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Thermal stability of phosphinated diethyl tartrate

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Abstract Organohalogen flame retardants, particularly brominated aromatics, are popular, effective, low cost, and widely used in the plastics industry. However, an increasing concern about persistence in the environment and potential negative health effects of these materials has generated intense interest in the development of alternatives. Ideally, these should have all the positive attributes of the materials that will be replaced. In addition, it is desirable that the new materials be as "green" as possible, e.g., based on renewable resources and be degradable to nontoxic products in the environment. A series of new, non-halogenated flame retardants based on tartaric acid is being developed. Tartaric acid is a by-product of the wine industry and is readily available locally on an annual basis (Michigan is the thirteenth largest producer of wine in the U.S.). It can be readily converted to the corresponding diethyl ester. This ester may serve as the base for the development of a series of new, non-halogenated flame-retarding agents. The presence of the reactive hydroxyl groups allows the introduction of a variety of phosphorus-containing moieties. For example, treatment of diethyl tartrate with diphenylphosphinyl chloride generates diethyl 2,3-di(diphenylphosphinato)-1,4-butanedioate. This material may serve as a monomer for the preparation of various phosphorus-containing polymers and oligomers via step-growth transesterification. The thermal stability of this compound has been assessed by thermogravimetry.

Keywords Green flame retardants · Bio-based polymer additives · Renewables · Degradation of phosphorus esters

Introduction

The high standard of living enjoyed by the citizens of developed nations of the world would not be possible without the development of polymeric materials which has occurred since WWII. For most applications, these materials must be flame retarded [1, 2]. Most commonly, flame retardants are introduced as additives during processing. A wide range of materials have been used as flame retardants but two classes, organohalogen and organophosphorus compounds, have been most prominent [3–8]. Organohalogen compounds, primarily bromoaromatics, decompose as the polymer substrate undergoes combustion to liberate halogen atoms and hydrogen halide to the gas phase where they effectively scavenge flame-propagating radicals, principally hydrogen atoms and hydroxyl radicals. The most widely used organohalogen flame retardant is decabromodiphenyl ether. It is readily available in good purity, relatively inexpensive, and effective. However, the increasing concern, particularly in Europe, about bioaccumulation of organohalogen compounds in the environment and potential associated health risks has provided motivation to seek alternatives [9–14]. The most likely alternatives are organophosphorus compounds. In general, these materials are significantly more expensive than their organohalogen counterparts and likely will not completely supplant organohalogens, particularly in the United States, until regulation demands it. Most organophosphorus compounds are solid-phase active. They promote char formation at the surface of the burning polymer which prevents

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heat feedback from the flame and pyrolytic decomposition of the polymer to generate volatile fuel fragments to feed the flame. These materials are most effective in oxygen-containing polymers. For flame-retarding polymers lacking oxygen in the structure, an oxygen rich promoter (pentaerythritol, dipentaerythritol, etc.) may be used in conjunction with the organophosphorus compound. It is thought that during combustion, phosphoric acid is generated which promotes crosslinking of the polymer and char formation. Recently, some remarkably effective gas-phase active organophosphorus flame retardants have been developed to replace tetrabromobisphenol A in the production of epoxy resins. Much of this is based on the incorporation of 9,10-dihydro-9-oxa-10-phosphaphenathrene 10-oxide (DOPO) into either the epoxy component or the hardener [15–21]. During polymer pyrolysis, these compounds extrude PO radical to the gas phase where it may function as an efficient scavenger of flame-propagating radicals. As a consequence, adequate flame retardance can be achieved at very low loading of these materials in the polymer matrix.

Tartaric acid, 2,3-dihydroxybutanedioic acid, is a principal by-product of the conversion of grape stock to wine by fermentation [22, 23]. This compound has a storied history. Crystals of a salt, potassium ammonium tartrate, were the object of the first resolution (by manual means) of a racemic mixture by Pasteur. This demonstrated the existence of enantiomeric compounds. Pasteur's interest in the formation of this compound led to the demonstration that the presence of yeast or bacteria is required for fermentation, i.e., that enzymes are required for the conversion of carbohydrates, primarily glucose and other simple monosaccharides, to ethanol. He also was able to demonstrate that spoilage due to bacterial contamination could be avoided by heating the medium to 52–60 °C for a short time, a process now known as pasteurization and which has been immensely useful for preservation by the food industry.

