



# Flame retardancy and hydrolysis resistance of waterborne polyurethane bearing organophosphate moieties lateral chain



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## ABSTRACT

A novel halogen-free flame retardant diol bearing pendant organophosphate group, 2-ethyl-2-(2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinanyl-2-methylene)-1,3-propanediol (EPPD), was designed and synthesized, and then covalently conjugated into polyurethane as chain extender to prepare a series of phosphorus-containing flame retardant waterborne polyurethanes (PWPU). The chemical structures of the resultant EPPD and PWPU were confirmed by FTIR, <sup>1</sup>H and <sup>31</sup>P NMR, respectively. Simultaneously, the flammability and thermal behavior of PWPU films were systematically investigated by limiting oxygen index (LOI) test, UL-94 vertical burning experiment and thermogravimetric (TG) as well as residual char analysis. An LOI value of 26.6% and a UL-94 V-0 rating can be achieved when the PWPU sample conjugated with 12 wt% EPPD, showing good inherent flame retardancy. TGA and residual char analysis indicate that the incorporation of EPPD induces a slight decrease of the thermal stability due to the relatively weaker bond energy of O=P–O, whereas the formed phosphoric and polyphosphoric acid during combustion can impart PWPU with nonflammability owing to the promoting of rugged carbonaceous char in the condensed phase which shields the underlying polyurethane from further attacking of heat flux. Meanwhile, hydrolytic stability study demonstrates that PWPU with organophosphate moieties linking in the side-chain exhibits better hydrolysis resistance than that with phosphoester bond conjugated in the backbone.

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## 1. Introduction

Waterborne polyurethane (WPU) is a versatile environmentally friendly polymer, which has gained speedy development and found extensive commercial applications in coatings, leather finishing, textile laminating, adhesives, biomaterials and other consumer products, by virtue of its overall balance features of good low-temperature flexibility, excellent abrasion resistance and toughness, controllable mechanical properties combined with outstanding adhesion to many surfaces that can be easily tailor-made by adjusting the compositions [1,2]. However, the high combustibility of WPU has notably restricted its further applications in stringent fire situation, thus, reducing the flammability is considerably imperative. Various fire retardants have been adopted to confer flame retardancy of WPU via blending and/or copolymerizing with the matrix. Traditionally, the halogenated compounds comprise the most widely applied method to endow WPU with

good flame resistance, due to the advantages of high efficiency and low cost. Nevertheless, halogen-based flame retardants can emanate toxic and potentially carcinogenic dioxins and furans along with obscuring smoke during combustion, which pollute environment, damage biota and compromise human health [3]. As a consequence, the development of environmentally friendly halogen-free fire retardants has become a hot topic in both academic and industrial communities.

Among the hopeful alternative flame retardants, the phosphorus-containing compounds are believed to be the most promising candidate owing to their multifold advantages including notable high-efficiency flame resistance, less toxic gases and smoke generation when burning [4–6]. Early studies primarily focused on investigating additive type phosphorus-based materials to enhance the flammability of WPU, but heterogeneous dispersion and poor compatibility with WPU were shown [7,8]. In this regard, copolymerization of flame-retardant monomers into polymer to render inherent and permanent flame retardancy as well as maintain the original physical and mechanical properties of WPU has hereby triggered tremendous research interest [2,9–13]. In our previous work, we synthesized a phosphorous–nitrogen

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intumescent flame retardant with reactive diamino groups and cyclic heteroaromatic structure: benzoguanamine spirocyclic pentaerythritol bisphosphonate (BSPB), and conjugated it into WPU backbone as hard segment to prepare flame-retardant WPU (FRWPU). A LOI value of 27.3% and a UL-94 V-0 rating could be achieved when the BSPB content was 8 wt%, and the mechanical properties of FRWPU were enhanced with the conjugation of BSPB [14]. Whereas, the corresponding reactive flame retardants are almost organophosphates and conjugated into the backbone of polyurethane, the hydrolysis rate of which was found to be twice as fast as the lateral chain type [15,16], and this would bring about serious reductions in fire resistance and mechanical properties of WPU. To remedy this problem, one possible solution is to introduce the phosphorus units into the reactive oligomer as side groups. Unfortunately, to the best of our knowledge, rational design of such “ideal” pendant group phosphorus-containing flame retardant is barely reported until quite recent.

As a continuous work, in this study, we designed and prepared a novel pendent organophosphorus group diol through a two-step reaction from neopentyl glycol, phosphorus oxychloride and trimethylolpropane, and then covalently conjugated it into WPU in the chain-extension step to acquire a series of flame retardant waterborne polyurethanes. As expected, the polyurethanes with pendant organophosphorus group exhibit intrinsic flame retardant features, and most importantly, fascinating hydrolysis resistance accompanied with favorable physical properties, thus unambiguously demonstrating the feasibility of our strategy.

