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Ryan Maguire
University of Dayton

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Honors Thesis
Ryan Maguire
Department: Chemistry
Advisor: Vladimir Benin, Ph.D.
April 2022

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Abstract

Melamine is an aromatic, nitrogen-containing compound used to produce a myriad of items ranging from kitchenware to laminates. In this project, it was attempted to determine whether another use for melamine, as a starting material for the production of a reactive flame retardant, could be achieved through synthetic modifications. A series of bifunctional derivatives were formed, and although some polymerization reactions were unsuccessful, alternate routes exist that can be attempted going forward.

Disclaimer

Acknowledgements

I wish to thank my thesis advisor, Dr. Vladimir Benin, for his constant guidance throughout the research, presentation, and writing process. I also wish to thank Dr. Judit Beagle for training and access to the microwave reactor and my academic advisor, Dr. Matthew Lopper, for his support during my time at the University of Dayton.

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Introduction

Flame-retardant compounds are a group of chemicals that are added to or incorporated into other materials, such as plastics, textiles, and coatings, to prevent fires from breaking out on their surfaces. These compounds are activated when a flame or some other ignition source is brought to the material's surface, and they utilize nonreactive properties to slow or completely stop the combustion process. This process can happen through physical mechanisms, in which the flame retardant alters the physical state of the ignited surface, such as decreasing its temperature, and through chemical mechanisms, in which the flame retardant causes certain reactions to occur that in turn serve to prevent combustion reactions due to the creation of new compounds that resist these processes.[1] These compounds have been applied in a myriad of settings, ranging from consumer goods to specialty items used for workers in jobs that require working with fire.

Two classes of flame retardants have been identified. The first of these, additive flame retardants, are simply mixed into the material, while the other class, reactive flame retardants, involve reacting the flame retardant as a co-monomer to generate the polymer chain with chemically incorporated flame retardant substructures. Additive flame retardants are the most common class and are often added through either a physical mixing process or by melting it into the system one wishes to add flame retardant properties to. Unfortunately, additive flame retardants can leach out of the polymer they have been added to, thus creating both environmental and toxicity issues.[1] Reactive flame retardants are chemically incorporated into the polymer chain, largely eliminating environmental and health concerns, but they are often more costly to prepare and can cause changes in the properties of the resultant polymers.[1] In this research, the goal was to determine and test synthetic routes to produce reactive flame-retardant compounds for nylon-type polymers, starting with melamine.

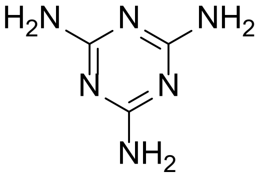


Figure 1: Melamine

Melamine is an aromatic compound that contains six nitrogen atoms, six hydrogen atoms, and three carbon atoms, with a core six-membered ring (Figure 1). The synthesis of melamine involves the decomposition of urea, which in turn forms cyanic acid and ammonia. A condensation reaction can then be performed on the cyanic acid to produce melamine. This synthesis can be performed as a liquid-phase reaction, which occurs under high pressure and utilizes melamine and ammonia in solvent, or as a gas-phase reaction, which occurs under low pressure and requires catalysts.[2] Melamine has been reacted with formaldehyde to produce tightly-bound resins used in a myriad of practical applications, such as cooking utensils, industrial coatings, fertilizers, and more. When used in food-related items, it has been found that melamine does not pose a significant threat to human health. The stability of these structures, caused by the aromatic stability of melamine, makes them sturdy and useful for these purposes. Furthermore, these structures are resistant to extreme temperature conditions, making them especially useful in fields where other compounds may more easily oxidize or degrade. Melamine can also be utilized in various other reactions to form a series of derivatives for practical use including corrosion-preventing substances and germicides.[2] Additionally, melamine itself has been shown to act as an additive flame retardant.

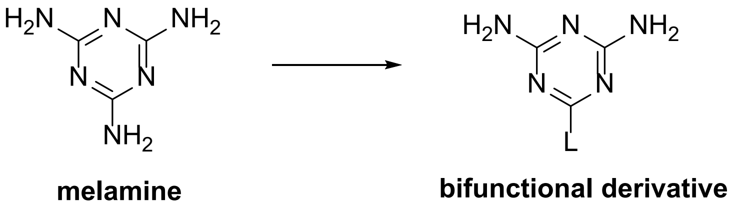


Figure 2: Bifunctional derivative of melamine

A specific goal of this project was to convert melamine into a bifunctional derivative, as shown in Figure 2. Such derivatives have been formed using cyanuric chloride (Figure 3) and other triazine derivatives as starting materials. The major goal of this research, however, was to determine whether melamine itself could be used as a starting material.

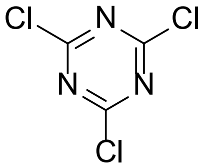


Figure 3: Cyanuric chloride

Specific challenges were anticipated at the onset of the project. The principal challenge revolved around melamine's low reactivity. Melamine contains a highly electron-withdrawing ring structure that is extremely stable due to its aromaticity. Since the electrons on the amino substituents are part of the conjugated system, melamine is a weak base with a pK_b of 9.0. Nonetheless, melamine is not entirely unreactive. It has been shown to react with mineral acids in the production of salts and complexes, meaning that melamine reactions are possible. Another concern entering this research involved reacting at only one amino substituent, but melamine's low reactivity rendered this concern unnecessary.

The resonance delocalization of π- and lone-pair electrons in melamine, seen in Figure 4, contributes significantly to its stability. In this resonance, a lone pair of electrons from an amino substituent can shift to the carbon atom attached to the substituent, leading the electrons in the carbon's double bond with a nitrogen atom to shift to that atom. This in turn leads the cyclic nitrogen to become negatively charged and the amino nitrogen to become positively charged. An electron pair on the cyclic nitrogen can shift to the next carbon atom in the ring, leading the resonance to continue around the entire melamine ring.

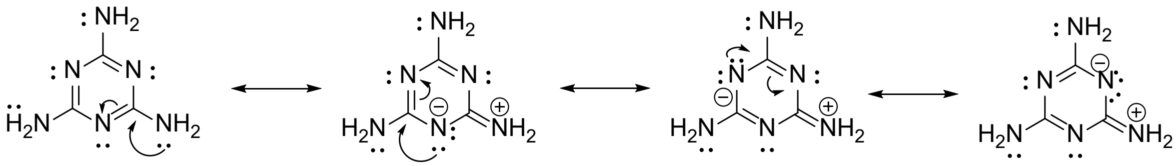


Figure 4: Resonance stability of melamine

Two major factors point to melamine having a behavior closer to an amide than to an aromatic amine. The first factor, that of the resonance available, shows significant similarities between melamine's resonance and the resonance of an amide, with a lone pair from a nitrogen atom conjugated to a C = O bond. The conjugation leads to a nitrogen atom from the ring (as in melamine) or the oxygen atom (as in an amide) becoming negatively charged. The initial nitrogen atom, meanwhile, becomes positively charged. These similarities are displayed in Figure 5.

