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Flame retardant polymeric materials achieved by incorporation of styrene monomers containing both nitrogen and phosphorus

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ABSTRACT

Organophosphorus compounds have a long history as effective flame retardants for polymeric materials. There is increasing interest in developing new phosphorus flame retardants as a consequence of the increasing worldwide regulatory pressure on the use of organohalogen flame retardants which are persistant in the environment, tend to bioaccumulate, and pose potential health risks for the human population. It has been widely suggested that the flame retardant activity of phosphorus compounds may be enhanced by the presence of nitrogen, sulfur, silicon and a few other elements. This has been tested by examining the flamability behavior of copolymers derived from styrene monomers containing phosphorus moieties in comparison to those containing similar monomers in which both phosphorus and nitrogen are present.

1. Introduction

Poly(styrene) is a commodity plastic encountered in daily life since it is used in numerous applications from computer housings to components for cars and airplanes, to toys and many household appliances and building insulation (expanded polystyrene foam).

As with many other polymers, poly(styrene) suffers from high flamability and lack of charrability which limits its use for many applications. Flame-retardant additives such as halogenated aromatics or organic and inorganic phosphorus compounds are commonly used to impart fire retardance to styrenic polymers. However, additive systems have the disadvantages of promoting undesirable changes in physical and mechanical properties of the polymer and of poor durability in long term use. Moreover, halogenated flame retardants have come under scrutiny because of perceived environmental and toxicological issues and there are movements to discontinue the use of halogen containing flame retardants [1,2].

One of the most promising alternatives to halogenated flame retardants seems to be organophosphorus compounds that can be chemically attached directly to the polymer chain. Several reports on the effect of the incorporation of phosphorus-containing styrenic comonomer units on the flame retardance of poly(styrene) have revealed significant increases in limiting oxygen index (LOI) together with increases in char yields on combustion of the polymers [3–8]. However, although some copolymers showed good flame retardant performance, no commercially valuable systems has come yet from this research [1]. It was noticed that in order to obtain UL-94 V-0 rating with commercial phosphorus FRs for styrenic plastics including ABS and HIPS, the additional incorporation of halogen-based phosphorus derivatives (e.g. aliphatic chlororethyl phosphonate), or a charring agent along with phosphorus FRs is inevitable [9].

Another very promising lead to flame-retard styrenics is the use of nitrogen–phosphorus compounds which are known to evolve little toxic gases or vapors as well as low levels of smoke during combustion and to be more convenient from a recyclability standpoint [9,10]. Among this type of compounds, the phosphoramidates are particularly promising since they showed a great potential as FRs for various polymeric systems, can be easily manufactured from relatively inexpensive raw materials with high yields, are less volatile as compared to analogous phosphates, have good thermal stability and exhibit enhanced char formation during the burning process [11,12]. The development of newer phosphoramidate compounds became even more important due to possible phosphorus–nitrogen synergism phenomena.

Encouraged by the recent findings, a series of four phosphoramidate-based styrene monomers was synthesized and fully characterized. Each monomer was homopolymerized in solution to

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provide a series of four new styrenic homopolymers. The thermal properties and fire behavior of this series were compared with an analog series of phosphorus-based styrenic homopolymers lacking the nitrogen atom.

2. Experimental

2.1. Materials

Diethylphosphite (98%), diphenyl phosphite (~85%), 4-*tert*-butylcatechol (TBC) and sodium hydride (NaH) as 60% dispersion in mineral oil were purchased from the Aldrich Chemical Company and dimethyl phosphite (98%) from Alfa-Aesar, and used as received. 4-(Chloromethyl)styrene (min. 90%), 4-aminostyrene and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) were supplied by TCI America and used as received. Styrene (≥99%, Sigma Aldrich) was passed through a column of basic alumina prior to use, in order to remove polymerization inhibitors. 2,2′-Azobis(isobutyronitrile) (AIBN) (Sigma Aldrich), which was used as a radical initiator, was recrystallized from methanol. All solvents and other common reagents were obtained from usual laboratory suppliers and were purified prior to use by standard methods.

In general, reactions were carried out in a dry three-necked, round-bottomed flask fitted with a Liebeg condenser bearing a gas-inlet tube, a magnetic stirring bar, and a pressure-equalizing dropping funnel. All glassware were flame-dried and allowed to cool under a stream of dry nitrogen prior to use. Chromatography was accomplished using ultrapure synthetic silica gel SilaFlash P60 (230–400 mesh silica) in a column of appropriate size, and combinations of hexane and ethyl acetate as eluents. Silica-coated (fluorescence UV_{254}) Whatman plates (Whatman Ltd.) were used for thin layer chromatography (TLC).

2.2. Monomer synthesis

The phosphorus- and phopshorus and nitrogen-containing monomers synthesized are: dimethyl-(4-vinylbenzyl)phosphonate (M_1), diethyl-(4-vinylbenzyl)phosphonate (M_2), diphenyl-(4-vinylbenzyl)phosphonate (M_3), 4-[(6-Oxido-6H-dibenz[c, e] [1,2] oxa-phosphorin-6-yl)]methyl styrene (M_4), phosphoramidic acid *N*-(4-vinyl-phenyl)-dimethylester (M_5), phosphoramidic acid *N*-(4-vinyl-phenyl)-diethylester (M_6), phosphoramidic acid *N*-(4-vinyl-phenyl)-diphenylester (M_7) and 4-[(6-Oxido-6H-dibenz[c, e] [1,2] oxaphosphorin-6-yl)]amino styrene (Fig. 1). The details of the monomer synthesis are given below (Fig. 2).

