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Heat release of polyurethanes containing potential flame retardants based on boron and phosphorus chemistries

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ABSTRACT

Using a polyurethane of methylene diphenyl isocyanate and 1,3-propane diol, several new non-halogenated aromatic boron and phosphorus flame retardants were evaluated for heat release reduction potential using the pyrolysis combustion flow calorimeter (PCFC). The polyurethanes were prepared in the presence of the potential flame retardants via solvent mixing and copolymerization methods, and were then analyzed via spectroscopic methods to determine if the flame retardant was still present in the final product. PCFC testing on the resulting products showed that the flame retardant molecule can have different effects on heat release depending upon how it is mixed into the polyurethane. Some materials showed strong effects on heat release reduction when reacted into the polyurethane during copolymerization, while others were more effective at heat release reduction when simply solvent blending into the polyurethane. The results from this screening study show that flame retardant chemical structure and its environment in the polymer (covalently bonded vs. noncovalent interactions) greatly affects flammability behavior. From the combined data, aromatic boronates were found to be very effective at reducing heat release and inhibiting melt flow during thermal decomposition, as were some aromatic phosphonic acid terephthalic acid and terephthalate derivatives.

1. Introduction

Flexible polyurethane foam remains the largest fuel load that could potentially lead to a flashover event (total loss of property and/or life) in the US [1]. There are regulations in place which require the use of flame retardants to lower the fire risk associated with flexible polyurethane foam [2–4], but some of the commercially available flame retardants are being deselected due to persistence, bioaccumulation, and toxicity (PBT) issues [5,6]. While some new flame retardants are becoming available which can meet existing regulations, the flammability tests themselves are in a state of flux, with arguments in place to have the tests focus on cigarette ignition, small flame ignition, and/or heat release [7,8]. Flame retardants, due to the complexity of fire physics and material flammability, must be optimized for a specific product in a specific test, and so when the flammability test is a "moving target" it becomes difficult for the flame retardant chemist to develop new chemistry. However, if one considers what makes polyurethane foam flammable, then one may have a "target" to begin developing new flame retardant chemistry. Such a target should address the polyurethane flammability problem while simultaneously addressing PBT issues. This is a problem with two inputs that need to be discussed separately before describing the approach in this paper which is focused on understanding and developing new flame retardant chemistries.

The first of the two inputs is the flammability of polyurethane foam. When flexible polyurethane foam ignites and burns, it will drip and flow thus forming a fuel pool fire event [9]. This formation of a pool fire, plus the high heat release of polyurethane, can rapidly lead to a flashover event. Therefore, to truly lower the flammability of polyurethane foam, the flame retardant must lower the heat release of the polyurethane and slow or prevent dripping/liquefaction of the foam during thermal decomposition. So when screening for new flame retardant chemistry at the small scale, lowered heat release should be one result to look for, and additional char formation along with inhibition of flow under thermal decomposition conditions should be another. Small scale heat release testing can be achieved via pyrolysis combustion flow calorimetry (ASTM D7309), which has been shown to be a proven

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technique for flame retardant material development and screening [10–13]. The technique does have some limitations [14,15], but provided those limitations are considered, the data generated by PCFC is still quite powerful in advancing new flame retardant chemistry. Addressing inhibition of liquefaction of a polymer is not easy to measure at small scale, and sometimes there is no substitute for actual vertical flame spread tests. However, studying increases in char yields and char residue structure from the PCFC test may be useful in determining the effectiveness of the flame retardant towards inhibition of foam liquefaction during burning. Admittedly, visual char studies can be qualitative (and subjective) in nature, but it is a place to start and should not just be dismissed out of hand, especially if the char structure generated by the flame retardant (FR) polyurethane is notably different than that of the non-FR polyurethane. In this case, looking for a lack of flow structure in the chars would suggest that the new flame retardant is inhibiting polyurethane liquefaction.

The second of the two inputs is the environmental impact of the flame retardant. There is convincing evidence that over time, some flame retardants will migrate out of polyurethane foam and become a PBT problem [16,17]. This also presents a fire safety problem in that the foam over time may lose its protection if enough of the flame retardant leaves the product. So the flame retardant chemist must now consider developing new flame retardants which either react into the polyurethane itself (cannot leave the polymer throughout its life cycle), or are polymeric in structure. Polymeric structures are preferred in that if they do get into the environment, they cannot easily bioaccumulate or become toxic should they be persistent. Environmental consideration must be included in new flame retardant design, but actual testing of chemical environmental impact can be expensive, and perhaps too expensive during early FR development. Predictive models for molecule toxicity exist as well, but these models have costs associated with them as well. At a minimum, determining if the FR covalently reacts into the polymer serves as useful screening criteria for ensuring low PBT profiles. If the FR cannot leave the polymer due to its covalent bonds with the main polymer chain, then it is less likely get into the environment to cause ecological damage. Therefore use of spectroscopic techniques that help show the FR is reacted into the polyurethane would be a good method to infer the environmental impact of the new FR.

