

Preparation and Application of Phosphorous-Containing Bio-Polyols in Polyurethane Foams

Qiang Zhang, Fangeng Chen, Lin Ma, Xuesong Zhou

State Key Laboratory of Pulp and Paper Engineering, School of Light Industry and Food Sciences, South China University of Technology, Guangzhou 510640, China

Correspondence to: F. Chen (E-mail: fgchen@scut.edu.cn)

ABSTRACT: A bio-polyol phosphonate acting as the polyol component in the preparation of polyurethane foam was synthesized from the liquefaction product of bagasse by the halogenation of the liquefaction product followed by the Michaelis–Arbuzov rearrangement. The FT-IR spectra showed that phosphorus-containing groups were introduced into the polyol chain. The data of the viscosity and the hydroxyl number suggested that the bio-polyol phosphonate would be a good polyol component in the preparation of polyurethane foam. The limiting oxygen index of polyurethane foam containing bio-polyol phosphonate varied in the range of 24–28, while that of polyurethane foam without bio-polyol phosphonate was 23, demonstrating that the introduction of the phosphorus-containing group into the polymer helped to improve the flame retardancy. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40422.

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INTRODUCTION

Biomass, especially lignocellulosic biomass, is recognized a good candidate to replace fossil resources in the production of fuels and materials. However, most lignocellulosic raw materials are not chemically reactive, and the high-valued utilization is thus restricted. Therefore, some procedures to convert lignocellulosic biomass into reactive chemicals, e.g., liquefaction, are required. The liquefaction products can be used as feedstock to synthesize various polymer materials such as phenolic resins, polyurethane foams and other polymer materials.^{1–3} Unfortunately, the liquefaction products used in the preparation of polyurethane, sometimes named as “bio-polyols” because they are similar to conventional polyols in structure, are flammable. This shortage prevents to improve the performances of the polyurethane and restricts the applications of these polyols. To solve this problem, various flame retardants are used to retard the burning of polyurethane. These flame retardants can be classified into two types: additive type and reactive type. The former one works by incorporating into the polymeric materials, and the latter works by the covalent bonding between the polymer and the flame retardant, or by dissolving in the polymer as additives.^{4,5} The former gives better performances than the latter due to its good compatibility to polymers.⁶

Phosphorus-containing compounds are frequently used flame retardants in polyurethane preparation. When burned at high temperature, a nonflammable film of phosphoric acid is formed. The film can cover the surface of the polymer material and

retard the burning. Phosphoric acid can also be transferred to polymetaphosphoric acid that can also protect polymer materials from burning. Phosphorus-containing groups can also be introduced into the polymer chain via the reaction of phosphorus-containing polyisocyanate and/or phosphorus-containing polyols. Some phosphorus-containing polyols, e.g., polyol phosphates and polyol phosphonates, have been reported to be used as flame retarding polyols in the preparation of polyurethane.^{7,8} Khatib et al.⁸ synthesized phosphonate diols from allyl or vinyl dialkyl phosphonate and 3-mercapto-1,2-propanediol by radical thiolene addition and used the phosphonate diols as both chain extenders and flame retardants in polyurethane preparation. A series of polyurethane samples with different phosphorus contents were prepared from hydroxytelechelic polybutadiene, phosphonate diol and modified MDI. The limiting oxygen index (LOI) of polyurethane was measured to be 23.2 when the phosphorus content was 3% whereas that of the non-phosphonated polyurethane was 17.2. However, the conversion yield in the synthesis of bio-polyol phosphonate is relatively low due to the relatively low reactivity of vinyl dialkyl phosphonates in radical polymerization.