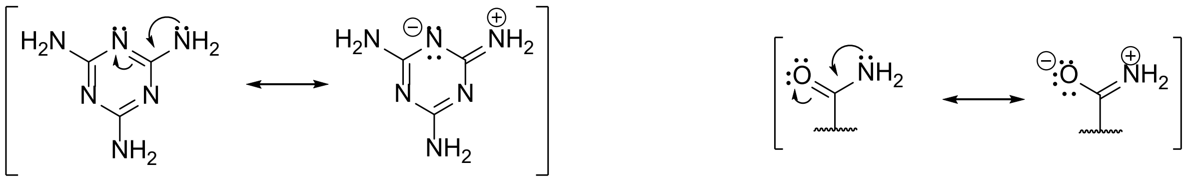
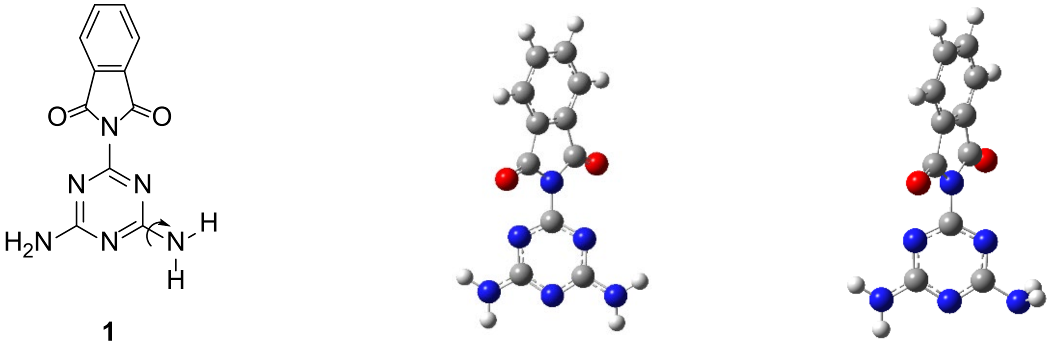


Figure 5: Similar resonance stabilization in melamine and amides

Furthermore, one can study the carbon-nitrogen bond rotation of an amino substituent in melamine. After reactions had been performed, the ^1H NMR spectrum of a phthalic anhydride-melamine derivative (**1**) was analyzed. Figure 6 displays the bond rotation under observation, with compound **1** on the left, a three-dimensional, calculated structure of compound **1** in the middle, and the calculated transition state for the bond rotation of compound **1** on the right.



1

Figure 6: Melamine-succinic anhydride amino group bond rotation

Figure 7 shows the ^1H NMR peak under study, with the hydrogen atoms under observation highlighted in blue. Two individual peaks for the amino hydrogens were observed rather than a coalescence of the two, implying that the atoms exist in different environments. The difference in frequencies of the two peaks, measured in Hertz, was used to calculate the rate constant of the rotation of the carbon-nitrogen bond using the equation

$$k = \frac{\pi(\Delta\nu)}{\sqrt{2}}$$

with $\Delta\nu$ representing the difference in frequency. From this equation and using the difference in frequency of 16.9 Hz, the rate constant k was found to be 37.4 Hz.

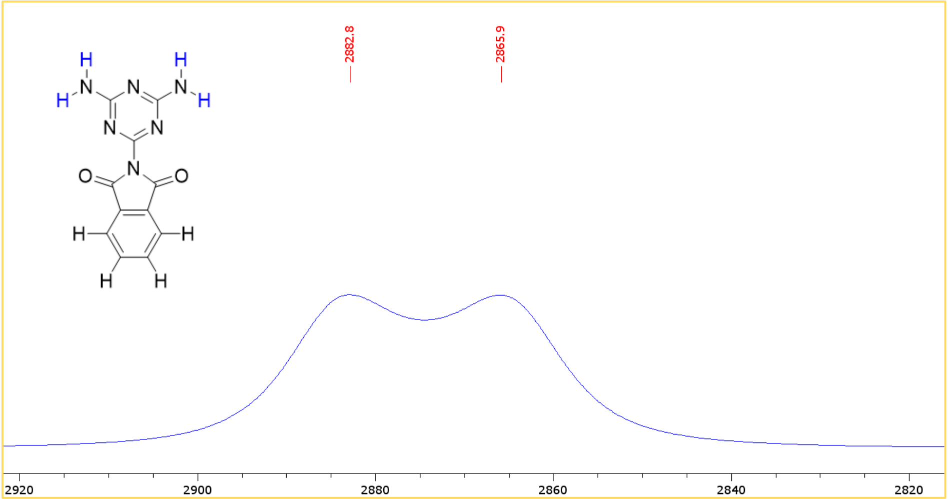


Figure 7: ^{1}H NMR peak for amino hydrogen atoms in compound **1**

This value was utilized with the Eyring equation:

$$k = \frac{\kappa T}{h} e^{-\Delta G^{\neq}/RT}$$

to find the activation energy, $\Delta G^{\neq}$, of the bond rotation. The value was determined to be 15.0 kcal/mol at 293 K, which was very similar to the theoretical value of 16.0 kcal/mol found using a *DFT/B3LYP//6-31+G(d)* method. This activation energy was compared to the C-N bond rotation activation energies in formamide, which is 15.7 kcal/mol, and in aniline, which is 3.7 kcal/mol. The value from the melamine derivative was far closer to that of the amide than to the cyclic, primary aromatic amine, further showing closer similarities between the behavior of melamine and amides compared to aromatic primary amines. This information sheds light on the reactivity of melamine, which will likely behave more like an amide than an amine in reactions.

Experimental

^{1}H NMR spectra were recorded at 300 MHz or 400 MHz and referenced to the solvent (DMSO-d_6: 2.49 ppm). Elemental analysis was provided by Atlantic Microlab, Norcross, GA.

Attempted formation of 2-((4,6-diamino-1,3,5-triazin-2-yl)amino)-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (4). Compound **2** (1.84 g, 0.01 mol) was introduced into a round-bottom flask equipped with a condenser. Water (10 mL) and K_2CO_3 (1.30 g, 0.01 mol) were added, and the mixture was stirred for 1 h at 60 ºC, Melamine (1.26 g, 0.01 mol) was then added and the resultant mixture was stirred for 5 h at 90 ºC. NaOH was added to the solution until the solution was no longer acidic. The mixture was then poured into ice water. Stirred for ~ 30 min, then filtered under reduced pressure (sintered glass filter, grade M). The solid was washed with water. The resultant material was air-dried. White solid. Yield: 56%. ^{1}H NMR (DMSO-d_6) δ 0.90 (s, 6H), 3.75 (d, J = 4.0 Hz, 4H), 7.54 (s, 7H). Anal. Calcd. For $C_8H_{17}N_6O_4P$: C, 32.88; H, 5.86; N, 28.76. Found: C, 32.97; H, 5.72; N, 28.58. The solid was determined to be the salt of melamine and the chlorophosphate. The reaction was attempted through multiple attempts, with the specific conditions displayed in Table A1 in the Appendix.