In this paper, we report on the use of PCFC to study how new phosphonate and boronate flame retardants synthesized previously [18] affect heat release in a polyurethane. A polyurethane based upon methylene diphenyl isocyanate and 1,3-propane diol was used as a system to quantify heat release reduction potential of these potential flame retardant chemistries which may be useful to address flexible polyurethane foam flammability. Flame retardants were incorporated into a polyurethane at 10 mol% through direct reaction with polyurethane monomers during polymerization, or via solvent blending with the polyurethane after the monomers had been polymerized in a separate flask. With the use of the PCFC, the effectiveness of the flame retardant chemistry in lowering heat release was studied. The best performing flame retardants were further studied with thermogravimetric analysis-Fourier Transform Infrared Spectroscopy (FTIR) to see if the mechanism of heat release reduction could be determined. The chars collected from PCFC testing were evaluated in a visual qualitative manner to see if any of the flame retardants had a positive effect on char formation and/or flow inhibition. Additionally, measurements were conducted to determine how these chemistries do/do not react into the polyurethane to screen for potential environmental impact. This was done through nuclear magnetic resonance (NMR) measurements of the polyurethanes formed to determine if the flame retardant was incorporated into the final structure or not. The results of this study should give insight into which new boron and phosphorus chemistry has potential to solve the polyurethane foam flammability problem and deliver new FR chemicals with greatly improved environmental profiles provided those new flame retardants are reacted into the polyurethane matrix.

2. Experimental procedures

2.1. General procedures and chemicals

^{1}H and ^{13}C spectra were recorded at 300 MHz and 75 MHz respectively and referenced to the solvent ($CDCl_3$: 7.27 ppm and 77.0 ppm; DMSO-d_6: 2.49 ppm and 39.5 ppm). ^{31}P NMR spectra were measured at 121 MHz, all in DMSO-d_6, and referenced to H_3PO_4 solution in DMSO-d_6 (0.0 ppm). The referencing was accomplished by measuring and calibrating the signal of the standard, followed by subsequent use of the Spectrum Reference (SR) feature of the NMR instrument, to standardize the rest of the spectra. ^{11}B NMR spectra were measured at 96 MHz, all in DMSO-d_6, and referenced to H_3BO_3 solution in DMSO-d_6 (0.0 ppm), again using the SR function. Elemental analysis was provided by Atlantic Microlab, Norcross, GA.

N-methylpyrrolidone, 1,3-propanediol and methylene diphenyl diisocyanate (MDI) were purchased from Acros Organics. Dibutyltin dilaurate was purchased from TCI America. The preparation of phosphonoterephthalic acid (**MPA**) [19,20], 2,5-diphosphonoterephthalic acid (**DPA**) [20], dimethyl 2,5-bis(dimethylphosphono)terephthalate (**DPME**) [20], boronoterephthalic acid (**MBA**) [18], diboronoterephthalic acid (**DBA**) [18] and dimethyl 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) terephthalate (**DBB**) [18] was accomplished following previously published synthetic protocols. 1,4-Dihydroxy-2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene (**MP**) and 1,4-dihydroxy-2,5-bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene (**DP**) have been reported recently [21,22], but we have included their preparation and isolation in the current manuscript, as the separation and purification protocol has been modified. 2*H*-5,5-Dimethyl[1,3,2]dioxaphosphorinane-2-oxide (**DDPO**) has also been reported in the literature [23,24], but the protocol was modified, and its preparation is described.

2.2. Synthesized flame retardants

In this effort we also used several synthetic flame retardants prepared in our laboratories which had shown effectiveness in reducing heat release when solvent blended with a thermoplastic polyurethane [18]. Their chemical structures with acronyms are shown in Fig. 1, and some additional details about the compounds are included in Table 1.

2*H*-5,5-Dimethyl[1,3,2]dioxaphosphorinane-2-oxide (DDPO). A mixture of 2,2-dimethyl-1,3-propanediol (62.4 g, 0.600 mol) and diethylphosphite (82.9 g, 0.600 mol, 77.3 mL) was stirred at 190 °C and atmospheric pressure, allowing for the continuous distillation of the ethanol formed during the reaction. Volatiles were removed under reduced pressure, followed by vacuum fractional distillation (0.05 mm Hg). The fraction distilling at 118–123 °C was collected, and NMR showed it to be pure for further use. Colorless oil, which solidifies upon standing. Yield: 34.9 g (38%). Mp 55 °C (Lit. [24] 58 °C). ^{1}H NMR ($CDCl_3$) δ 0.87 (s, 3H), 1.20 (s, 3H), 3.86–4.06 (m, 4H), 6.85 (d, $J = 676.3$ Hz, 1H).

1,4-Dihydroxy-2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene (MP) and 1,4-dihydroxy-2,5-bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphane-2-yl)benzene (DP). A solution of *p*-benzoquinone (2.00 g, 18.50 mmol), toluene (20 mL), and acetic acid (0.1128 g, 1.90 mmol) was added dropwise