The United States ranks fourth behind Italy, France, and Spain in wine production accounting for about 10% of the total. Wine is widely produced in the United States but large-volume production is localized in a few regions [24, 25]. Michigan ranks fourth among the US states in acreage devoted to grape growing and thirteenth in the production of wine [26]. Vineyards are located in southwest Michigan near Fennville and in the peninsular region near Traverse City. All are located within 25 miles of the Lake Michigan shore. The lake effect provides a favorable microclimate for grape production. The presence of this robust wine industry provides an annual, renewable source of tartaric acid. Tartrates occur naturally in winery pomace, in still slops from brandy distillation, in lees that settle in wine tanks, and in argols that separate as a crystalline coating of nearly pure cream of tartar (potassium bitartrate) on the walls and bottoms of wine storage tanks [27–30]. Cream of tartar also crystallizes in tanks of filtered wine undergoing refrigeration [30].

Tartaric acid may be readily converted to the corresponding diethyl ester [31, 32]. This compound represents a useful starting point for the synthesis of "green" flame-retardant materials based on a plentiful, inexpensive, and renewable by-product of the thriving Michigan wine industry.

Experimental

General

In general, reactions were carried out in a dry (all glassware was dried in a oven overnight at 120 °C and allowed to cool under a stream of dry nitrogen prior to use) three-necked, round-bottomed flask fitted with Liebig condenser bearing a gas-inlet tube, a magnetic stirring bar (or Trubore stirrer), and a pressure-equalizing dropping funnel (or syringe port). Chromatography was accomplished using SilaFlash P60 (230–400 mesh silica; Silicycle) in a column of appropriate size and hexane/ethyl acetate as eluant. Silica-coated Mylar plates (ThermoFisher Scientific) were used for thin layer chromatography (TLC). Melting points were determined by differential scanning calorimetry (DSC) using TA Instruments 2910 MDSC. All samples were analyzed at a heating rate of 5 °C min^{-1} in a constant nitrogen purge of 50 $\mathrm{cm}^3\ \mathrm{min}^{-1}$. Thermal decomposition temperatures were obtained using a TA Instruments 2950 Hi-Res TGA instrument interfaced with the Thermal Analyst 2100 control unit. Most generally, a heating rate of 5 °C min^{-1} was used. TA Thermal Advantage software was used for data analysis. Samples (5–10 mg) were contained in a platinum pan. The sample compartment was purged with dry nitrogen at 50 $\mathrm{cm}^3\ \mathrm{min}^{-1}$ during analysis. Nuclear magnetic resonance (NMR) spectra were obtained using a 10 to 25% solution in deuterochloroform or dimethyl sulfoxide-d_6 and a Varian Mercury 300 MHz spectrometer. Proton and carbon chemical shifts are reported in parts-per-million (δ) with respect to tetramethylsilane (TMS) as internal reference ($\delta = 0.00$). Phosphorus chemical shifts are in δ with respect to 85% aqueous phosphoric acid solution as external reference ($\delta = 0.00$). Infrared (IR) spectra were obtained using thin films between sodium chloride plates or solid solutions (1%) in anhydrous potassium bromide (as discs) and a Nicolet MAGNA-IR 560 spectrometer. Absorptions were recorded in wave numbers (cm^{-1}), and absorption intensities were classified in the usual fashion as very weak (vw), weak (w), and medium (m), strong (s), and very strong (vs) relative to the strongest band in the spectrum. Mass spectra were obtained using a Hewlett-Packard 5890A gas chromatograph/mass spectrometer (MSD) with an ionizing potential of 70 electron volts and temperature programmed elution into the spectrometer inlet (90–200 °C).

Materials

Common solvents and reagents were obtained from ThermoFisher Scientific or the Aldrich Chemical Company. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride prior to use; methylene chloride from calcium hydride. Chlorodiphenylphosphine (diphenylphosphinous chloride), 1,4-dihydroxybenzene (hydroquinone) and diethyl tartrate were obtained from the Aldrich Chemical Company and used as received.

