Polymer Degradation and Stability 107 (2014) 53–63

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Decomposition and combustion studies of phosphine oxide containing aromatic polyethers

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ARTICLE INFO

Article history:
Received 26 November 2013
Received in revised form
16 April 2014
Accepted 4 May 2014
Available online 17 May 2014

Keywords:
Combustion
Decomposition
Mechanical properties
Poly(arylene ether)
Phosphine oxide

ABSTRACT

A comparative study of the decomposition and combustion behavior of systematically varied linear polyether analogs is reported. Properties of aromatic polyethers of bisphenol A/or 4,4′-dihydroxy biphenyl with bis(4-fluorophenyl) derivatives with phosphorus, $-CF_3$ and methoxy $-OCH_3$ constituents were systematically evaluated. All polyethers were synthesized by nucleophilic aromatic polycondensation. The polymers obtained covered a wide range of weight average molar masses (40,000–125,000 g/mol) as determined by size exclusion chromatography with multi-angle light scattering detection. FTIR and NMR spectroscopy revealed formation of the desired polymer structure of the linear polyarylene ethers. All polymers were easily soluble in common organic solvents, thus enabling processing from solution. Film casting from dichloromethane solution yielded transparent, free standing films with high mechanical stability (tensile strengths up to 63 MPa, E-moduli up to 2.5 GPa and elongations at break up to 35%). The thermal decomposition under nitrogen was accessed by thermogravimetry (TGA) and TGA combined with infrared spectroscopy, while the combustion was examined by pyrolysis combustion flow calorimetry (PCFC). The fire behavior was examined for one polymer (P3) by limiting oxygen index that revealed that the phosphine oxide moieties have a measurable influence on flame retardancy compared to the PSU control.

1. Introduction

Poly(arylene ether)s belong to the class of high performance polymers due to physical properties such as high mechanical strength, toughness, high thermal, thermo-oxidative stability and chemical resistance [1–4]. In most cases, they are synthesized by nucleophilic aromatic substitution reaction of an activated dihalide with an aromatic diphenol [5,6].

Among the large number of aromatic poly(arylene ethers), those containing phenylphosphine oxide (PhPO) groups have been an important area of research. McGrath et al. reported the synthesis and flame retardant properties of arylene ether-phenyl phosphine oxide-containing polymers [7–10]. According to them the presence of phosphorus in the char after such high temperature heating implied that these materials should also be resistant to aggressive oxygen plasma environments.

McGrath [11,12] and Carbasso [13] further studied the synthesis of linear poly(arylene ether phosphine oxide)s via metal catalyzed coupling reaction and also studied metal complexation of phosphorous containing polymers. Polymers containing PhPO units exhibited excellent adhesion properties to metal substrates. They are usually amorphous and showed a very high refractive index due to the non-coplanar structure of the triarylphosphine oxide units and the highly polar P]O bonds. Connell et al. reported the high resistance of polymers with PhPO groups against atomic oxygen [14,15].

Significant research has been done to develop poly(arylene ether)s with high glass transition temperature and thermal stability. Because of their low water absorption and low dielectric constant fluorine containing poly(arylene ether)s are of special interest. The presence of trifluoromethyl groups increases the fractional free volume that improves the gas permeability and chemical resistance without sacrificing thermal and thermo-oxidative stability [16–20], thus making them interesting for membrane based applications.

Braun et al. [21] and Hoffmann et al. [22] have further studied the fire behavior of PSUs and blends containing phosphorus-PSUs

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http://dx.doi.org/10.1016/j.polymdegradstab.2014.05.002
0141-3910/

with different phosphorus environment. The influence of the chemical structure, charring and phosphorus release was discussed based on the mass loss, kinetics and products [21]. They have also studied the phosphorus polyesters with systematically altered phosphorus environment. They have incorporated monomer with phosphorus containing substituents into aromatic-aliphatic polyesters to develop flame retardant as additive for poly(butylene terephthalate) [22].

Previously, we have reported a series of linear poly(arylene ether phosphine oxide)s (PAEPOs) containing trifluoromethyl groups [23,24]. In pyrolysis combustion flow calorimetry (PCFC) and thermal analysis, indications were found that these polymers will behave flame retardant properties. This observation matches the expectation and experience for halogen-containing flame retardant polymers.

In the present investigation, we report about a comparative study of a series of PAEPOs, some of them newly synthesized and some in relation to the previous reports [23,24]. The synthetic strategy led to a series of PAEPOs allowing for the first time a direct comparison of the effect of phosphine oxide, trifluoromethyl- and methylether groups. The basic goal was to synthesize highly efficient flame retardant PAEPOs without halogen substituents. The thermal decomposition and combustion behavior and the burning behavior of selected samples were extensively studied. Based on the characterization results, decomposition mechanisms were derived in order to select a proper structure suitable to improve the physical and flame retardant properties of high performance polymers.

