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Novel flame retardant polyarylethers: synthesis and testing

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Abstract

Three new polyarylethers **A–C** based on bisphenol C and its derivatives have been synthesized and tested. These new polymers all show a glass transition temperature and are inherently flame resistant and do not require the use of any flame retardant synergist. The new polyarylethers can all be made in 2–3 steps from available raw materials, keeping cost to a minimum. The thermal and flame retardant properties, such as DSC and UL-94 rating, are examined.

Keywords: Polyarylethers; Polymer synthesis; Flammability

1. Introduction

The development of flame retardant polymers has been an important area of research over the last 40 years. The drive for new materials can be attributed to the aerospace industry and government regulations for fire safety [1,2]. The use of flame retardant additives for making commercial polymers flame resistant consumes 909,000 tons/yr of additives [3]. While increasing the flame resistance of the polymers, these additives are known to compromise the polymer's physical and mechanical characteristics, such as decreasing the strength and stress modulus. The impetus of the polymer industry is the design of a low-cost flame retardant polymer that does not require additives yet still has favorable physical and mechanical properties. New flame resistant engineering plastics that have been commercialized are used in specialty applications, for example, polyarylsulfone and polyetheretherketone (PEEK). These polymers work as heat/flame resistant polymers, but due to high cost of production and poor processibility, their commercial use has been limited. There are several research polymers that have focused on the use of non-halogenated functionalities to impart flame resistance, but these polymers are still under investigation [4]. Furthermore, a polymer system is sought that does not burn even when it is exposed to a constant flame source. Currently there is no such polymer available.

The compound that we have explored as a backbone for the flame retardant polymers is commonly called bisphenol C (BPC) or 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene. It is derived from an acid-catalyzed condensation of chloral hydrate and phenol, followed by a dehydrohalogenation reaction to yield BPC [5]. As has been shown by many research groups, BPC can be used as a blendable additive in a commercial plastic or as part of a polymer back bone to effectively impart flame resistance to certain polymeric materials [5–12]. When thermally decomposed, BPC exothermically produces volatile products such as HCl and CO_2 [11–13]. It is these pyrolysis by-products and the high char-forming nature of BPC that cause flame resistance in these polymers and blends.

The thrust of our research has been to incorporate the BPC moiety into a polymer backbone that can impart flame retardancy without additives. Two different methods have been used for the polymerizations: (a) phase transfer catalysis (PTC) through an interfacial nucleophilic displacement mechanism [14], and (b) acyclic diene metathesis (ADMET) polymerization which involves the formation of two metallocyclobutane intermediates in the presence of a catalytic amount of ruthenium; the intermediates dissociate from the metal to yield a newly metathesized double bond and an ethylene by-product [15,16]. The attractiveness of the ADMET polymerization is that, unlike a condensation

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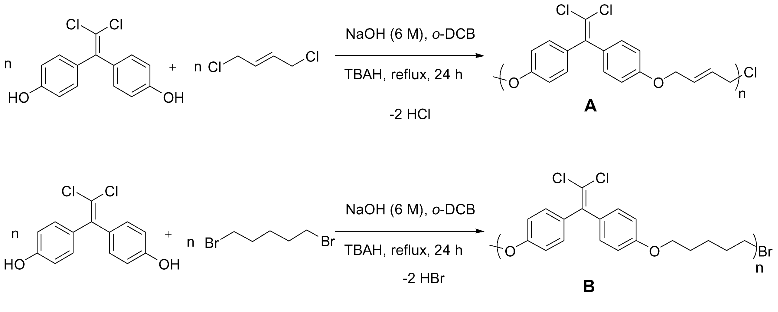


Scheme 1. Synthesis of Polyarylether **A** and **B**, PTC conditions.

polymerization, the stoichiometry of the monomers is not as crucial for obtaining high molecular weight polymer.

To determine the properties of the newly synthesized compound, two methods were used as a test for flame retardancy. The first testing method was the Underwriters Laboratories test for flammability of plastic materials (UL-94). The second method, developed within the last few years, was pyrolysis-combustion flow calorimeter (PCFC) [17–19]. Evaluation of the polymers' chemical and physical properties was done using standard thermal analysis techniques such as differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis.

