

Conclusion

Our work describes the preparation and the dehydrogenative polymerization of new alkylsilanes, substituted 3-phenyl-1-silabutanes, catalyzed by Cp_2MCl_2 ($M=Ti, Hf$)/Red-Al combined system. The polymers with degree of polymerization (DP) of 5 through 16 were obtained. The dehydrogenative polymerization of the monomer silanes with Cp_2TiCl_2 /Red-Al catalyst system occurred at a faster rate and produced higher molecular weights of polysilane than that with Cp_2HfCl_2 /Red-Al catalyst system, opposite trend to the polymerization of phenylsilane with Cp_2MCl_2 /RLi system.

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A Potential Flame-retardant by Intumescence. Melaminium 2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-methoxy-sulfates

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New compounds of melaminium 2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-methoxy-sulfate have been synthesized and characterized by means of chemical analysis, 1H , ^{13}C , and ^{31}P NMR, and IR spectroscopies. When the compounds are subjected to an open flame, they foam without melting to produce a light char with about 50 times volume of the initial compounds. The evaluation of these flame-retardants proves to be efficient for polypropylene. Thermogravimetric analysis discloses that the compounds are also thermally stable for compounding into polypropylene without decomposition.

Introduction

In recent years, the use of some traditional halogenated flame-retardants is limited on account of the possible forma-

tion of extremely toxic halogenated dioxines or dibenzofurans.^{1,2} Among alternative candidates intumescent materials have a considerable attention because they provide fire protection with minimum of overall fire hazard.³ Since the first

intumescent coating material was patented in 1938,⁴ the mechanism of an intumescent flame-retardant refers to the forming of a cohesive foam which acts as an insulating barrier between the fire and substrate.⁵ In particular, such an intumescence depends significantly on the ratio of C, N, and S atoms in a compound.^{3,5} Although intumescent coatings are capable of exhibiting good fire protection for the substrate, they have several disadvantages such as water solubility, brushing problem, and relatively high cost etc.⁶ The fire retardation of plastic materials is generally achieved by incorporating fire-retardant additives into the plastic during processing.⁷⁻⁹ Since the processing requires that the additives withstand up to above 200 °C, the intumescent systems without sufficient thermal stability cannot be incorporated into various plastics. Phosphate-pentaerythritol system was investigated and developed as the intumescent materials.³ For example, a systematic study on a mixture of ammonium polyphosphate and pentaerythritol has shown that intumescence occurs on flaming.^{2,10-12} Thus, new intumescent materials with appropriate thermal stability have been synthesized for better fire-retardance.^{13,14}

In this paper, in an effort to understand the chemistry of intumescent materials, we have synthesized the melamine salt of pentaerythritol containing sulfate group which is useful for flame retardation,¹⁵ and characterized them based on spectroscopic data and thermal properties.

Experimental

Reagents and Instrumentation. Pentaerythritol (Aldrich), phosphoryl chloride (Merck), chlorosulfonic acid (Nakarai), melamine (Junsei) were used as received. Acetonitrile and dioxane were used as solvents after distillation by standard methods. 2,6,7-Trioxa-1-phosphabicyclo[2.2.2]octane-4-methanol was prepared by the literature method.³

Chemical analyses were carried out by the Advanced Analysis Center at KIST. IR spectra were recorded on a MIDAC 101025FT-IR spectrophotometer as KBr pellets. NMR spectra were measured on a Varian Gemini 300 NMR spectrometer operating at 300.00 MHz (¹H), 75.48 MHz (¹³C), and 121.44 MHz (³¹P) in pulse mode with Fourier transform at ambient temperature. The chemical shift were relative to internal Me₄Si (¹H and ¹³C) and external (C₆H₅O)₃PO(³¹P) for the indicated nuclei. Thermogravimetric analyses were achieved by a DuPont TGA 2950 with scan rate of 20 °C/min.

Synthesis of 2,6,7-Trioxa-1-phosphabicyclo[2.2.2]octane-4-methoxy hydrogen sulfate (TPMHS). Chlorosulfonic acid (32.63, 0.28 mole) was added dropwise into 2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-methanol (50.0 g, 0.28 mole) dissolved in 350 mL of acetonitrile. The reaction solution was stirred and refluxed for 6 h. The resultant slurry was cooled to room temperature. The solid product was filtered and washed with cold acetonitrile. The white solid product (mp 100 °C) was obtained in 80% yield. Anal. found (Calcd. for C₈H₉O₈PS): C, 24.80 (24.88); H, 3.39 (3.49). ¹H NMR (DMSO-d₆, ppm): 3.6 (s, 2H); 4.6 (s, 6H); 9.1 (br, 1H). ¹³C NMR (DMSO-d₆, ppm): 37, 62, 76. IR (KBr, cm⁻¹): 1314 (s), 1251 (s), 1011 (s), 862 (s).