2-(4,6-Diamino-1,3,5-triazin-2-yl)isoindoline-1,3-dione (1). Melamine (2.52 g, 0.020 mol) was introduced into a round-bottom flask, equipped with a condenser and a Dean-Stark trap. DMSO (20 mL) and toluene (15 mL) were added, followed by phthalic anhydride (3.25 g, 0.022 mol), and the resultant mixture was stirred for 90 min at 150 ºC. The mixture was then poured into *aq.* $NaHCO_3$ (50 mL, 5% w/v soln.). Stirred for ~ 20 min, then filtered under reduced pressure (sintered glass filter, grade M). The solid was washed successively with water, methanol and diethyl ether. The resultant material was air-dried. White solid. Yield: 71%. 1H NMR (DMSO-*d₆*) δ 7.18 (d, J = 20.0 Hz, 4H), 7.91-7.99 (m, 4H). Anal. Calcd. For $C_{11}H_8N_6O_2$: C, 51.56; H, 3.15; N, 32.80. Found: C, 51.28; H, 3.03; N, 33.01. The reaction was carried out in multiple attempts, with the specific conditions displayed in Table A2 in the Appendix.

1-(4,6-diamino-1,3,5-triazin-2-yl)pyrrolidine-2,5-dione (7). Melamine (2.52 g, 0.020 mol) was introduced into a round-bottom flask equipped with a condenser, and DMF (12 mL) was added, followed by succinic anhydride (6.00 g, 0.060 mol), and the resultant mixture was stirred for 24 h at 120 ºC. The mixture was then poured into water for 20 minutes before being added to *aq.* $NaHCO_3$ (50 mL, 5% w/v soln.). Stirred for ~ 30 min, then filtered under reduced pressure (sintered glass filter, grade M). The solid was washed successively with water, methanol and diethyl ether. The resultant material was air-dried. White solid. Yield: 37%. ^1H NMR (DMSO-d_6) δ 2.78 (s, 4H), 7.12 (s, 4H). Anal. Calcd. For $C_7H_8N_6O_2$: C, 40.39; H, 3.87; N, 40.37. Found: C, 40.16; H, 3.75; N, 40.22. The reaction was carried out in multiple attempts, with the specific conditions displayed in Table A3 in the Appendix.

A melamine monophthalate salt was formed in all runs and was isolated. ^1H NMR (DMSO-d_6) δ 7.07 (s, 7H), 7.52-7.54 (m, 2H), 7.97-8.00 (m, 2H). Anal. Calcd. For $C_{11}H_{12}N_6O_4$: C, 45.21; H, 4.14; N, 28.76. Found: C, 45.03; H, 3.97; N, 28.64.

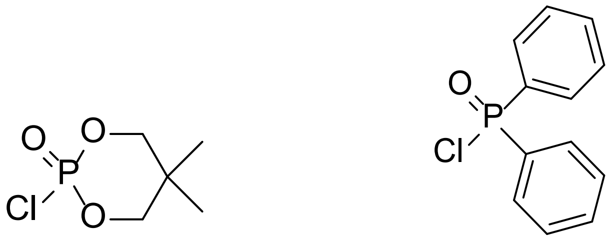
Attempted Polymerization of compound 7 using oil bath. Compound **7** (1.04 g, 0.005 mol) was introduced into a round-bottom flask equipped with a condenser, and NMP (15 mL) and triethylamine (1.01 g, 0.010 mol, 1.40 mL) were added, followed by sebacoyl chloride (1.20 g, 0.005 mol, 0.992 mL). The resultant mixture was stirred for 24 h at 100

°C. The mixture was then poured into *aq*. $NaHCO_3$ (50 mL, 5% w/v soln.). Stirred for ~ 30 min and became soluble.

Attempted polymerization of compound 7 using a microwave reactor. Compound **7** (0.42 g, 0.003 mol) was introduced into a small glass container and NMP (10 mL) and triethylamine (0.674 g, 0.007 mol, 0.93 mL) were added, followed by sebacoyl chloride (0.8 g, 0.003 mol, 0.660 mL), and the resultant mixture was placed into the microwave reactor for 5 minutes at 170 °C using 60 W. The mixture was then poured into 50 mL of water before being suspended in *aq*. $NaHCO_3$ (50 mL, 5% w/v soln.). Stirred for ~ 30 min then filtered under reduced pressure (sintered glass filter, grade M). The solid was washed successively with water, methanol and diethyl ether. The resultant material was air-dried. The polymerization reaction was carried out through multiple attempts, with the specific conditions displayed in Table A4 in the Appendix.

Results and Discussion

The formation of a bifunctional derivative was initially attempted by reacting melamine with chlorophosphates and chlorophosphinates. These classes of compounds typically react readily with aromatic amines, such as aniline, in the presence of a base.[3] These reactions can occur very quickly, often at room temperature. In this same vein, 2-chloro-1,3,2-dioxaphosphinane 2-oxide (Compound **2**) and diphenylphosphinic chloride (Compound **3**), both shown in Figure 8, were employed in reactions with melamine.

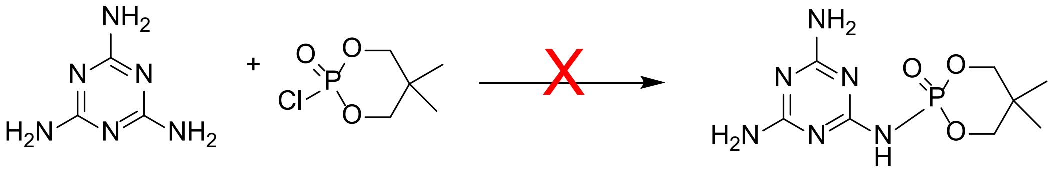


2 **3**

Figure 8: Chlorophosphate and chlorophosphinate Reactants

Scheme 1 shows the attempted reaction with compound **2** and the desired product. When analyzing the products from the chlorophosphate and chlorophosphinate reactions, it was determined that all reactions performed in water led to the formation of a salt (Compound **5**).

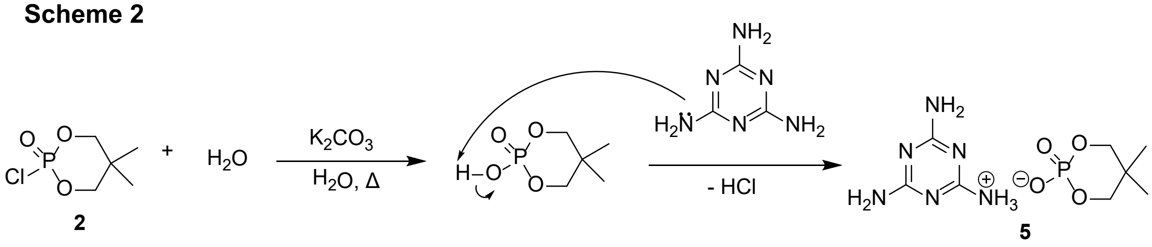
Scheme 1



2 **4**

In this process, a proposed reaction schematic, shown in Scheme 2, involved first the hydrolysis of the chlorophosphate or chlorophosphinate, with a hydroxyl group replacing the chlorine. Then, a lone pair of electrons in an amino substituent on melamine could have attacked the hydrogen from the hydroxyl group, leading the electrons in the hydroxy bond to be claimed by the oxygen, giving the oxygen a negative charge and the amino substituent a positive charge.