Synthesis

Diphenylphosphinic chloride

To a stirred solution of 1.15 cm^3 (1.41 g, 6.40 mmol) of chlorodiphenylphosphine in 10 cm^3 of anhydrous dichloromethane was added, dropwise, over a period of 0.5 h, a solution of 0.65 cm^3 (1.08 g, 8.00 mmol) of thionyl chloride in 5 cm^3 of dichloromethane [33]. The resulting mixture was allowed to stir one hour at room temperature. The solvent and excess thionyl chlorides were removed by rotary evaporation at reduced pressure to afford diphenylphosphinic chloride as slightly yellow oil.

Diethyl 2,3-diphosphinato-1,4-butanedioate

To a stirred solution of 8.7 cm^3 (10.79 g, 45.6 mmol) of diphenylphosphinic chloride in 80 cm^3 of dry benzene was added, dropwise over a period of 0.5 h, a solution of 4.5 cm^3 (5.42 g, 26.3 mmol) of diethyl tartrate and 6.3 cm^3 (4.45 g, 60.9 mmol) of triethylamine in 40 cm^3 of benzene [34]. The resulting mixture was allowed to stir for 36 h at room temperature. The solution was washed, successively, with 50 cm^3 of water and two 50-cm^3 portions of saturated aqueous sodium chloride solution. The solution was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporation at reduced pressure. Recrystallization of the residual material from ethyl acetate afforded diethyl 2,3-diphosphinato-1,4-butanedioate (5.01 g, 31.4% yield) as a white crystalline solid, mp 150 °C (DSC).

1,4-(Diphenylphosphinato)benzene

To a stirred solution of 0.24 g (2.18 mmol) of hydroquinone and 1.2 cm^3 (1.49 g, 6.29 mmol) of diphenylphosphinic chloride in 10 cm^3 of dry THF was added, dropwise over a period of 0.5 h, a solution of 0.87 cm^3 (0.62 g, 8.41 mmol) of triethylamine in 10 cm^3 of dry THF [35]. The resulting mixture was allowed to stir 12 h at room temperature. The solvent was removed by rotary evaporation at reduced pressure to afford a white solid which was dissolved in 50 cm^3 of dichloromethane. The dichloromethane solution was washed, successively, with two 30-cm^3 portions of saturated aqueous sodium bicarbonate solution and two 30-cm^3 portions of saturated aqueous sodium chloride solution. The solution was dried over anhydrous sodium sulfate, and the solvent was removed by rotary evaporation at reduced pressure to provide 1,4-(diphenylphosphinato)benzene (3.38 g, 27.2% yield) as a white solid (Fig. 1).

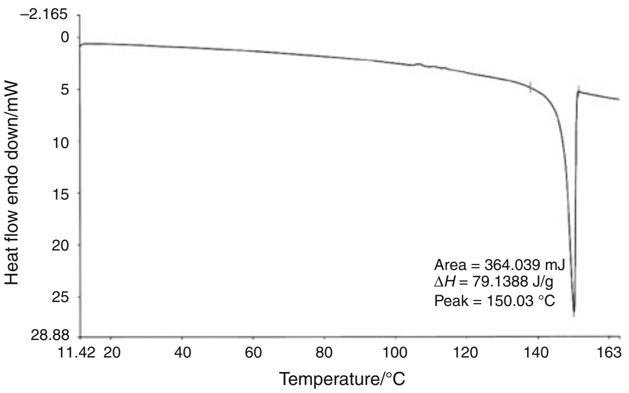
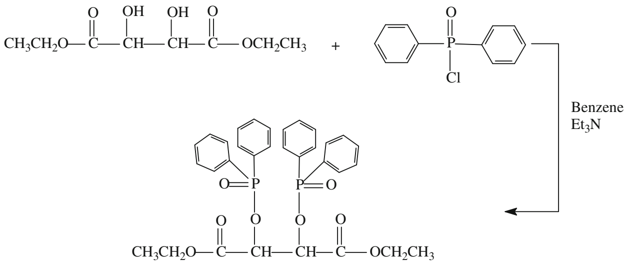


Fig. 1 DSC thermogram for diethyl 2,3-diphosphinato-1,4-butanedioate

Results and discussion

Tartaric acid, a common byproduct of the wine industry, may serve as a base for the development of a new class of “green” flame retardants for polymeric materials. The presence of the two hydroxyl groups in this compound permits the ready incorporation of phosphorus-containing moieties. In this case, this has been accomplished by treating tartaric acid, as the diethyl ester, with diphenylphosphinic chloride (Scheme 1).