2. Experimental section

2.1. Materials

4-Methoxyphenylphosphonic dichloride and phenylphosphonic dichloride were purchased from TCI Europe (Germany) and were used as received. 5-Bromo-2-fluorobenzofluoride was purchased from Fluorochem (UK). 1-Bromo-4-fluorobenzene was purchased from Aldrich (Germany) and used as received. The bisphenols, 4, 4′-isopropylidenediphenol (BPA) and 4,4′-dihydroxy biphenyl (DHB) were purchased from Aldrich (Germany) and were also used as received. Potassium carbonate (K_2CO_3, Aldrich, Germany) was dried before use. The solvent dichloromethane (DCM, Acros, Germany) was also used as received. N-Methyl-2-pyrrolidone (NMP, Merck, Germany) was stored over NaOH and distilled from phosphorus pentachloride (P_2O_5) before use. Dry toluene (Aldrich, Germany) was used as received. Magnesium turning was purchased from Merck, Germany, and was used as received. Tetrahydrofuran (Merck, Germany) was distilled from sodium metal before use.

2.2. Synthesis procedures

2.2.1. Synthesis of the monomer bis(4-fluorophenyl) phenylphosphine oxide

The procedure that we followed in the previous work [10,23,24] was applied for synthesizing the monomer bis(4-fluorophenyl) phenylphosphine oxide (chemical structure see Fig. 1). In a 250-mL three-necked round-bottom flask equipped with a condenser, nitrogen inlet, and stir bar a solution of 4-bromo fluorobenzene (19.45 g, 110 mmol) in THF was added slowly to magnesium turnings (3.7 g, 152 mmol). The reaction was initiated by addition of a trace of iodine. The resulting mixture was stirred at 25 °C for 4–5 h, until consumption of almost all magnesium turnings. After complete addition of the bromide the resulting brown solution was heated to reflux for 2.5 h. After that the reaction mixture was cooled to 0 °C with an ice bath. Subsequently, a solution of 10.0 g (50 mmol) of phenylphosphonic acid dichloride in 35 mL of THF was added over a period of 30 min. The reaction mixture was allowed to warm to room temperature and kept for overnight under stirring. Finally, the excess Grignard reagent was quenched with 50 mL saturated ammonium chloride solution. The organic material was extracted into ether; washed with water, 5% NaOH, and water; followed by drying over magnesium sulfate. The solvents were removed via rotary evaporation followed by vacuum.

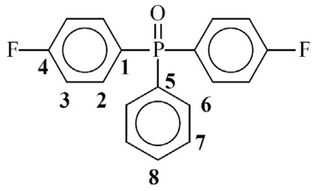

Fig. 1. Chemical structure and ^{1}H NMR assignments of bis(4-fluorophenyl) phenylphosphine oxide with assignment of NMR signals.

An amber colored, highly viscous oily liquid was obtained which was purified by column chromatography using dichloromethane/methanol as eluent. The separated fractions were dried to yield 10.8 g (67.03%) of a white solid.

Yield: 10.8 g (67.03%). Melting point: 124 °C.

Elemental analysis: Calcd. for $C_{18}H_{13}$ F_2OP (314.27 g/mol): C: 68.79%; H: 4.17%; found: C: 68.29%; H: 4.10%. FTIR (KBr) $\bar{\upsilon}$: 3025, 1611, 1498, 1325, 1055, 875, 845, 645 cm^{-1}.

^{1}H NMR ($CDCl_3$) δ: 7.66 (4H, m, H-2), 7.64 (2H, m, H-6), 7.57 (1H, m, H-8), 7.48 (2H, m, H-7), 7.16 (4H, m, H-3) ppm.

^{13}C NMR ($CDCl_3$) δ:165.08 (d, C-4), 134.46 (dd, C-2), 132.17 (d, C-8), 132.09 (d, C-5), 131.84 (d, C-6), 128.61 (d, C-7), 128.35 (dd, C-1), 115.93 (dd, C-3) ppm.

^{19}F NMR ($CDCl_3$) δ: -107.40 (s) ppm.

^{31}P NMR ($CDCl_3$) δ: 28.19 (s) ppm.

2.2.2. Synthesis of bis(4-fluoro-3-trifluoromethyl phenyl) phenylphosphine oxide

The monomer (see Fig. 2) was synthesized according to the early stated procedure [23,24]. Here in place of 4-bromo fluorobenzene, 5-bromo-2-fluorobenzotrifluoride (27.01 g, 110 mmol) was being used for 10 g of phenylphosphonic acid dichloride. A slightly yellowish colored, highly viscous oily liquid was obtained which was purified by column chromatography using dichloromethane/methanol as eluent. After drying the fractions, 13.5 g (73.09%) of a pale yellow solid was obtained.

Yield: 13.5 g (73.09%). Melting point: 92 °C.

Elemental analysis: Calcd. for $C_{20}H_{11}$ F_8OP (450.26 g/mol): C: 53.35%; H: 2.46%; Found: C: 53.85%; H: 2.73%.

NMR and FTIR spectroscopy: Observed data matched data reported in Ref. [24].

2.2.3. Synthesis of the monomer bis(4–fluoro-3-trifluoromethyl phenyl)-4′-methoxyphenyl phosphine oxide

The monomer (see Fig. 3) was prepared according to [14]. 5-Bromo-2-fluoro benzotrifluoride (23.4 g, 100 mmol) was being

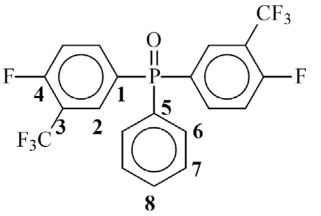

Fig. 2. Chemical structure and ^{1}H NMR assignments of bis(4-fluoro-3-trifluoromethyl phenyl) phenylphosphine oxide.