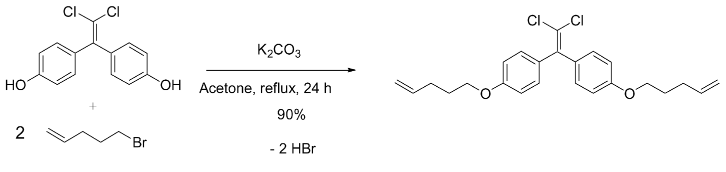
2. Experimental

2.1. Synthesis

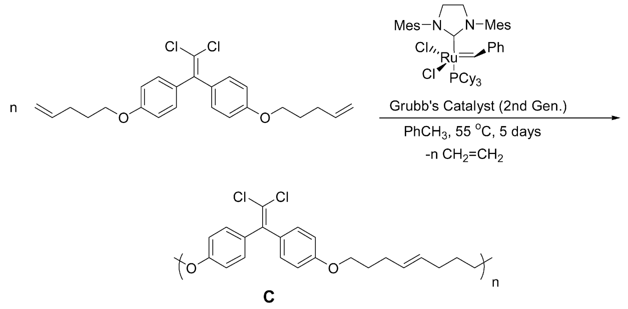
Two of the polyarylethers **A** and **B** were synthesized using BPC and as a co-monomer with either *trans*-1,4-dichloro-2-butene (DCB) or 1,5-dibromopentane (DBP) in a phase transfer-catalyzed (PTC) interfacial polycondensation [14]. It is important to note that the order of addition of the reagents was critical to produce optimal products. To a resin kettle equipped with a mechanical stirrer and a reflux condensor was added BPC, sodium hydroxide solution (6 M), tetrabutlyammonium hydrogen sulfate (TBAH) (5 mol% as the PTC), *o*-dichlorobenzene (*o*-DCB), and finally DCB or DBP. The reaction was vigorously stirred and heated at reflux for 1 day. The reaction was then cooled and separated into two layers and diluted with a suitable organic solvent (toluene or ethyl acetate). The organic layer was washed with a dilute acidic aqueous solution (HCl, 0.1 M) and with water (× 2). The organic layer was then poured into MeOH to precipitate the polymer. The precipitated polymer was then filtered and dried in a vacuum oven at 60 °C for 16 h. (Scheme 1) Polyether **A**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, $J = 8.5$ Hz, 4H), 6.85 (d, $J = 8.5$ Hz, 4H), 6.06 (s, 2H), 4.55 (s, 4H). Polyether **B**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, $J = 8.8$ Hz, 4H), 6.83 (d, $J = 8.7$ Hz, 4H), 3.96 (t, $J = 6.4$ Hz), 1.84 (m, 4H), 1.65 (m, 2H).

The ADMET monomer was prepared by an alkali condensation of BPC and 5-bromo-1-pentene. To a round bottom flask equipped with a stir bar and reflux condensor were added BPC and potassium carbonate (dried in an oven, 5 equiv.). Acetone and 5-bromo-1-pentene (2.7 equiv.) were added via syringe. The reaction was heated at reflux with vigorous stirring for 24 h. The reaction was then diluted with ethyl acetate, followed by a water workup. The organic layer was dried over magnesium sulfate, filtered, and the solvent was removed via rotary evaporation. The white powder was dried in a vacuum desiccator over P_2O_5 for 12 h. The final product was purified by several recrystallizations from MeOH to afford white needles in 92% yield, and stored in a dry box (Scheme 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dt, $J = 8.9$, 2.5 Hz, 4H), 6.83 (dt, $J = 8.9$, 2.5 Hz, 4H), 5.85 (ddt, $J = 17.0$, 10.3, 6.7 Hz, 2H), 5.06 (dtd, $J = 17.1$, 1.7, 1.7 Hz, 2H), 4.99 (dtd, $J = 10.2$, 1.6, 1.6 Hz, 2H), 3.96 (t, $J = 6.4$ Hz, 4H), 2.23 (q, $J = 7.3$ Hz, 4H), 1.87 (quin, $J = 6.9$ Hz, 4H).

The above monomer was polymerized in a typical ADMET procedure using 1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)-(tricyclohexylphosphine)ruthenium (Grubbs Catalyst, 2nd Generation). A dry Schlenk flask, mechanical stirrer, and reflux condensor was assembled in a drybox. To the reaction set up was added the monomer and catalyst (1–2 mol%). The reaction hardware was sealed with a glass stopcock, removed from the dry box, set up in the hood, and then placed under vacuum overnight. Toluene was added via syringe and the reaction was heated to 55 °C for 5 days using a positive pressure of argon exiting through a mineral oil bubbler to facilitate the removal of ethylene. Opening the



Scheme 2. Synthesis of the monomer for the subsequent ADMET polymerization.