The phosphorus ester is a white crystalline solid, mp 150 °C. The proton NMR spectrum of this material is shown in Fig. 2. The stereochemistry of the compound is



Scheme 1 Synthesis of diethyl-2,3-diphosphinato-1,4-butanedioate

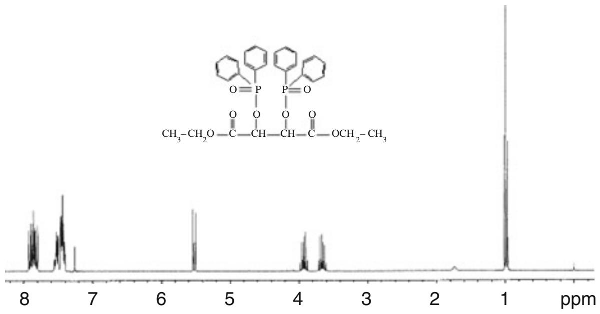


Fig. 2 Proton NMR spectrum of diethyl 2,3-diphosphinato-1,4-butanedioate

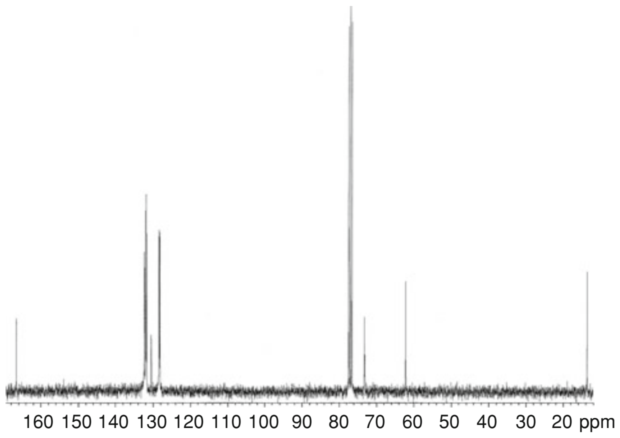


Fig. 3 Carbon-13 NMR spectrum of diethyl 2,3-diphosphinato-1,4-butanedioate

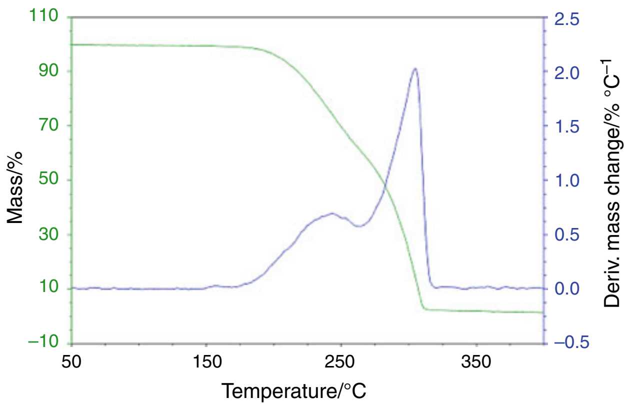
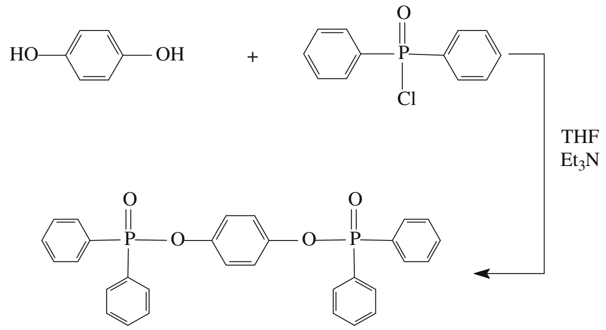


Fig. 4 Thermal decomposition of diethyl 2,3-diphosphinato-1,4-butanedioate

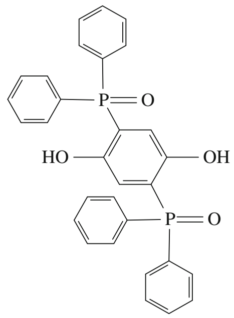


Scheme 2 Synthesis of 1,4-(diphenylphosphinato)benzene

reflected in the two quartets of doublets (coupling to phosphorus) for the methylene protons at δ 3.8. The corresponding carbon-13 spectrum is displayed in Fig. 3.

