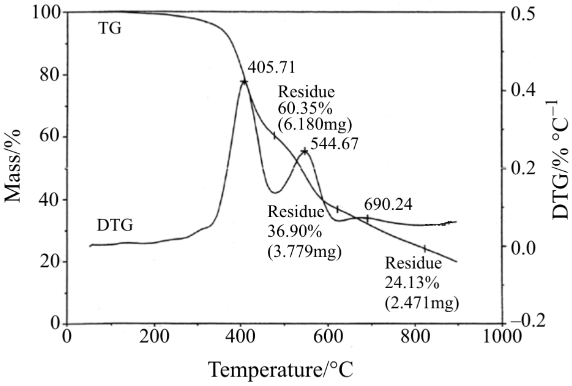


Fig. 1 Thermal decomposition of 2,4,6-tri(4-bromoanilino)-1,3,5-triazine

The products are stable solids which may be characterized by spectroscopic and thermal methods. All these compounds contain high levels of both nitrogen (six nitrogen atoms per molecule) and bromine (three to fifteen bromine atoms per molecule). The thermal degradation characteristics for these compounds were determined by thermogravimetry. A TG and DTG curves for the decomposition of

Table 1 Decomposition data for 2,4,6-Tri[(bromo)$_x$anilino]-1,3,5-triazines

Compound (number of bromine atoms)	First stage		Second stage		Third stage		
	dp[a]/°C, DTG	Mass loss[b]/%	dp[a]/°C, DTG	Mass loss[b]/%	dp[a]/°C, DTG	Mass loss[b]/%	Residue/%
1	405.7	39.65	544.7	23.45	690.2	12.77	24.13
2	418.9	42.05	551.3	25.06	865.6	29.21	3.68
3	447.1	38.02	534.7	36.57	758.1	23.06	2.35
4	430.5	42.41	529.8	39.92	691.9	15.32	2.35

[a] Decomposition point taken as the maximum in a derivative plot of mass loss *vs.* temperature

[b] Mass loss as a percentage of the initial sample mass

2,4,6-tri(4-bromoanilino)-1,3,5-triazine is shown in Fig. 1. The decomposition process consists of three stages. The first centered at 406°C represents a loss of 39.7% of the initial mass and probably reflects the loss of a 4-bromoanilino group. The second stage is centered at 545°C and corresponds to an additional loss of mass (23% of the initial mass present) and probably reflects the loss of a second bromoanilino group. The final stage of decomposition is centered at 690°C and corresponds to the loss of the final 4-bromoanilino group. The residue, 24.13% of the initial mass of the sample, corresponds to the triazine core of the compound. Other (bromoanilino)triazines degrade similarly. The degradation data are collected in Table 1.

All these compounds undergo initial decomposition at temperatures greater than 400°C and degradation occurs in a stepwise manner reflecting, in the main, sequential loss of bromoanilino groups. As the level of bromine present increases the initial decomposition temperature increases somewhat. These observations suggest that the compounds may be good candidates for high temperature flame retardants and further that both gas-phase action (volatilization of bromine-containing fragments) and solid phase action (formation of a nitrogen-rich residue) will be present.

Conclusions

A series of 2,4,6-tri[(bromo)$_x$anilino]-1,3-5-triazines have been synthesized and characterized by spectroscopic techniques. The thermal decomposition characteristics of these compounds have been determined by thermogravimetry. All undergo stepwise decomposition above 400°C. These compounds offer potential as superior flame retardants – capable of displaying good gas phase activity coupled with the simultaneous promotion of char formation in the solid state.

Acknowledgements

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