Scheme 3. ADMET polymerization of Polyarlyether **C**.

flask to air quenched the reaction. The mixture was then diluted with enough toluene to dissolve the solid. Pouring the reaction mixture into a large excess of MeOH precipitated the polymer. The collected solids were dried in a vacuum oven at 60 °C for 16 h (Scheme 3). Polyarylether **C**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (m), 6.82 (m), 5.84 (m), 5.50 (m), 5.03 (m), 3.95 (m), 2.50 (m), 2.22 (m), 1.83 (m).

2.2. Characterization

The TG analysis was done on a TA Instruments TGA Q50, under a nitrogen atmosphere heating from 22 to 1000 °C at 10 °C/min. The sample sizes ranged from 10 to 20 mg, with a sample purge pressure of 20 and 40 psi for the balance purge pressure. The TG was calibrated using the Curie point temperature of a pure sample of nickel, adjusted to the theoretical value (Fig. 1). The DSC measurements were taken on a TA Instruments DSC Q10, under a nitrogen atmosphere heating from 30 to 450 °C at 10 °C/min. Two successive heating cycles were programmed into the analysis of each DSC sample. To drive off solvent and/or water, the first cycle was from 30 to 200 °C (10 °C/min). The sample was cooled, followed by a second heating cycle from 30 to 450 °C (10 °C/min). These cycles are differentiated in Figs. 2–4 with the broken and solid lines, respectively. The nitrogen pressure was set at 20 psi and sample sizes ranged from 5 to 10 mg. The DSC was calibrated using an internal baseline adjustment procedure; the temperature calibration was done using a pure sample of indium with the result adjusted to the theoretical value.

The molecular weights of the polymers were analyzed on a Waters GPC 150 C and/or a Polymer Laboratory GPC 220, using THF (40 °C, 1 ml/min) as the elutent. The GPC samples were analyzed using both refractive index and UV absorption detection. The synthesized polymers were compared with polystyrene standards of known molecular weights of 1 000 000, 900 000, 435 500, 96 000, 30 300, 22 000, 5050, 1250, and 580.

The flame resistance of the new polymers was tested using the horizontal and vertical Underwriters Laboratory test for flammablility of plastic materials (HVUL-94). Two 1/8 inch thick × 1/2 inch wide × 3 inches long plastic (polymer + anti-drip additive) rectangular bars were used for this test. All flame tests were done in an Atlas Electric HVUL-94 flame test station. The methane tank pressure regulator was set to 20 psi. The pressure regulator on the HVUL-94 test station was set to 4.5 psi. The Bunsen burner flame height was 125 mm, and the height from the top of the Bunsen burner to the bottom of the test bar was 70 mm. The flame was blue with an intense blue inner cone at a flow rate of 90 cc/min. All test bars underwent two trials; each trial consisting of ignition for 10 s, followed by flame removal and a recording of the time for the bar to be considered self-extinguished.

PCFC is a new method used to characterize the potential flame retardancy of a polymeric material [17–19]. It gives three important data points that are used to evaluate the materials performance:

(a) Heat release capacity: a calculated variable derived from the polymeric structure. This is a true material property that is dependent upon thermodynamic state variables, and independent of sample size and heating rate.
(b) Total heat release: a measured value that is derived from the controlled pyrolysis of the polymer in an inert gas (to avoid oxidizing the char). The fuel gas is then mixed with oxygen at elevated temperatures (900 °C) and the heat of combustion is measured [19].
(c) Char yields, which are important because char does not burn and it helps to add an insulating layer between the flame front and the polymeric fuel. It has been shown by Filipczak and Lyon that PCFC data obtained from this method correlates well to other pyrolysis methods such as Cone Calorimetry, the UL-94 test for flamability of plastic materials, and oxygen bomb calorimetry [18].

PCFC measurements were taken using 0.1–0.2 mg of the polymer sample at an interface temperature just below the onset of decomposition. The samples were pyrolyzed to a temperature of 930 °C at 4.3 °C/s in a nitrogen atmosphere. The polymer was then completely combusted at 900 °C. The sample results are an average of five measurements (Table 1) [19].