Absorptions due to the presence of the ethyl group are present at δ 13.6 and 62.2, those for the butane main chain at δ 73.2 and 166.6, and those for the carbon atoms of the phenyl groups attached to phosphorus at δ 128.2, 130.4, 131.8 and 132.2. The thermogram for the decomposition of this compound is displayed in Fig. 4. The decomposition occurs in two steps with an initial onset of decomposition at 185 °C. In the first step, approximately 45% of the initial sample mass is lost. The larger mass loss (48% of the initial mass) occurs somewhat later with approximately 7% residue remaining at 400 °C. The initial decomposition probably reflects loss of the phosphinato groups as the corresponding acid. This decomposition profile suggests that this material will degrade with the liberation of acid at the combustion temperature of many polymers.

This should promote char formation at the surface of the polymer such that heat feedback from the flame, and consequent polymer pyrolysis to generate fuel fragments, will be strongly inhibited. The nature of this compound can be readily manipulated by varying the carboxyl ester functionality. In addition, it may be converted to high phosphorus content oligomers by condensation with 2,5-(diphenylphosphonato)-1,4-dihydroxybenzene (structure shown below).



This compound may be obtained by treatment of 1,4-(diphenylphosphinato)benzene with strong base. The synthesis of this precursor compound is outlined below in Scheme 2. It has been isolated and thoroughly characterized spectroscopically.

The infrared spectrum of this compound is shown in Fig. 5.

The spectrum contains aromatic C–H absorption at 3058 cm^{-1}, absorption for an aromatic nucleus at 1598 cm^{-1},

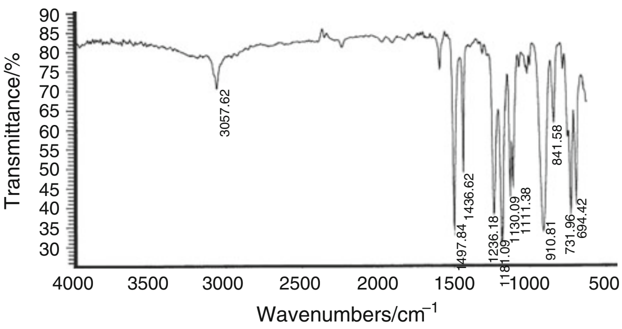


Fig. 5 Infrared spectrum of 1,4-(diphenylphosphinato)benzene

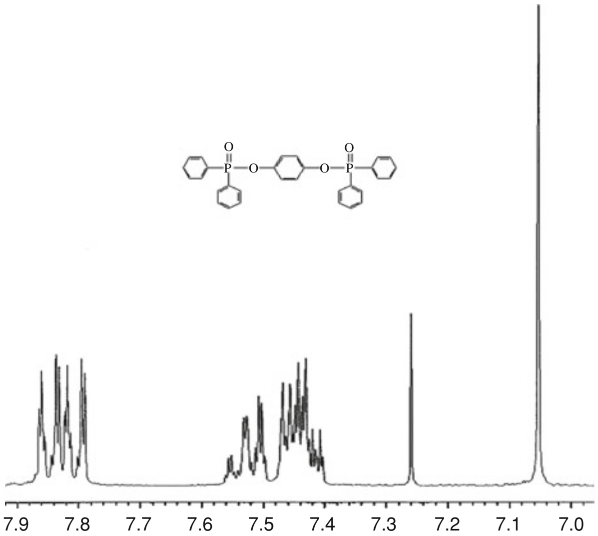


Fig. 6 Proton NMR spectrum of 1,4-(diphenylphosphinato)benzene

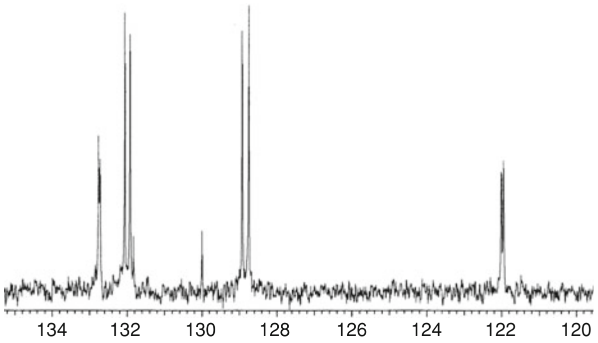


Fig. 7 Carbon-13 NMR spectrum of 1,4-(diphenylphosphinato)benzene

P=O absorption at 1236 cm^{-1} and P–O–C (aromatic) absorption at 1081 and 911 cm^{-1} [36, 37]. The proton NMR spectrum of this compound is displayed in Fig. 6 and the corresponding carbon-13 spectrum in Fig. 7.