Scheme 2



The formation of a salt with this chemical structure was confirmed by elemental analysis, showing that the desired bifunctional derivative was not formed. On the other hand, the reactions performed in acetonitrile instead of water showed only the recovery of the starting materials rather than the occurrence of any reaction. These results led to the assumption that melamine does not behave as typical amines and that melamine cannot be reacted with this class of compounds. Figure 9 shows the ^{1}H NMR spectrum for this salt, which was used in conjunction with elemental analysis to confirm the salt's identity. In this spectrum, one can note the three unique hydrogen atom signals present, with the melamine hydrogen atoms appearing with a shift around 7.5 and the hydrogen atoms from the chlorophosphate anion appearing further upfield.

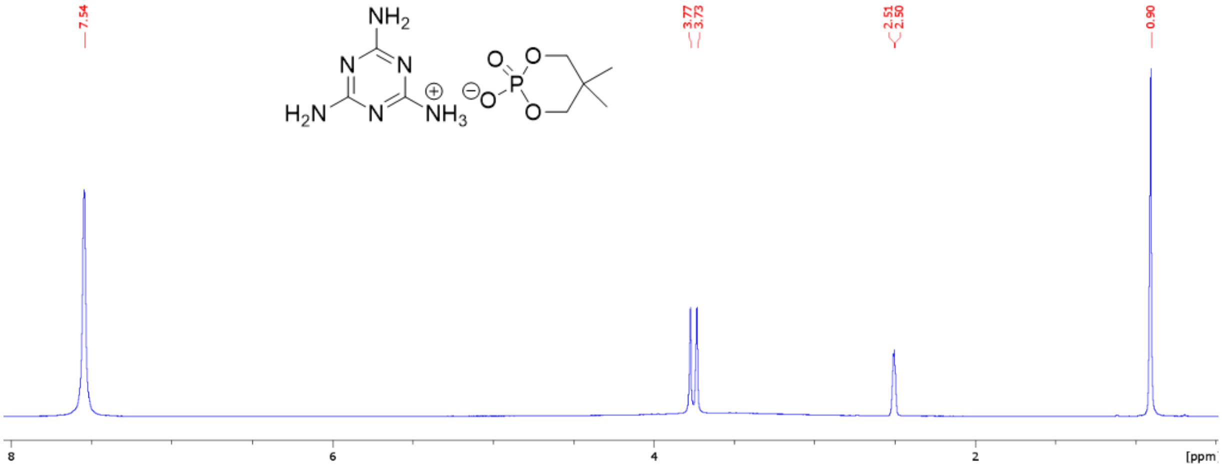
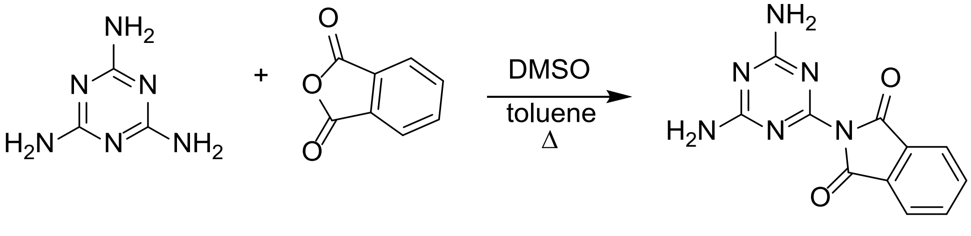


Figure 9: ^{1}H NMR spectrum of compound **5**

The reaction between melamine and PAH is shown in Scheme 3.

Scheme 3



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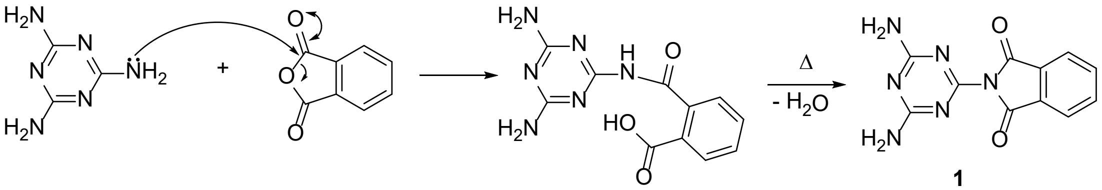
A proposed reaction mechanism (Scheme 4) involves a lone pair from an amino group attacking an acyl carbon in the anhydride. This could in turn cause the ring to break open, leading to the formation of a carboxylic acid from the oxygen originally in the ring. By heating the reaction, a dehydration process could occur, eliminating water and closing the ring to create the desired bifunctional derivative.

Scheme 4



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This product formed was confirmed through elemental analysis and through the ^{1}H NMR spectrum, which can be seen in Figure 10. As expected, there are only two unique hydrogen atoms in this species, with one corresponding to hydrogen atoms on the benzene ring and the other corresponding to the melamine hydrogen atoms.

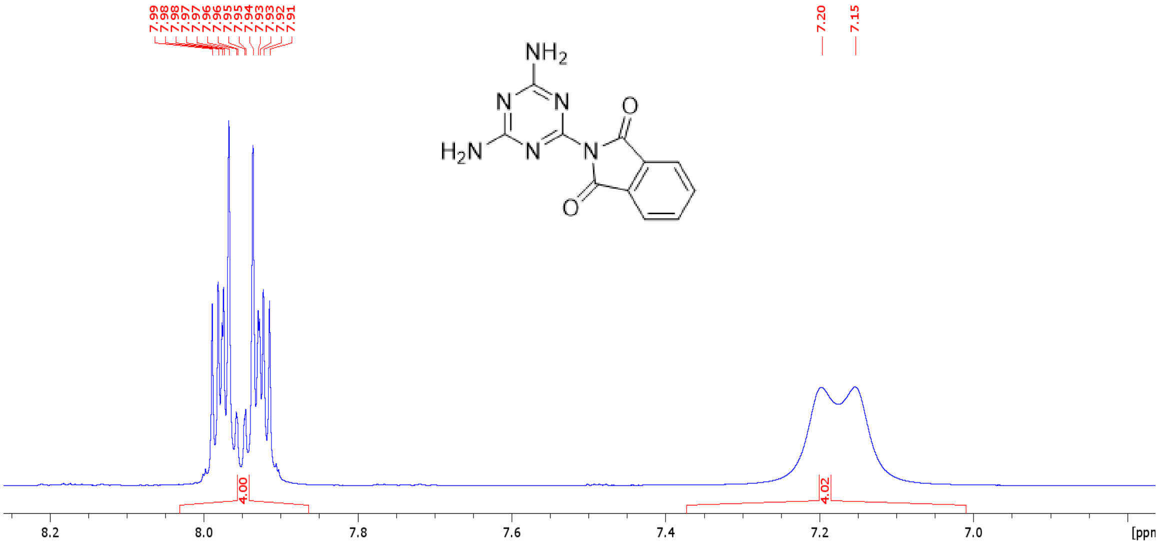
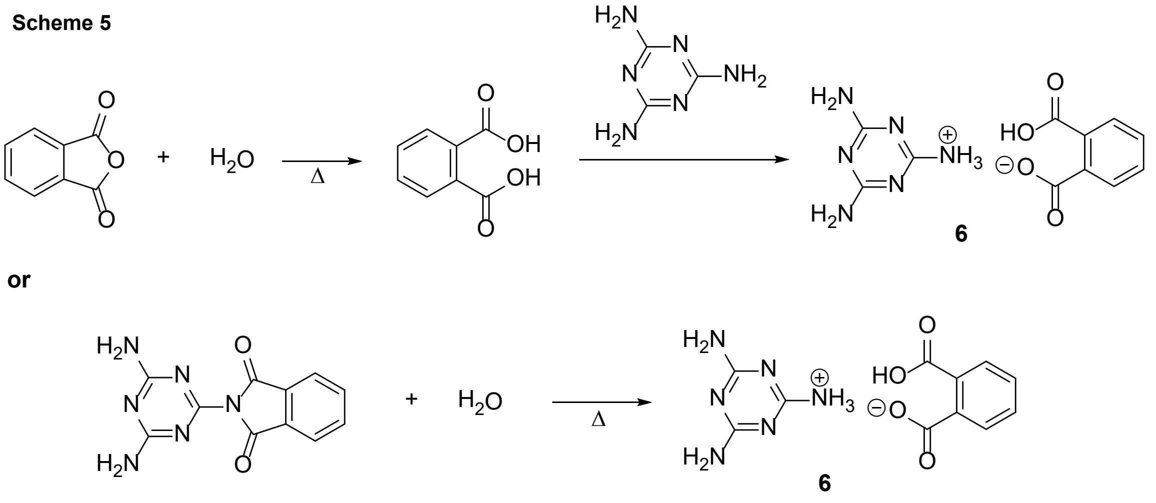