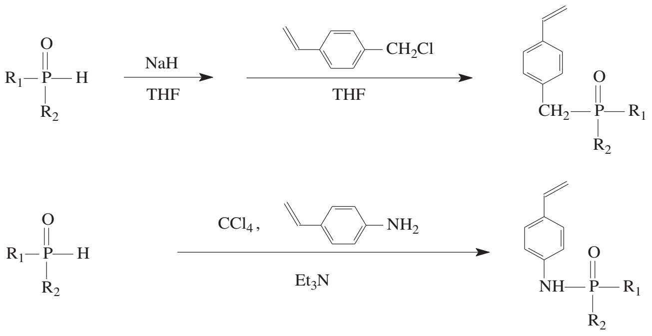

Fig. 2. Synthesis of styrene monomers containing flame-retarding moieties.

2.2.1. Dimethyl-(4-vinylbenzyl)phosphonate (M_1) [13,14]

Sodium hydride (0.55 g, 0.024 mmol) as a suspension in 60% mineral oil was added to 20 mL dry THF and the suspension was stirred at room temperature, under nitrogen for 0.5 h. A solution of dimethyl phosphite (2.6 g, 0.024 mol) and 10 mL THF was added slowly and the mixture was allowed to cool at 0–5 °C and stirred for 0.5 h 4-(Chloromethyl)styrene (3 g, 0.02 mol) and TBC (100 mg, 0.6 mmol) in 25 mL of THF were added dropwise. The reaction mixture was stirred at ambient temperature for 2 h and then at the solvent reflux for 12 h. The salt which formed during the reaction was removed by filtration. The solvent was removed from the filtrate by rotary evaporation at reduced pressure. The residual material was dissolved in 100 mL of methylene chloride. The solution was washed, successively, with two 100-mL portions of distilled water and 100 mL of saturated aqueous sodium chloride solution. The solution was dried over anhydrous magnesium sulfate and the solvent was removed by rotary evaporation at reduced pressure. The residue was purified by flash chromatography (eluant: ethyl acetate/hexane 50/50, v/v). The pure product was obtained as a pale yellow oil (4.02 g, yield 90.13%):**IR** (thin film, cm^{-1}) 3003 (w, Ar–H), 2909 (m, CH_2), 1630 (m, vinyl), 1515 ($C{=}C_{aromatic}$), 1410 (m, P–C), 1250, vs (P=O), 1030 (vs, P–O–C); ^{1}**H NMR** (300 MHz, $CDCl_3$, δ) 2.75 (d, 2H, $J_{PH} = 21.7$ Hz, $C\underline{H}_2$–P); 3.1 (d, 6H, $J_{PH} = 10.89$ Hz, $C\underline{H}_3$–O); 5.09 (d, 1H, $J_{HH} = 10.8$ Hz, $CH{=}C\underline{H}_2$); 5.42(d, 1H, $J_{HH} = 17.6$ Hz, $CH{=}C\underline{H}_2$); 6.61–6.71 (dd, 1H, *cis* $J_{HH} = 10.8$ Hz, *trans* $J = 17.6$ Hz, $C\underline{H}{=}CH_2$); 6.95–7.33 (m, $4\underline{H}_{aromatic}$); ^{13}**C NMR** (75.46 MHz, $CDCl_3$, δ) 33.5 (d, $J_{PC} = 127.8$ Hz, $C\underline{H}_2$–P), 53.3 (d, $J_{PC} = 6.8$ Hz, $C\underline{H}_3$–O); 113.6 (1C, $CH{=}\underline{C}H_2$), 130.04, 131.10 (d, $J = 9.8$ Hz, $\underline{C}H{=}CH_2$), 126.15, 126.25 (d, $J_{PC} = 3.45$ Hz, $1\underline{C}_{aromatic}$), 130.5, 136.3 (2C aromatic); ^{31}**P NMR** (121.48 MHz, $CDCl_3$, δ) + 34.5; **GC–MS**: calcd. for $C_{11}H_{15}O_3P$: 226, found: 226.

$R_1 = R_2 = OCH_3$ Dimethyl-(4-vinylbenzyl)phosphonate (**M_1**)

$R_1 = R_2 = OC_2H_5$ Diethyl-(4-vinylbenzyl)phosphonate (**M_2**)

$R_1 = R_2 = OC_6H_5$ Diphenyl-(4-vinylbenzyl)phosphonate (**M_3**)

R_1, R_2 = DOPO 4-[(6-Oxido-6H-dibenz[c, e][1, 2]oxa-phosphorin-6-yl)]methyl styrene (**M_4**)

$R_1 = R_2 = OCH_3$ Phosphoramidic acid, *N*-(4-vinyl-phenyl)-dimethylester (**M_5**)

$R_1 = R_2 = OC_2H_5$ Phosphoramidic acid, *N*-(4-vinyl-phenyl)-diethylester (**M_6**)

$R_1 = R_2 = OC_6H_5$ Phosphoramidic acid, *N*-(4-vinyl-phenyl)-diethylester (**M_7**)

R_1, R_2 = DOPO 4-[(6-Oxido-6H-dibenz[c, e][1, 2]oxa-phosphorin-6-yl)]amino styrene (**M_8**)

Fig. 1. The monomers synthesized and used in homopolymerization.