It should be noted that all the absorptions in the carbon spectrum appear as doublets due to coupling to phosphorus.

Conclusions

Diethyl 2,3-diphenylphosphinato-1,4-butanedioate may be readily obtained from tartaric acid, an abundant by product of the wine industry. This compound undergoes thermal decomposition, most likely to liberate diphenylphosphinic acid to promote char formation, at the combustion temperature of several common polymers. It may also serve as one component of high-phosphorus content oligomers with flame-retarding properties. Therefore, it may serve as a base for the development of a family of bio-based, environmentally friendly flame retardants for polymeric materials.

References

1. Troitzsch J. Plastics flammability handbook: principles, regulations, testing and approval. 3rd ed. Cincinnati: Hanser Gardner Publications; 2004.
2. Georlette P, Simons J, Costa L. Halogen-containing fire-retardant compounds. In: Grand AF, Wilkie CW, editors. Fire retardancy of polymeric materials. New York: Marcel Dekker Inc.; 2000. pp. 245–84.
3. Gann RC. Flame retardants: overview. In: Kroschwitz J, Howe-Grant M, editors. Kirk-Othemer encyclopedia of chemical technology, vol. 10. New York: Wiley; 1993. pp. 930–936.
4. Green J. A review of phosphorus-containing flame retardants. J Fire Sci. 1992;10(6):470–87.
5. Weil ED. Phosphorus-based flame retardants. In: Engel RE, editor. Handbook of organophosphorus chemistry. New York: Marcel Dekker; 1992.
6. Weil ED, Levchik SV, Ravey M, Zhu WM. A survey of recent progress in phosphorus-based flame retardants and some mode of action studies. Phosphorus Sulfur Silicon Relat Elem. 1999;144–146:17–20.
7. Lu SY, Hamerton I. Recent developments in the chemistry of halogen-free flame retardant polymers. Prog Polym Sci. 2002;27(8): 1661–712.
8. Davis J. The technology of halogen-free flame retardant additives for polymeric systems. Eng Plast. 1996;9(5):403–19.
9. Law RJ, Allchin CR, de Boer J, Covaci A, Herzke D, Lepom P, Morris S, Tronczynski J, de Wit CA. Levels and trends of brominated flame retardants in the European environment. Chemosphere. 2006;64:187–208.
10. de Wit C, Alace M, Muir D. Levels and trends of brominated flame retardants in the Arctic. Chemosphere. 2006;64:209–33.
11. Pepich BV, Prakash B, Domino MM, Dattilio TA. Development of U.S. EPA method 527 for the analysis of selected pesticides and flame retardants in the UCMR survey. Eviron Sci Technol 2005;39(13):4996–5004 (references cited therein).
12. Birnbaum LS, Staskal DF. Brominated flame retardants: cause for concern? Environ Health Perspect. 2004;112(1):9–17.
13. Alaee M, Wenning RJ. The significance of brominated flame retardants in the environment: current understanding, issues and challenges. Chemosphere. 2002;46:579–82.
14. Wheler EK, Hovander L, Bergmen A. New organohalogens in human plasma. Identification and quantification. Organohalog Compds. 1997;33:420–5.
15. Artner J, Ciesielski M, Walter O, Doring M, Perez RM, Sandler JKW, Altstadt V, Schartel B. A novel DOPO-based diamine as

hardener and flame retardant for epoxy resin systems. Macromol Mater Eng. 2008;293(6):503–14.

