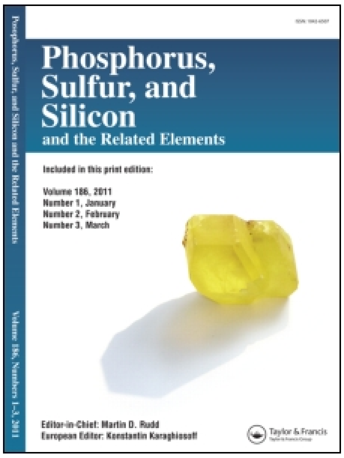

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Pentaerythritol Phosphate Derivatives as Flame Retardants for Polyolefins

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A building block of our experimental char-forming flame retardants is pentaerythritol phosphate alcohol or PEPA. We present examples of the synthesis of several PEPA derivatives, notably bis-PEPA carbonate (BPC) and bis-PEPA PEPA-phosphonate (BP3). The syntheses are complicated by steric hindrance to reaction, and the choice of solvent and reaction conditions is important. All compounds can be formulated to give UL 94 V-0 flame retardant properties in polypropylene.

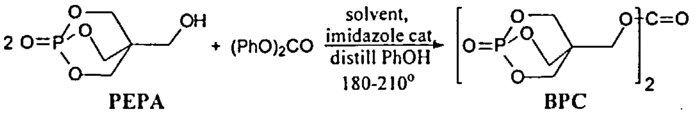
Keywords: flame retardant; pentaerythritol; phosphates; phosphonates

INTRODUCTION

Pentaerythritol has long been known as a char-former in flame retardant (FR) compositions. Its cheapness is offset by its undesirably high water solubility. To satisfy market needs for new polyolefin FR's, we wanted water-insoluble, thermally stable, nonhalogenated char-formers. We made some new pentaerythritol derivatives, high in phosphorus, to allow formulation of intumescent FR's for polypropylene.

SYNTHESIS

The raw material for our experimental compounds is pentaerythritol phosphate alcohol or PEPA (2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-methanol-1-oxide), made by reaction of pentaerythritol with $POCl_3$.[1] We made several derivatives of PEPA, such as bis-PEPA carbonate or BPC,[2] the H-phosphonate BPHP,[3] the methylphosphonate BPMP[4] and something we call bis-PEPA PEPA-phosphonate or BP3.[5] All of these were made by transesterification of PEPA with an appropriate ester. An example of reaction conditions is shown for BPC (Equation 1).



(1)

We needed a very high-boiling, nonreactive, moderately polar solvent from which we could distill phenol without contamination. We chose an isopropylated triphenyl phosphate with the trade name Phosflex® 41P.[6] PEPA, a hindered neopentyl-like primary alcohol, requires rather high temperatures for transesterification and is moderately soluble in hot 41P.

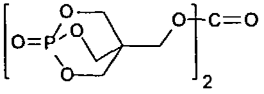
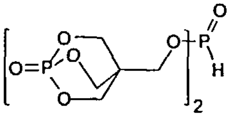
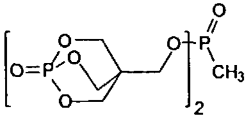
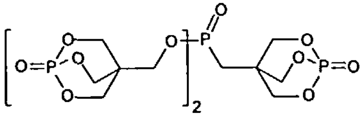
Experimental

A typical synthesis of our PEPA derivatives used a 250 mL 4-necked flask fitted with mechanical stirrer, pot thermometer and distilling head. The flask was charged with about 0.3 mole of PEPA, about 100-125 mL of Phosflex® 41P solvent, about 2 mole % (vs. PEPA) of a catalyst and one equivalent of a phenyl ester. Alkyl esters were not sufficiently reactive to exchange with PEPA under practical reaction conditions.

Heating the reaction mixtures at 10-50 mm pressure at 160-180° caused phenol to distill as it formed. To make **BP3**, further heating at 220°/16 hr was needed to complete an Arbuzov reaction of the intermediate tris-PEPA phosphite. The insoluble reaction products could be filtered from the cooled reaction mixtures and washed with a more volatile nonsolvent, such as acetonitrile, before drying. The highly polar products have no melting point; they decompose at temperatures ~300°. All are insoluble in water and most solvents except **BPHP**, which is quite water soluble and deliquescent.