Synthesis of Melaminium 2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-methoxy sulfate (1). TPMHS (50.0 g, 0.19 mole) and melamine (24.0 g, 0.19 mole) in 350

mL of acetonitrile were refluxed for 10 h. The slurry was cooled to room temperature. The solid product was filtered and washed with cold acetonitrile. The white solid was thoroughly dried *in vacuo* at 80 °C and yielded quantitatively. Anal. found (Calcd. for C₈H₁₅N₆O₈PS): C, 24.90 (24.88); H, 3.90 (3.91); N, 22.54 (21.76). ¹H NMR (DMSO-d₆, ppm): 3.6 (s, 2H); 4.6 (s, 6H); 7.6 (s, 7H). ¹³C NMR (DMSO-d₆, ppm): 37, 61, 76, 160. ³¹P NMR (DMSO-d₆, ppm): 15. IR (KBr, cm⁻¹): 1726 (s), 1699 (s), 1304 (s), 1013 (s).

Synthesis of Melaminium bis(2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-methoxy hydrogen sulfate) (2) and Melaminium tris(2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-methoxy hydrogen sulfate) (3). TPMHS (50.0 g, 0.19 mole) and melamine (12.0 g, 0.095 mole and 16.7 g, 0.063 mole, respectively) were treated in the same manner as above-mentioned. Anal. found (Calcd. for C₁₃H₂₄N₆O₁₆P₂S₂ (2)): C, 23.90 (24.15); H, 3.72 (3.74); N, 12.70 (13.00). ¹H NMR (DMSO-d₆, ppm): 3.6 (s, 4H); 4.6 (s, 12H); 7.6 (s, 8H). ¹³C NMR (DMSO-d₆, ppm): 37, 61, 76, 160. ³¹P NMR (DMSO-d₆, ppm): 15. IR (KBr, cm⁻¹): 1732 (s), 1682 (s), 1298 (s), 1018 (s).

Anal. found (Calcd. for C₁₈H₃₃N₆O₂₄P₃S₃ (3)): C, 23.70 (23.85); H, 3.63 (3.67); N, 9.12 (9.27). ¹H NMR (DMSO-d₆, ppm): 3.6 (s, 6H); 4.6 (s, 18H); 7.6 (s, 9H). ¹³C NMR (DMSO-d₆, ppm): 37, 61, 76, 160. ³¹P NMR (DMSO-d₆, ppm): 15. IR (KBr, cm⁻¹): 1725 (s), 1676 (s), 1310 (s), 1012 (s).

Flame Retardance Test. The title compounds were incorporated into polypropylene by mixing for 10 min at 190 °C on a Brabender Mixer. The samples for standard LOI test¹⁶ (13.0×62.5×1.6 mm) were prepared by using a pressure operating at 180 °C. The LOI test was accomplished by Suga Test Instrument Model ON-1.

Results and Discussion

Synthesis. The compounds 1, 2, and 3 were smoothly prepared in acetonitrile solvent according to Eqs. (1) and (2). The structures of 1, 2, and 3 were established by chemical analysis, ¹H, ¹³C, and ³¹P NMR, and IR spectroscopic data. In particular, IR and ¹H NMR were useful in identifying the products by disappearance of the OH group in the starting material, TPMHS. The solid products are insoluble or slightly soluble in common organic solvents at room temperature, but moderately soluble in water, which is generally unfavorable for a flame-retardant.

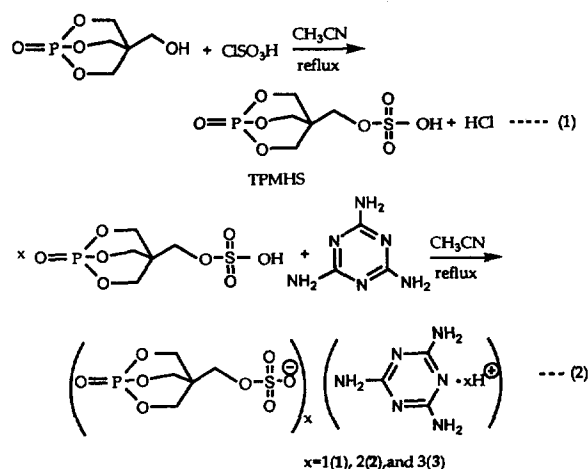
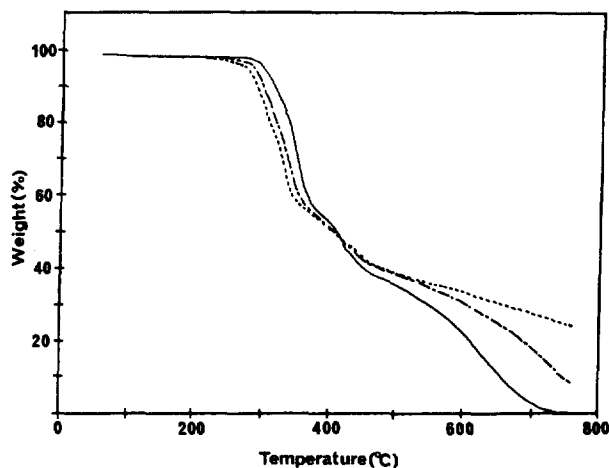