16. Ciesielski M, Schafer A, Doring M. Novel efficient DOPO-based flame-retardants for PWB relevant epoxy resins with high glass transition temperatures. Polym Adv Technol. 2008;19(6):507–15.
17. Schartel B, Balabanovich AI, Braun U, Knoll U, Artner J, Ciesielski M, Doring M, Perez RM, Sandler JKW, Altstadt V, Hoffman T, Pospiech D. Pyrolysis of epoxy resins and fire behavior of epoxy resin composites flame-retarded with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide additives. J Appl Polym Sci. 2007;104(4):2260–9.
18. Perez RM, Sandler JKW, Altstadt V, Hoffman T, Pospiech D, Artner J, Ciesielski M, Doring M, Balabanovich AI, Knoll U, Braun U, Schartel B. Novel phosphorus-containing hardeners with tailored chemical structures for epoxy resins: synthesis and cured resin properties. J Appl Polym Sci. 2007;105(5):2744–59.
19. Perez RM, Sandler JKW, Altstadt V, Hoffman T, Pospiech D, Artner J, Ciesielski M, Doring M, Balabanovich AI, Schartel B. Effective halogen-free flame retardancy for a monocomponent polyfunctional epoxy using an oligomeric organophosphorus compound. J Mater Sci. 2006;41(24):8347–51.
20. Perez RM, Sandler JKW, Altstadt V, Hoffman T, Pospiech D, Artner J, Ciesielski M, Doring M, Braun U, Knoll U, Schartel B. Effective halogen-free flame retardants for carbon fiber-reinforced epoxy composites. J Mater Sci. 2006;41(15):4981–4.
21. Perez RM, Sandler JKW, Altstadt V, Hoffman T, Pospiech D, Ciesielski M, Doring M. Effect of DOP-based compounds on fire retardancy, thermal stability, and mechanical properties of DGEBA cured with 4, 4′-DDS. J Mater Sci. 2006;41(2):341–53.
22. Amerine MA, Berg HW, Cruess WV. The technology of wine making. Westport: The Avi Publishing Company Inc.; 1972.
23. Austin C. The science of wine. London: University of London Press Ltd.; 1968.
24. Pinney T. A history of wine in America: from prohibition to the present. Berkeley: University of California Press; 2005.
25. Wine regions of the United States. http://www.wineforeveryone.com/wine_regions_united_states.html. Accessed 11 July 2009.
26. Michigan wine and grape council. http://www.michiganwines.com/page.php?menu=maps. Accessed 11 July 2009.
27. Rivas B, Torrado A, Moldes AB, Dominguez JM. Tartaric acid recovery from distilled lees and use of the residual solid as an economic nutrient for *Lactobacillus*. J Agric Food Chem. 2006;54(20):7904–11.
28. Versari A, Castellari M, Spinabelli U, Galassi S. Recovery of tartaric acid from industrial enological wastes. J Chem Technol Biotechnol. 2001;76(5):485–8.
29. Brown EM, Henriques VD. Vinification in California wineries. Ind Eng Chem. 1935;27:1235–40.
30. Marsh GL, Joslyn MA. Effect of temperature on the precipitation rate of cream of tartar from wine. Ind Eng Chem. 1935;27: 1252–7.
31. Zhou X, Lin W-J, Ye J-L, Huang P-Q. A versatile approach to pyrrolidine azasugars and homoazasugars based on a highly diastereoselective reductive benzyloxymethylation of protected tartarimide. Tetrahedron. 2007;63(7):6346–57.
32. Lemieux RU, Howard J. The O-inside conformation of 1,3:2,4-di-*O*-methylene-L-threitol. Can J Chem. 1963;41:393–8.
33. Baolina TV, Groyvnova IB, Petrovskii PV, Matroscov EI, Groyunova EI, Nifantev EE. One-pot synthesis of *N*-diphenylphosphorylureas. Doklady Chem. 2006;409:129–32.
34. Tyssee DA, Bausher LP, Haake P. Displacement at phosphorus by a mechanism with A1 character. Acid-catalyzed hydrolysis of phosphinanilides. J Am Chem Soc. 1978;95(24):8066–72.
35. Dhawan BD, Redmore D. *o*-Hydroxyaryl diphosphonic acids. J Org Chem. 1984;49(21):4018–21.
36. Annakutty KS, Kishore K. Flame retardant polyphosphate esters. 2. Condensation polymers of bisphenol A with alkyl phosphorodichloridates: synthesis, characterization and thermal studies. Polymer. 1988;29(4):762–4.
37. Liu Y-L, Hsiue G-H, Chiu Y-S, Jeng R-J, Ma C. Synthesis and flame-retardant properties of phosphorus-containing polymers based on poly(4-hydroxystyrene). J Appl Polym Sci. 1996;59(10): 1619–25.