Table 1
PCFC results for Polyarylether **A**–**C**, and other commercial polymers

Polymer	HR capacity (J/g K)	Total Heat (kJ/g)	Char yields (%)[a]
Polyarylether **A**	37	8	58
Polyarylether **B**	205	13	37
Polyarylether **C**	146	18	20
Polyethylene	1676	42	0
Polystyrene	927	39	0

[a] PCFC results.

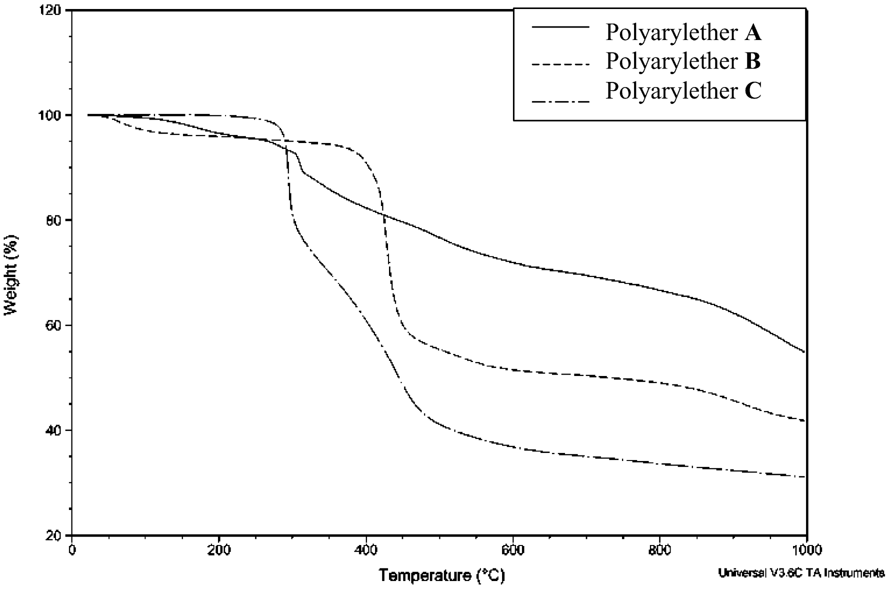


Fig. 1. TG analysis results from Polarylether **A**–**C**.

3. Results and discussion

3.1. Thermal analysis characteristics

Most aliphatic or olefinic polymers have no flame resistant properties. However, we have found that some BPC polymers are indeed flame retardant but have poor processibility due to their rigid structure. The incorporation of the aliphatic (pentane) and olefinic (butene, octene) functionalities in the present work has yielded polymers having glass transition temperatures (T_gs) and flame resistance with little to no additives being required (1 wt% PTFE was used as an anti-drip additive).

Polyarylether **A** was the first to be synthesized using PTC conditions. It is the most thermally stable of the three polymers. Comparisons of the TG analysis and PCFC data from the three polyarylethers show that **A** gives the highest char yields (58%) followed by **B**, and **C**. (Table 1). The thermal stability of the polymers is reduced with the incorporation of more aliphatic/olefinic groups, resulting in the lower char yields. This is apparent when one compares heat release capacity and char yields of polyarylether **A** and **C**. The PCFC total heat release data correlates well with the TG char yields. Polyarylether **C** has a lower heat release capacity than polyarylether **B**, but also has a lower char yield. The thermal stability of these polymers can be attributed to the bisphenol C structure. The increased thermal resistance may also be due, in part, to the olefin