The Michaelis–Arbuzov rearrangement, one of the most versatile pathways for the formation of carbon-phosphorus bonds by the reaction of an ester of trivalent phosphorus with alkyl halides, can be used to prepare phosphonates, phosphinic acid esters, and phosphine oxides.⁹ Vidil et al.¹⁰ synthesized methyl

2,3,4-tri-O-benzyl-6-bromo-6-desoxy- α -D-mannopyranoside from methyl 2,3,4-tri-O-benzyl-6-desoxy- α -D-mannopyranoside and LiBr. Then the product was reacted with trimethylphosphite to obtain the mannose 6-phosphonate by the Michaelis–Arbuzov rearrangement. Though seldom reported, it is expected that polyol phosphonates can be prepared by this method.

In this study, liquefied bagasse was modified with epichlorohydrin to obtain a halogenated product. Then, the halogenated product reacted with trimethylphosphite via the Michaelis–Arbuzov rearrangement to form a “bio-polyol phosphonate.” The physical and chemical properties of the bio-polyol phosphonate as well as its performances in rigid polyurethane foam were characterized to verify the possibility to be used in building insulation engineering.

EXPERIMENTAL

Materials

Bagasse was provided by Jiangmen Sugarcane Chemical Factory, Guangdong, China. Polyethylene glycol 400 (PEG 400), silicongtungstic acid, epichlorohydrin, dibutyltin dilaurate (DBTDL, a catalyst used in polyurethane preparation), dimethylpolysiloxane (PDMS, a surfactant), triethylene diamine (DABCO, a catalyst), and trimethyl phosphite were of reagent grade. Two polyether polyol products, namely 4110 (a polyol with the hydroxyl number 450 mgKOH/g synthesized from sucrose, propylene glycol and propylene oxide) and 635 (a polyol with the hydroxyl number 490 mgKOH/g synthesized from sorbitol, glycerol and propylene oxide) respectively, were obtained from Shanghai Fengwei Chemical, Shanghai, China. Diphenyl methane-4, 4'-diisocyanate (MDI) was the commercial product of BASF China. Dichloroethane (HCFC-141b) was purchased from Solvay GmbH.

METHODS

Liquefaction of Bagasse

Bagasse was liquefied in PEG 400 in the presence of silicongtungstic acid as the catalyst. Nearly 30 g of polyethylene glycol that contains 4% silicongtungstic acid as the catalyst were added into a three-necked flask and heated to 130°C by oil bath. After that, 3 g of bagasse was added to the flask and heated the flask to 160°C. After 2 h, the flask was immersed in cold water to terminate the reaction. The liquefaction product was centrifuged to remove the catalyst and the residue, and the liquefaction product, which would be used as the polyol component in the preparation of polyurethane foam, was thus obtained.

Synthesis of Bio-polyol Phosphonate

The liquefaction product and epichlorohydrin were mixed by 1 : 1 molar ratio of hydroxyl-to-epoxy groups and stirred at 45°C for 3 h. After that, the mixture was vacuum-evaporated with a rotary evaporator at 80°C for 1 h to remove the excess epichlorohydrin. The halogenation of the liquefaction product was thus finished.

Subsequently, the halogenated liquefaction product and predetermined amount of trimethyl phosphite were mixed and stirred at 160°C for 6 h under nitrogen atmosphere. After that, the mixture was vacuum-evaporated with a rotary evaporator at 90°C for 1 h to remove the excess trimethyl phosphite. The bio-polyol phosphonate, named as BPP, was thus obtained.

Preparation of Rigid Polyurethane Foam

The rigid polyurethane foams were prepared based on the formulations (shown in Table I) according those in our previous paper.¹¹ The polyol components (BPP and other polyols), DBTDL, DABCO, PDMS, and HCFC-141b were mixed thoroughly in a paper cup with continuous stirring. Then, the predetermined amount of MDI was added into the mixture. The mixture was stirred at 2500 rpm for 8–10 s to rise at ambient conditions for 30–60 s. The resulting foam was allowed to cure at ambient conditions for 1–2 h.

CHARACTERIZATION

FT-IR Spectra

The FT-IR spectra were recorded on a TENSOR27 spectrometer (Bruker, Germany) over the range of 400–4000 cm^{-1} .