Figure 10: ^{1}H NMR spectrum of compound **1**

In all runs, a melamine monophthalate salt (Compound **6**) was also formed, the identity of which was confirmed through elemental analysis as well. The ^{1}H NMR spectrum can be seen in Figure 11, which displays three unique hydrogen atoms as opposed to the desired product, which only has two unique hydrogen atoms. This spectrum is extremely similar to the spectrum for the potassium monophthalate salt, which was used to help characterize this species.[7] The two upfield peaks correspond to two unique hydrogen atoms on the benzene ring, which exists in different environments in the salt.

Two possible mechanisms for the salt formation have been proposed. The first involves the initial reaction of PAH with water, causing a hydrolysis that leads to a dicarboxylic acid. The dicarboxylic acid could then undergo a proton exchange with melamine to produce the salt. In the second mechanism, the already-formed derivative could react with water that would reverse the final step of the proposed schematic for its formation, leading to the breaking of the nitrogen-carbonyl carbon bonds and forming the salt. These schematics are shown in Scheme 5. Because melamine has been found to resist reactions with carboxylic acids, the second mechanism is more likely.

Scheme 5



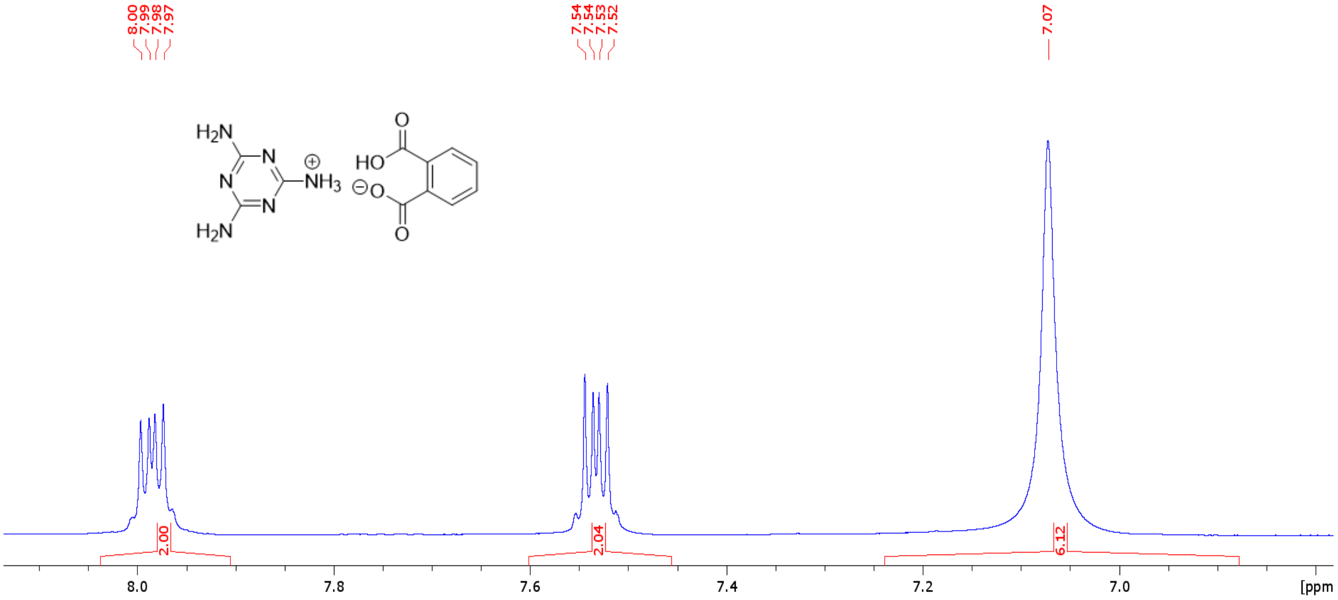
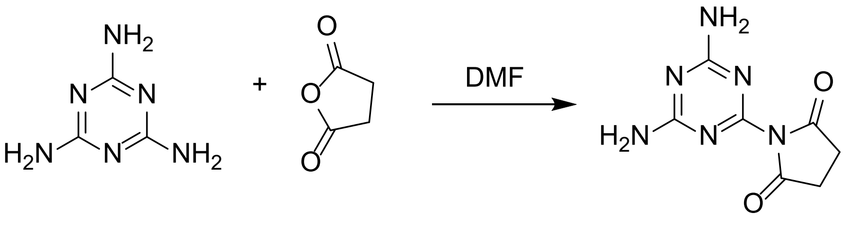


Figure 11: ^{1}H NMR spectrum of compound **6**

A second reaction of melamine with a cyclic anhydride, which also worked successfully, was the reaction with succinic anhydride (SAH), reflected in Scheme 6.

Scheme 6



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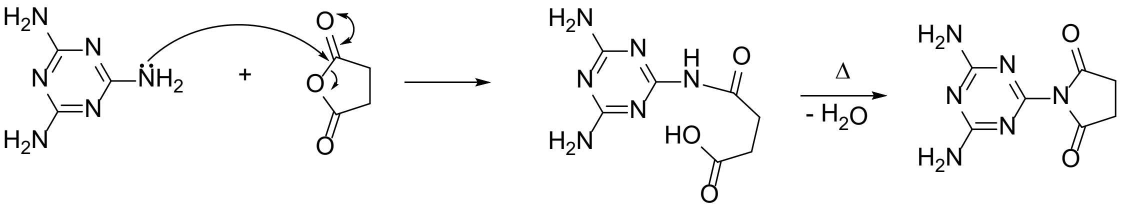
The formation of compound **7** follows a similar mechanism, with an amino lone pair attacking a carbonyl carbon, the anhydride ring breaking open, and the removal of water leading to the ring's closing, forming the desired derivative (Scheme 7).