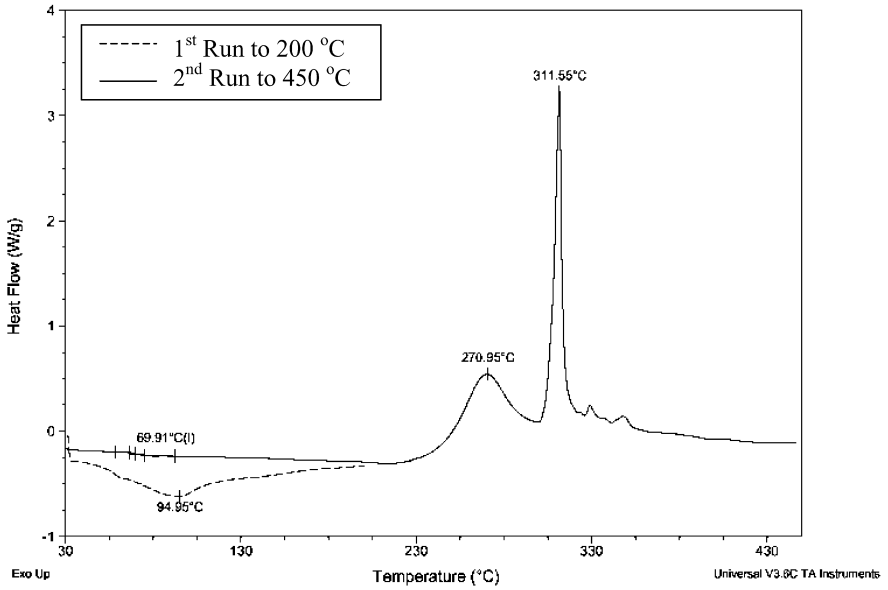


Fig. 2. DSC result for Polyarylether **A**.

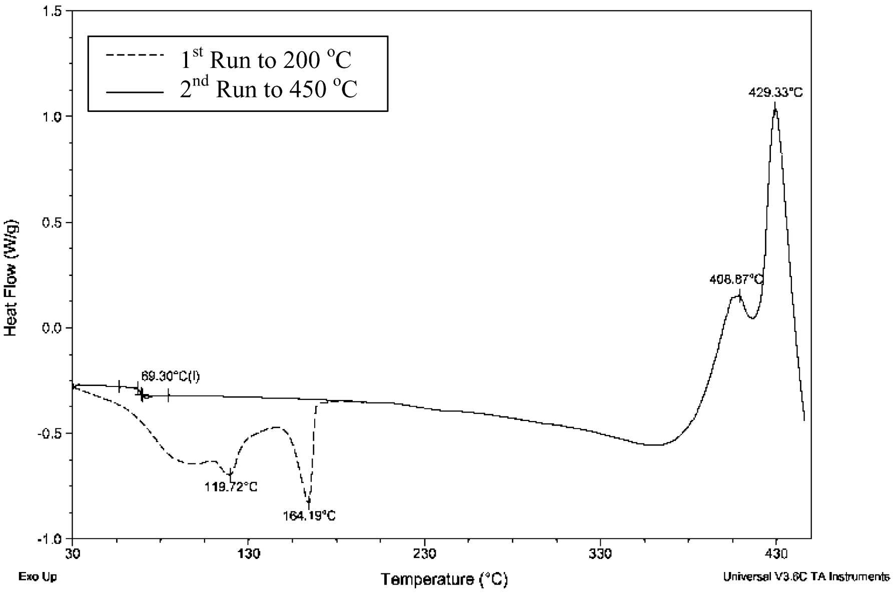


Fig. 3. DSC results for Polyarylether **B**.

functionality in polyarylethers **A** and **C**. Wagener has observed high thermal stability in vinyl ether polymers from ADMET polymerization [16]. Our data analysis supports this conclusion; while char yields are low for polyarylether **C**, the heat release capacity is also low. The initial loss of mass in polymers **A** and **B**, which is not observed in polymer **C**, may be a result of water or solvent loss; the most important result is the overall weight loss of the material. (Fig. 1).

The DSC analysis for polyarylether **A** indicates that this material is an amorphous polymer with $T_g = 70$ °C. This polymer forms an amorphous glass after the first heating cycle. Several batches were made, with an average molecular weight of $M_w = 14\,700$; $M_n = 4500$. One batch had a higher molecular weights of $M_w = 27\,000$ and $M_n = 6800$. Polyarylether **A** exhibited two distinct exothermic peaks in the DSC. The first peak occurred at 270 °C and we assume this was due to the crosslinking of the olefins, which would help increase char formation. The second peak was 311 °C, and is attributed to the exothermic decomposition products of BPC polymers (Fig. 2) [11–13].

Polyarylether **B** is also an amorphous polymer with a T_g at 69 °C. This polymer had a molecular weight of $M_w = 23\,000$ and $M_n = 7700$. This polymer also forms an amorphous glass after the first heating cycle and shows the characteristic BPC exothermic decomposition peak at 429 °C with a shoulder at 409 °C. (Fig. 3).