³¹P-NMR spectra

The ³¹P NMR spectra of the bio-polyol phosphonate were recorded using Bruker DRX-400 spectrometer equipped with a BBO NMR probe operating at the frequency of 202.05 MHz and room temperature. The samples were dissolved in 450 μL of solvent of DMSO-*d*₆/pyridine mixture containing tri-*meta*-tolylphosphate (0.7 mg mL^{-1}) and chromium-acetyl acetonate (0.9 mg mL^{-1}). A 90° pulse was used with a 5-s pulse delay along with inverse-gated broad-band proton decoupling. A line-broadening factor of 5 Hz was used and the time domain (TD) size was 64 K. For each spectrum 2000 scans were conducted.

Gel Permeation Chromatography

The molecular weight and molecular weight distribution of bio-polyol phosphonate were determined by gel permeation chromatography using an Agilent 1100 apparatus equipped with an Agilent PL column and a differential refraction detector (RID). The samples were eluted by tetrahydrofuran at the flow rate 1.0 mL min^{-1} . The column was calibrated by mono-dispersed polystyrene standards. The average molecular weights were calculated based on the chromatogram and calibration line.

Viscosity

The viscosities of liquefaction product and bio-polyol phosphonate were measured with a NDJ-7 rotary viscometer (Shanghai Balance Instrument Factory, China).

Hydroxyl Number

The hydroxyl numbers of the bio-polyol were estimated according to ASTM D2849 (Methods of Testing Urethane Foam Polyol

Table I. Formulation to Prepare Rigid Polyurethane Foam (Weight Parts)

BPP	Polyol 4110	Polyol 635	PDMS	DABCO	DBTDL	HCFC-141b	MDI
60	20	20	2	2	1	7	165

Raw Materials) by the esterification of the polyol and subsequent base titration.

Thermal Stability

The thermal stability of the polyurethane foams was evaluated by thermogravimetric analysis (TGA) with a Q500 apparatus (TA Instruments, U.S.A.) from room temperature to 700°C at a rate of 10°C per minute under nitrogen flow.

Limiting Oxygen Index

The LOI was measured with a M606B apparatus (Qingdao Shanfang Instrument, China) according to ISO 4589-1984. The oxygen contents increased at an interval 0.2%.

Density

The foam density was measured according to ISO 845:1988 with specimens of 50 mm × 50 mm × 50 mm (width × length × thickness).

Compressive Strength

The compressive strength of foams was measured according to ISO 844:2004 with specimens of 50 mm × 50 mm × 50 mm (width × length × thickness) at a compressive speed of 5.0 mm min⁻¹ on an Instron-5565 Universal Testing Machine (Instron Corporation, USA).

RESULTS AND DISCUSSION

Synthesis of the Bio-polyol Phosphonate

Figure 1 shows the reaction to synthesize bio-polyol phosphonates. The bio-polyol phosphonates are synthesized via two steps. First, the liquefaction product was halogenated with epichlorohydrin. Then the halogenated bio-polyol reacted with trimethyl phosphite via the Michaelis–Arbuzov rearrangement to obtain bio-polyol phosphonate.

As shown in Figure 1, one hydroxyl group was consumed when one molecule of bio-polyol reacted with one molecule of epichlorohydrin. Simultaneously, another hydroxyl group was formed by this reaction. Therefore, the total amount of hydroxyl groups did not change.