Table 1. LOI^a Test Result against Polypropylene of the Title Compounds

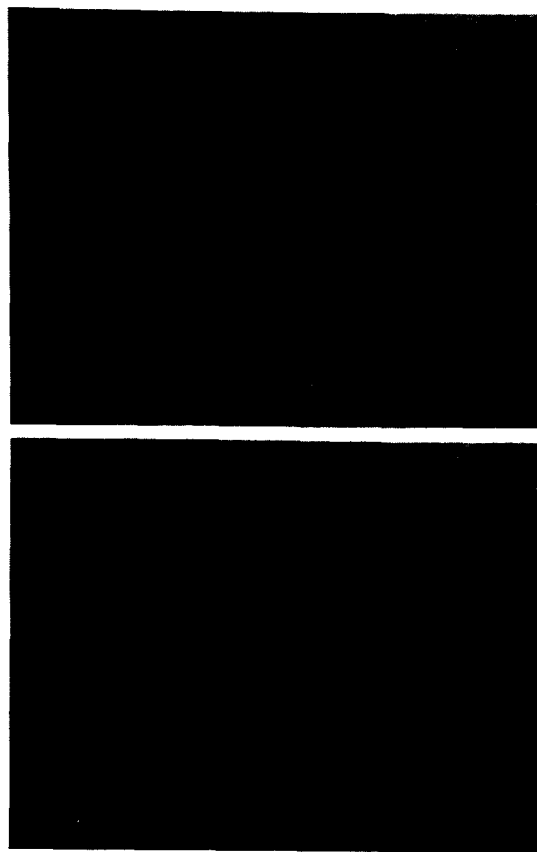
Conc. (%) Compds	25	30	35
1	20.5	21.0	21.0
3	19.5	19.5	20.0
CN-1197 ^b	20.5	22.0	22.0

^aLimiting Oxygen Index: minimum oxygen content needed to support combustion of sample in an upward-flowing mixture of nitrogen and oxygen. ^bAn industrial flame-retardant from Great Lakes (U. S. A).

**Figure 1.** Thermogram curves of 1 (—), 2 (---), and 3 (···) under N₂ with heating rate of 20 °C/min.

Physical Properties. Thermogravimetric analyses (TGA) for the title compounds are depicted in Figure 1. The TGA curves exhibit thermal stability up to about 300 °C, which is suitable for compounding the flame-retardant into plastics. The onset temperature of weight-loss for each compound is approximately 250 °C, and T₁₀ values for 1, 2, and 3 are 326, 304, and 298 °C, respectively. The residual weights of all compounds were decreased to half at about 400 °C, and to 0, 8.5, and 24.1% at 770 °C for compounds 1, 2, and 3, respectively. The most interesting feature in the TGA curves is the T₁₀ values and the residual weights as 770 °C. The mass loss for the compounds directly depends on the number of TPMHS group in the present compounds.

When the compounds are subjected to an open flame, they foam without melting to produce a light char with about 50 times volume of the initial compounds. Figure 2 shows compound 1 before and after exposure to flame. The insulative properties of this char is illustrated by the fact that, while the surface of the material was foaming and charring in the flame, the inside bulk remained as a white free-blowing powder. A prominent difference in char-volume change among compounds 1, 2, and 3 was not observed. The title compounds are less intumescent than *b*-MAP^{3,17} but the char after intumescence for the present compounds is harder than that for *b*-MAP. Such a difference seems to stem from the presence of sulfate in the present compounds in contrast

**Figure 2.** Top: Compound 1 before exposure to flame. Bottom: Compound 1 after exposure to flame.

to *b*-MAP composed of only phosphate.

Flame Retardation. The preliminary evaluation of the present compounds 1 and 3 for polypropylene proved to be efficient intumescent fire-retardant additives. The compounds are tested and compared with commercial compound CN-1197¹⁸ (Great Lakes, U. S. A.). Compound 1 is slightly more effective than 3. A prominent trend by the contents (25, 30, and 35%) of the intumescent materials was not observed. However, the flame-retardant effect of the present compounds is comparable to that of commercialized CN-1197. Further evaluation for other plastics is underway.

Conclusion. The present compounds foam efficiently on exposing to open fire, and are thermally stable for compounding into polypropylene. The presence of additional sulfates in the compounds causes them to be less intumescent and harder char-forming than the commercialized CN-1197, and no remarkable improvement was observed in flame retardance. It may be concluded that the kind of atom and the ratio of the atoms be the key in the development of molecule that exhibits desirable intumescent flame-retardant.

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 18. Commercialized from Great Lakes, U. S. A.: 2,6,7-Trioxa-1-phosphabicyclo[2.2.2]octane-4-methanol.