Polarylether **C** is an amorphous polymer with a T_g of 42 °C and forms an amorphous glass after the first heating

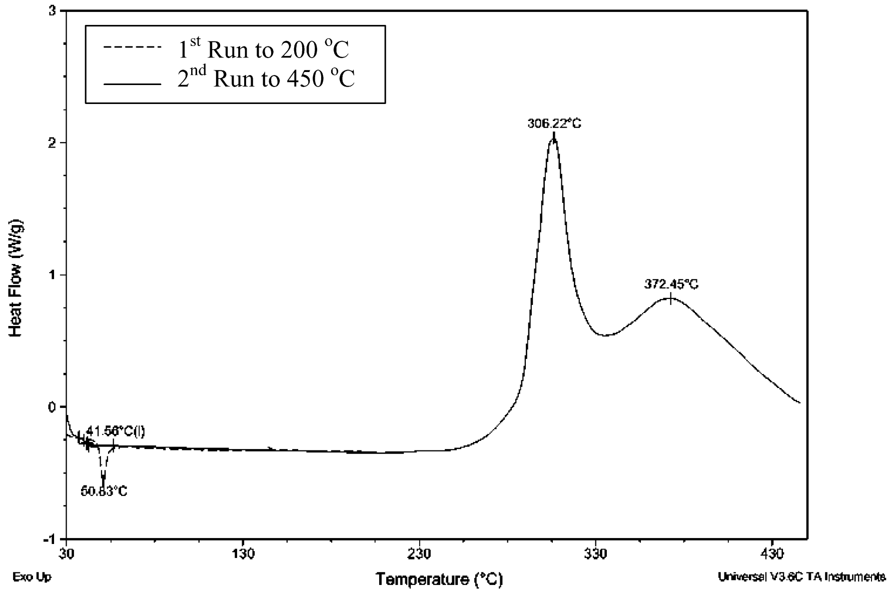


Fig. 4. DSC results for Polyarylether **C**.

Table 2
UL-94 Results for Polyarylether **A**–**C**

Polymer	First ignition[a]	Observed dripping[b]	Second ignition[a]	Observed dripping[b]	UL-94 rating
Polyarylether **A**	3, 0	No, no	0, 0	No, no	V-0
Polyarylether **B**	1, 6	No, no	3, 0	No, no	V-0
Polyarylether **C**	6, 0	No, no	0, 2	No, no	V-0

All samples were blended with 1 wt% PTFE (polytetrafluoroethylene, as an anti-drip additive).

[a] Time to self-extinguishing in seconds after the first and second 10 s ignition in two sample runs.

[b] Indicates that molten plastic did (Yes) or did not (No) drip on to a cotton patch suspended below the ignited bar during the UL-94 test.

cycle. The molecular weight of the polymer was measured at $M_w = 16\,250$ and $M_n = 7800$. This polymer also has two distinct exothermic peaks that can be seen in the DSC. The first peak at 306 °C has been attributed to olefinic crosslinking. A distinctive BPC decomposition peak was observed at 372 °C (Fig. 4). As with the other polymers made in this paper, several batches were made with higher T_gs (85 °C) and molecular weights ($M_w = 19\,000$ and $M_n = 8500$).

3.2. Flammability of the polymers

The flammability of these polyarylethers was measured using the standard UL-94 test for plastic flammability. All three samples obtained a V-0 rating when two sample bars were exposed to two, 10-second flame ignitions. All sample were mixed with 1 wt% PTFE as an anti-drip additive. It is important to note that the samples were also tested without anti-drip additive. They did not burn but dripped excessively, making characterization impossible. It is for this reason that an anti-drip additive was used. The polymer samples all gave good results without the need for a synergist such as antimony oxide to impart flame retardancy. It was observed that when these polymers were subjected to prolonged exposure to the Bunsen burner flame, the fire never consumed the samples. The UL-94 sample results can be seen Table 2.

4. Conclusions

Three new polymers have been made that are inherently flame retardant without the need for a synergist, even after prolonged exposure to a flame. These polymers can be made in 2–3 steps from common raw materials. The flame retardant polymers **A**–**C** represent one part in a larger process to make airline travel safer. The aircraft industry, led by the FAA, has established goals for the development of a flame retardant plastic that is both economical and structurally sound.

Acknowledgements

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