Scheme 7



7

The resulting product's identity was confirmed through elemental analysis and through the ^{1}H NMR spectrum, shown in Figure 12. This structure only has two unique hydrogen atoms, with the more downfield peak corresponding to the melamine hydrogen atoms and the more upfield peak corresponding to the hydrogen atoms from the original succinic anhydride ring. Similarly, these reactions also led to the production of a salt that had to be purified.

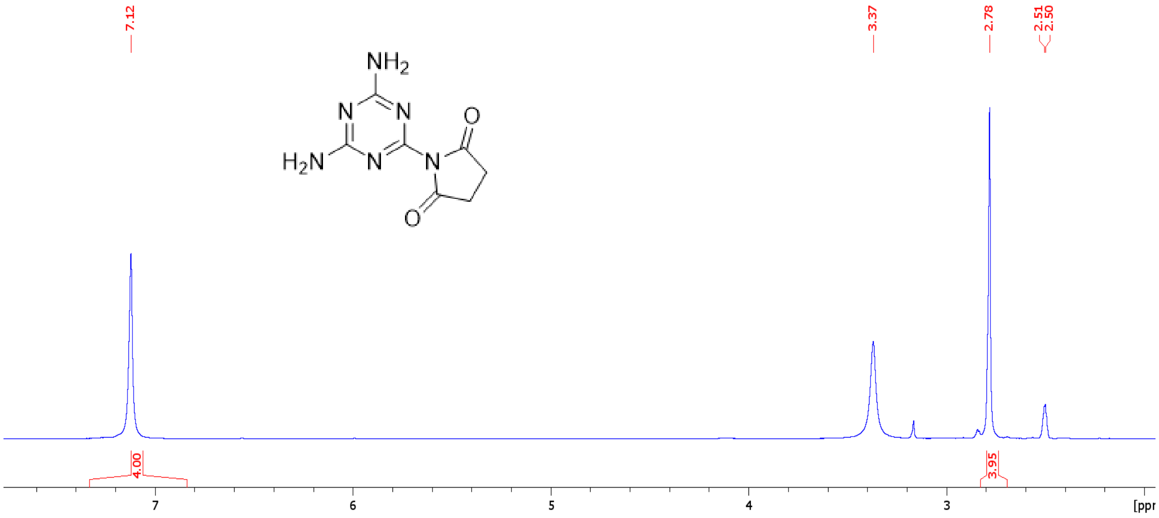
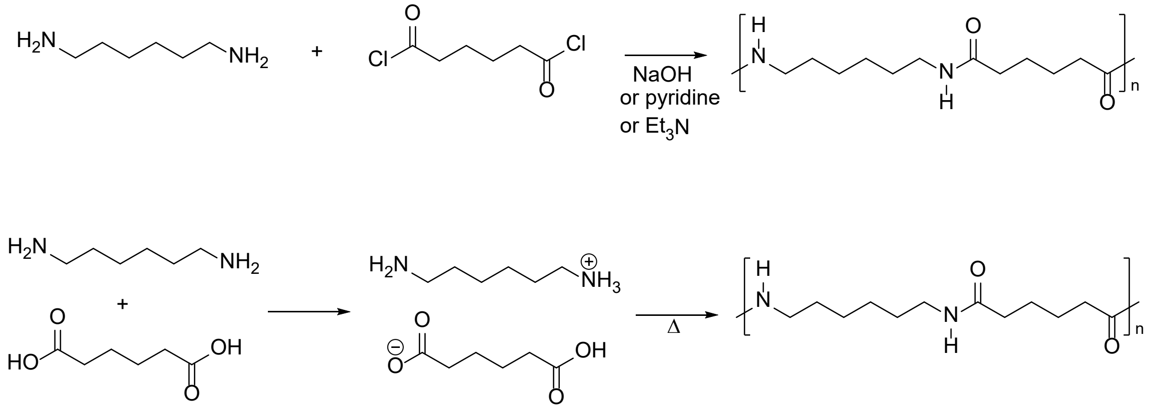


Figure 12: ^{1}H NMR spectrum of compound **7**

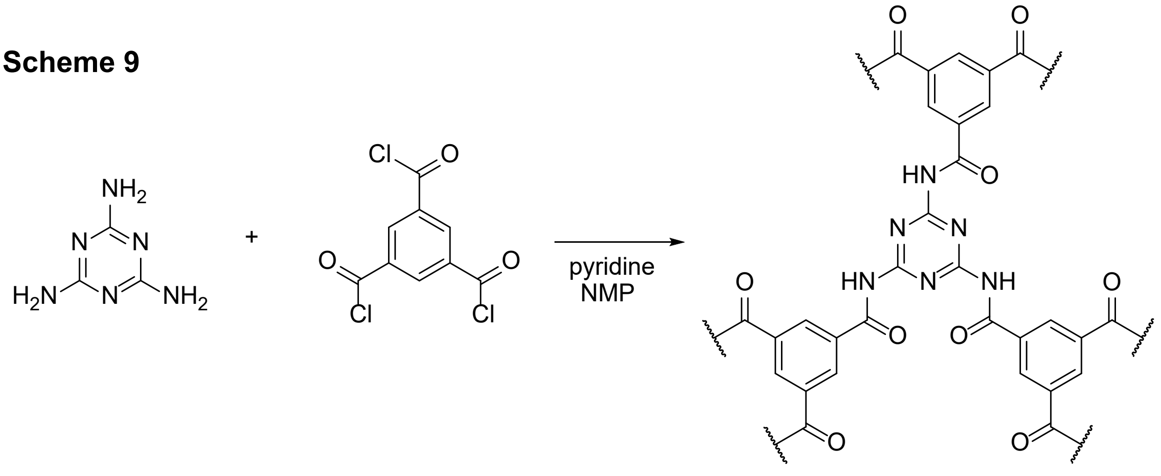
The attempted polymerization reactions with compound **1** were based on protocols used in the preparation of Nylon *6,6*. Traditionally, this instant reaction is performed with 1,6-hexanediamine and adipoyl chloride as reactants in the presence of some kind of base, often sodium hydroxide, pyridine, or triethylamine.[4,5] The reaction is shown on the top in Scheme 8. The lone pairs of electrons on the amino nitrogen atoms can attack the carbonyl carbons in a reaction that keeps repeating, creating the desired chain. Similarly, this reaction is performed using adipic acid instead of adipoyl chloride in industry, leading to the formation of a salt with an amino nitrogen taking a proton from the hydroxyl group of the dicarboxylic acid before ultimately forming the bonds between both. This industrial reaction is shown on the bottom in Scheme 8. Because melamine resists reactions with carboxylic acids, the acid chloride route was used as a model for this process.