## 2. Experimental

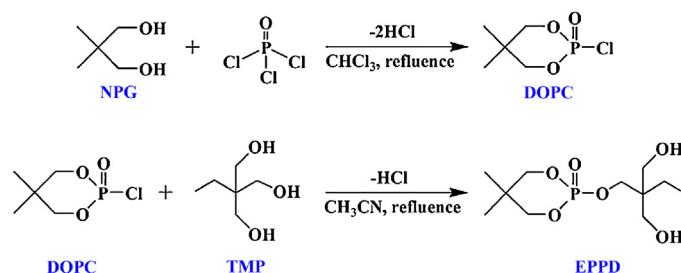
### 2.1. Materials

Polypropylene glycol with number-average molecular weight of 2000 (PPG220) was acquired commercially from Junsei Chemical Co., Ltd. (Tokyo, Japan) and was degassed and dehydrated under high vacuum (0.8 mmHg) at 120 °C overnight prior to synthesis. Dicyclohexylmethane diisocyanate ( $H_{12}$ MDI) of extra pure grade was provided by Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and was dried with 4 Å molecular sieves before use. Neopentyl glycol (NPG), trimethylolpropane (TMP) and 2,2-bis(hydroxymethyl) propionic acid (DMPA) were analytical reagents and supplied by Kanto Chemical Co., Inc. (Tokyo, Japan). Phosphorus oxychloride ( $POCl_3$ ) was received from Alfa Aesar (China) Chemical Co., Ltd. (Shanghai, China) and distilled at reduced pressure prior to use. Dibutyltin dilaurate (DBTDL) and triethylamine (TEA) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). *N,N*-dimethylformamide (DMF), chloroform, hexane, ether, acetonitrile and acetone of reagent grade were purchased from Aladdin Industrial Corporation (Shanghai, China) and were purified before use. Deionized water was self-prepared. Benzoguanamine spirocyclic pentaerythritol bisphosphonate (BSPB) was synthesized according to our reported literature [14] and used as a chain-extender to prepare flame retardant waterborne polyurethane with organophosphate moieties conjugated in the backbone.

### 2.2. Synthesis of

#### 2-chloro-2-oxy-5,5-dimethyl-1,3,2-dioxaphosphorinane (DOPC)

A 250 mL four-necked round-bottom glass flask equipped with a thermometer, addition funnel, mechanical stirrer and reflux condenser with aqueous sodium hydroxide trap was charged with 31.25 g of neopentyl glycol (0.30 mol) and 150 mL chloroform. The mixture was stirred and heated slowly. When the reaction temperature reached 50 °C, 45.60 g of phosphorus oxychloride (0.30 mol)



Scheme 1. Synthesis procedure and molecular structure of EPPD.

was carefully added dropwise into the flask with constant pressure funnel over a period of 2 h. Thereafter, the reaction mixture was raised to 62 °C gradually and kept under reflux until no HCl gas emitted. After cooling to room temperature, the chloroform solvent was removed by rotary evaporator under reduced pressure, and the white precipitate was filtered and washed thoroughly with hexane and ether sequentially. Then the powdery product was dried under reduced pressure at 80 °C to constant weight. The white powder was obtained with 88% efficiency.

### 2.3. Synthesis of 2-ethyl-2-(2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinanyl-2-methylene)-1,3-propanediol (EPPD)

In a 250 mL four-neck and round-bottom separable flask fitted with a dropping funnel, mechanical agitator, temperature controller and a condenser with a tail gas absorber, 29.52 g of trimethylolpropane (0.22 mol) was dispersed by 80 mL dry acetonitrile at 60 °C. Subsequently, the mixture of 36.90 g DOPC (0.20 mol) dissolved in 70 mL acetonitrile and 22.26 g triethylamine (0.22 mol) was dropped into the glass reactor within about 2 h. After the addition, the reaction mixture was gradually heated up to 82 °C and stirred strongly, refluxing for 8 h. Then the acetonitrile was removed by vacuum distillation and the white solid was further purified by washing three times with acetone and chloroform. Successively, the white extract, named EPPD, was dried for overnight at 80 °C under high vacuum to obtain a pure product with a yield of 72%, and then subjected to analysis. The molecular structure of EPPD together with the schematic process is depicted in Scheme 1.

### 2.4. Synthesis of flame retardant waterborne polyurethanes

The flame-retardant waterborne polyurethanes with pendant organophosphorus group (PWPU) were synthesized using the prepolymer method in a three-step procedure. The molar ratio of isocyanate groups with respect to hydroxyl groups was maintained at 1.31. At the first step, a stoichiometric mixture of PPG220,  $H_{12}$ MDI, DMPA together with 0.05 wt% DBTDL catalyst was fed into a 500 mL four-neck round-bottom glass reactor equipped with a mechanical stirrer, nitrogen inlet, temperature meter and condenser with a drying tube, and allowed to react at  $(80 \pm 2)$  °C for 2 h at dry nitrogen atmosphere to obtain a liner NCO-terminated prepolymer. Thereafter, the intermediate was chain extended by adding calculated amount of NPG and EPPD under moderate stirring at that temperature until the theoretical isocyanate value was reached, which was monitored intermittently with the dibutylamine back titration method. Particularly, DMF was added occasionally to reduce the viscosity of reaction mixture. After cooling the system to 50 °C, the ionic centers of DMPA were neutralized with TEA. Finally, the resultant mixture was dispersed by demineralized water under vigorous stirring conditions to obtain a series of transparent organophosphonate-containing waterborne

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