The reagents and conditions for these transesterifications are summarized in Table 1. The sodium used in these reactions forms sodium phenoxide, the actual catalyst. Imidazole catalyst gave somewhat purer **BPC** than sodium, but comparable reaction rates required about twice as much imidazole (~4 mole %).

TABLE 1 PEPA derivatives from transesterification

Catalyst, Temp.	Ester	Product (% Yield)	^{31}P NMR (ppm, d$_6$-DMSO)
Na or imidazole, 180-210°	diphenyl carbonate	 Bis-PEPA Carbonate, BPC (94)	-6.5
Na or $MgCl_2$, 180°	diphenyl phosphite	 Bis-PEPA H-phosphonate, BPHP (53)	+11.0 -6.4
Na, 180-200°	diphenyl methylphos-phonate	 Bis-PEPA Methylphosphonate, BPMP (<30)	+34.2 -6.3
Na, 180° then up to 210°	triphenyl phosphite	 Bis-PEPA PEPA-phosphonate, BP3 (92)	+28.8 -7.2 -6.2

FLAME RETARDANCY

Because of high char yields, these new compounds show promise as the char-forming component of intumescent FR's for thermoplastics. The high thermal stability allows compounding into polypropylene (PP), for example, at high processing temperatures (up to ~275° for some highly filled cases).

An interesting discovery during this work was the synergy of our synthesis solvent Phosflex® 41P with the components of the FR composite.[7] Addition of this liquid phosphate (or other similar ones) had several benefits to the polypropylene formulation:

1) Char increased.
2) Less of the PEPA-derivative was needed to achieve V-0 FR performance.
3) Dispersion of the additives improved.
4) Compounding and extrusion were easier.

Preblended formulations were compounded in a 60 mL Brabender Bowl Mixer at ~164° for 5 minutes at 50-75 RPM. Compression molding for 3-5 min. in a 200° hydraulic press gave a 1/16" plaque, from which test specimens were cut. Standard UL 94 testing protocol provided the flammability results. Examples of PP composites incorporating the PEPA derivatives are shown in Table 2.

TABLE 2 PEPA-derivative flame-retardant formulations in polypropylene

Material (amounts in parts by weight)	**BPC**	**BPHP**	**BPMP**	**BP3**
PP-6323, Himont polypropylene	69.8	69.1	68.7	69.8
Experimental PEPA-derivative	7.5	10.9	12.0	7.5
Melamine phosphate, Akzo Fyrol® MP	18.0	18.0	19.8	18.0
THEIC*, BASF Corp.	2.0	2.0	-	2.0
Phosflex® 41P, Akzo Nobel	2.5	-	-	2.5
Calcium stearate	0.2	-	-	0.2
UL 94 at 1/16"	V-0	V-0	V-0	V-0

* THEIC is tris(2-hydroxyethyl)isocyanurate, a char-enhancing additive

CONCLUSION

Carbonate and phosphonate ester derivatives of pentaerythritol phosphate alcohol are promising components of intumescent flame retardants for polypropylene. The higher synthetic yields for **BPC** and **BP3** make them especially attractive candidates.

Acknowledgements

I thank Paul Moy and Gerry Alessio for polymer compounding and flame retardant testing.

References

[1] Y. Halpern and R. H. Niswander, US 4,454,064 (1984).

[2] J. E. Telschow and E. D. Weil, US 5,235,085 (1993).

[3] J. E. Telschow, US 5,420,326 (1995).

[4] J. E. Telschow, US 5,486,639 (1996).

[5] J. E. Telschow, US 5,536,862 (1996).

[6] Phosflex® 41P is available from Akzo Nobel Chemicals Inc. See J. E. Telschow and E. D. Weil, US 5,237,085 (1993) for other examples of its use as a solvent for making phosphorus heterocycles from pentaerythritol.

[7] P. Y. Moy, J. E. Telschow, and G. R. Alessio, WO 97/41173 (1997).