Scheme 8



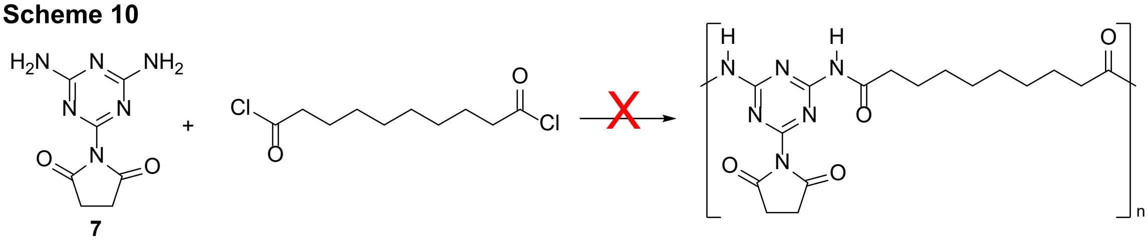
MIT researchers recently published the first reported instance of melamine reacting with an acid chloride to produce a polymer. In this process, trimesic acid chloride was reacted with melamine in a mixture of pyridine and NMP to produce the desired polymer (Scheme 9).[6] This process was used as a model for some of the attempted polymerizations. Initially, reactions were attempted at 100 ºC in an oil bath with triethylamine as the base and NMP as the solvent. Later reactions were attempted in a microwave reactor and used pyridine rather than triethylamine, much like the MIT paper.

Scheme 9



All polymerization reactions attempted were unsuccessful in forming the desired product. The attempted reaction would have resulted in lone pairs from the amino substituents on compound **1** attacking the acyl carbons of the respective acid dichlorides, leading to hydrogen chloride as a byproduct and forming the polymer. These reactions were attempted using triethylamine, with the attempted reaction and desired product shown in Scheme 10.

Scheme 10



However, the reactions performed under nitrogen in an oil bath showed no evidence for the formation of a polymer when tested through NMR. These reactions utilized a similar system to similar reactions reported in literature, with a condenser placed on top of a round-bottom flask, which was in turn placed in an oil bath. Similar reaction specifications were attempted in the microwave reactor. For these reactions, the starting materials were scaled down and placed in a small glass vial, which was placed in the microwave reactor. Three parameters can be controlled on the microwave reactor, namely the reaction's temperature, time, and the machine's power. When triethylamine was used as the base for the reaction in the microwave reactor, the NMR results remained uncertain. In a follow-up trial, pyridine was used as the base instead, much like the MIT paper. The machine's power, temperature, and reaction time were all increased, but this trial led to a water-soluble result that was not the desired polymer. Research is ongoing for this portion of the project.

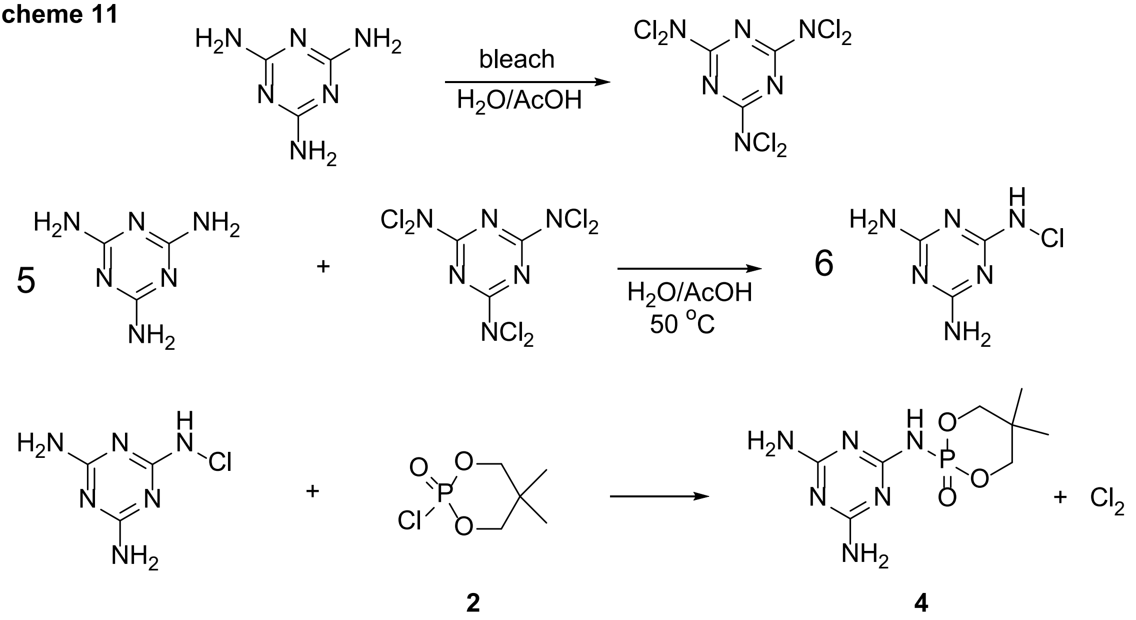
Conclusion

From this research, four major conclusions were reached. First, it is possible to form bifunctional derivatives of melamine when cyclic anhydrides are used as reactants. These reactions are favorable and can be controlled through such conditions as reaction temperature and solvent. Second, the formation of these derivatives always results in the formation of a salt byproduct, but the derivative can be purified so as to remove this salt from the desired product. The use of a sodium bicarbonate bath during the workup of all reactions helped to serve this purification purpose. Third, melamine is unreactive with phosphoric chlorides and phosphinic chlorides. Although melamine has some structural similarities to aromatic amines, which tend to react with these classes of compounds, it clearly does not behave in the same manner. Its inability to react with a chlorophosphate or a chlorophosphinate under any conditions, including at high temperatures, shows that it does not behave as a typical aromatic amine. Finally, melamine derivatives are, as yet, unable to be reacted with acid chlorides to form polymers. This, much like melamine's unreactive nature towards chlorophosphates and chlorophosphinates, is likely due to the unique stability of this starting material.

Future research will be continued on the polymerization process, especially because the microwave reactor has shown more promise that merely performing these reactions in an oil bath. Using pyridine as the only solvent may be another parameter that can be adjusted to impact the results.

Additionally, recent literature has suggested that melamine can be reacted with bleach to substitute an amino hydrogen atom with a chlorine atom, forming several chlorinated melamines. These new derivatives could be further reacted with phosphoric chlorides, acid dichlorides, or epoxides to produce a bifunctional derivative that may more easily polymerize to produce the desired flame retardants, thus offering another possible route to produce this class of compounds. This possible route, leading to a bifunctional derivative formed in a reaction with compound **2**, is shown in Scheme 11.[8]

Scheme 11



This investigation has not yet been successful in incorporating melamine derivatives into polymers, but research is still ongoing and remains a possibility. This discovery, as well as other possible routes to form bifunctional melamine derivatives, showcases a myriad of routes that may make this class of compounds a reality for future usage.

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Appendix

Table A1: Melamine-Chlorophosphate and Melamine-Chlorophosphinate Reaction Conditions

Melamine to Reactant Ratio	Temperature	Reaction Time	Solvent(s)	Workup and Alternate Reaction Conditions	Percent Yield	Purity Estimate
1:1 melamine to 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide ratio (1.26 g and 1.84 g)	60 ºC for first hour, 90 ºC for last 5 hours	6 hours	10 mL H_2O	1.30 g K_2CO_3 used in reaction, NaOH added at end of reaction; Worked up in ice water	46%	0%
1:1 melamine to 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide ratio (0.62 g and 0.91 g)	90 ºC	24 hours	10 mL acetonitrile	0.65 g K_2CO_3 used in reaction; Worked up in ice water	56%	0%
1:1.1 melamine to diphenylphosphinic chloride ratio (1.26 g and 1.9 mL)	90 ºC	24 hours	20 mL acetonitrile	Worked up in ice water and recrystallized	31%	0%

Table A2: Melamine-Phthalic Anhydride (PAH) Reaction Conditions

Melamine to PAH Ratio	Temperature	Reaction Time	Solvent(s)	Workup and Alternate Reaction Conditions	Percent Yield	Purity Estimate
1:1.4 melamine to PAH ratio (3.18 g and 5.21 g)	100 ºC	5 hours	20 mL DMSO	Worked up in ice water and sodium bicarbonate, dried with methanol	63%	53%
1:1.1 melamine to PAH ratio (2.52 g and 3.25 g)	100 ºC	3 hours	20 mL DMSO	Worked up in ice water and sodium bicarbonate, dried with methanol and ether	61%	58%
1:1.1 melamine to PAH ratio (2.52 g and 3.25 g)	120 ºC	5 hours	20 mL DMSO	Worked up in ice water and sodium bicarbonate, dried with methanol and ether	7%	57%
1:1.1 melamine to PAH ratio (2.52 g and 3.25 g)	100 ºC	1 hour	20 mL DMSO	Worked up in ice water and sodium bicarbonate, dried with methanol and ether	67%	69%
1:1.1 melamine to PAH ratio (2.52 g and 3.25 g)	100 ºC	45 minutes	20 mL DMSO	Worked up in ice water and sodium bicarbonate, dried with methanol and ether, recrystallized from water	76%	43%
1:1.1 melamine to PAH ratio (2.52 g and 3.25 g)	100 ºC	1 hour	20 mL DMSO	Worked up in sodium bicarbonate, dried with methanol and ether	84%	50%
1:1 melamine to PAH ratio (12.60 g and 16.30 g)	100 ºC	100 ºC	100 mL DMSO	Worked up in sodium bicarbonate, dried with methanol and ether	80%	82%
1:1.1 melamine to PAH ratio (2.52 g and 3.25 g)	100 ºC	1 hour	20 mL DMSO	Worked up with 20-minute suspension in sodium bicarbonate, dried with methanol and ether	97%	54%
1:1.1 melamine to PAH ratio (2.52 g and 3.25g)	100 ºC	1 hour	20 mL DMSO	Worked up with 30-minute suspension in sodium bicarbonate, dried with methanol and ether	49%	94%
1:1.1 melamine to PAH ratio (2.52 g and 3.25 g)	150 ºC	90 minutes	20 mL DMSO, 15 mL toluene	Under nitrogen with Dean-Stark trap; Worked up in sodium bicarbonate, dried with methanol and ether	71%	97%
1:1 melamine to PAH ratio (12.60 g and 16.30 g)	150 ºC	90 minutes	100 mL DMSO, 10 mL toluene	Under nitrogen with Dean-Stark trap; Worked up in sodium bicarbonate, dried with methanol and ether	52%	40%
1:1.1 melamine to PAH ratio (2.52 g and 3.25 g)	100 ºC	90 minutes	10 mL DMSO	Worked up in sodium bicarbonate, dried with methanol and ether	59%	64%

Table A3: Melamine-Succinic Anhydride (SAH) Reaction Conditions

Melamine to SAH Ratio	Temperature	Reaction Time	Solvent(s)	Workup and Alternate Reaction Conditions	Percent Yield	Purity Estimate
1:1.1 melamine to SAH ratio (2.52 g and 2.20 g)	100 ºC	1 hour	20 mL DMSO	Worked up in sodium bicarbonate ice bath	0%	n/a
1:3 melamine to SAH ratio (2.52 g and 6.00 g)	115 ºC	5 hours	12 mL DMF	Worked up in ice water bath and sodium bicarbonate, recrystallized twice in water	4%	29%
1:3 melamine to SAH ratio (2.52 g and 6.00 g)	115 ºC	24 hours	12 mL DMF	Worked up in ice water and sodium bicarbonate, dried with methanol	37%	100%
1:3 melamine to SAH ratio (2.52 g and 6.00 g)	140 ºC	5 hours	12 mL DMA	Worked up in ice water and sodium bicarbonate, dried with methanol	26%	58%
1:3 melamine to SAH ratio (2.52 g and 6.00 g)	120 ºC	5 hours	12 mL DMF	Reacted under nitrogen; Worked up in ice water and sodium bicarbonate, dried with methanol and ether	23%	65%
1:3 melamine to SAH ratio (2.52 g and 6.00 g)	120 ºC	24 hours	12 mL DMF	Cooled in freezer, worked up in ice water and sodium bicarbonate, dried with methanol and ether	53%	50%
1:3 melamine to SAH ratio (2.52 g and 6.00 g)	145 ºC	2 hours	No solvent	Worked up in water and sodium bicarbonate	96%	0%

Table A4: Polymerization Reaction Conditions

Derivative to Reactant Ratio	Temperature	Reaction Time	Solvent(s)	Workup and Alternate Reaction Conditions	Percent Yield
1:1 mel-SAH to adipoyl chloride ratio (1.04 g and 0.74 mL)	100 ºC	24 hours	15 mL NMP, 1.4 mL Et_3N	Worked up in water, suspended in acetone	24%
1:1 mel-SAH to adipic acid ratio (0.62 g and 0.44 mL)	130 ºC	5 hours	16 mL NMP, 4 mL pyridine, 1.57 mL $(PhO)_3$	Reacted with 1 g LiCl; Worked up in methanol	0%
1:1 mel-SAH to sebacoyl chloride ratio (1.04 g and 1 mL)	100 ºC	24 hours	15 mL NMP, 1.4 mL Et_3N	Reacted under N_2; Worked up in water, suspended in sodium bicarbonate	30%
1:1 mel-SAH to sebacoyl chloride ratio (0.63 g and 1 mL)	100 ºC	24 hours	15 mL NMP, 1.4 mL Et_3N	Worked up in sodium bicarbonate	56%
1:1 mel-SAH to sebacoyl chloride ratio (0.42 g and 0.5 mL)	170 ºC	5 minutes	0.9 mL Et_3N, 7 mL NMP	Reacted at 60 W in microwave reactor; Worked up in ice water and sodium bicarbonate, dried with methanol and ether	20%
1:1 mel-SAH to sebacoyl chloride ratio (0.5 g and 0.6 mL)	25 ºC	24 hours	22 mL NMP, 0.7 mL pyridine	No precipitate appeared, no workup used	0%
1:1 mel-SAH to sebacoyl chloride ratio (0.17 g and 0.2 mL)	200 ºC	8 minutes	7 mL NMP, 0.2 mL pyridine	Reacted at 80 W in microwave reactor; Worked up in water and sodium bicarbonate	0%