Characterization of the Bio-polyol Phosphonate

FT-IR Spectroscopy of the Bio-polyol Phosphonate. Figure 2 shows the FT-IR spectra of trimethyl phosphite, the liquefaction product and the bio-polyol phosphonate. The absorption at 1100 cm⁻¹ is assigned to the C—O—C bond in polyethylene glycol (the liquefying reagent). The bands at 1738, 1315, 1251, 1037, and 735 cm⁻¹ are assigned to the stretching vibrations of C=O, PC—H, P=O, P—O—C (aliphatic), and P—C, respectively.¹² The band at 1738 cm⁻¹ representing carbonyl derived

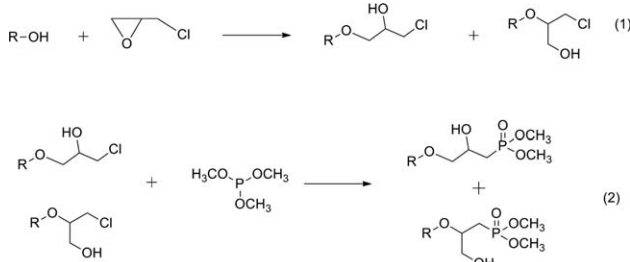


Figure 1. Reaction in the synthesis of the bio-polyol phosphonate.

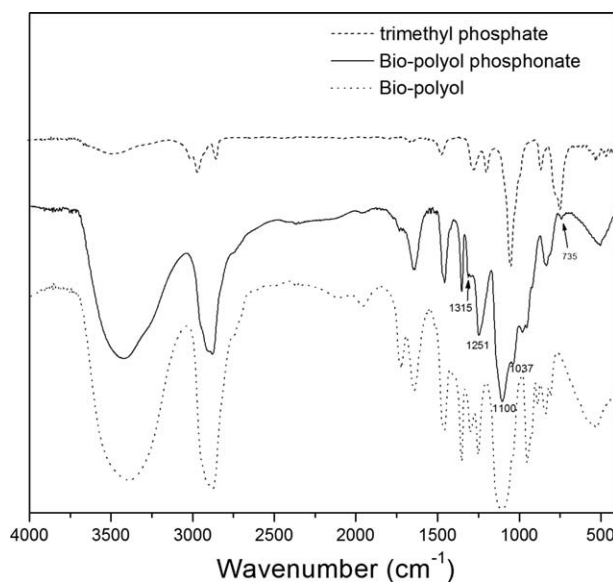


Figure 2. FT-IR spectra of trimethyl phosphite, liquefaction product and bio-polyol phosphonate.

from the lignin existed in the plant fiber or the oxidation product of the plant fiber. Anyway, no absorption appeared at 1251 cm⁻¹ within the FTIR spectra of trimethyl phosphite and the liquefaction product. The bands representing the P—C and P=O bonds illustrated the existence of phosphonyl groups. These results indicated that phosphorus-containing groups have been introduced into the bio-polyol, which helped to improve the flame retardancy of polyol and polyurethane. The band appeared at 1100 cm⁻¹ can be assigned to the stretching vibrations of C—O—C. The absorption of this band can be used as referent, because the content of C—O—C band remained unchanged after modification. The absorption of the 3386 cm⁻¹ band representing the O—H stretching vibration had no significant change in the spectrum of the bio-polyol phosphonate, suggesting that the amount of hydroxyl groups did not change after the modification.

³¹P NMR Spectroscopy of the Bio-polyol Phosphonate. Only one signal of phosphorus atom appeared at 141 ppm in the ³¹P NMR spectrum because there existed only one P—O bond in the molecule of trimethyl phosphite. However, there existed different linkages between phosphorus and other atoms (P—O and P—C bonds). The ³¹P NMR spectroscopy also confirmed the presence of phosphonate in the backbone, with a broad signal in the chemical shift range 0–20 ppm (centered at 12.7 ppm). A great number of sharp signals appeared in the spectra demonstrating the existence of various phosphorus-containing groups.

The Molecular Weight and Molecular Weight Distribution of the Bio-polyol Phosphonate. The gel permeation chromatograms of the liquefying reagent, the liquefaction product, the halogenated liquefaction product and the bio-polyol phosphonate were shown in Figure 3. The sequence of the elution time was found to be bio-polyol phosphonate < halogenated liquefaction product < liquefaction product < liquefying reagent. It was estimated from the chromatograms that sequence of the molecular weight of the three samples is bio-polyol

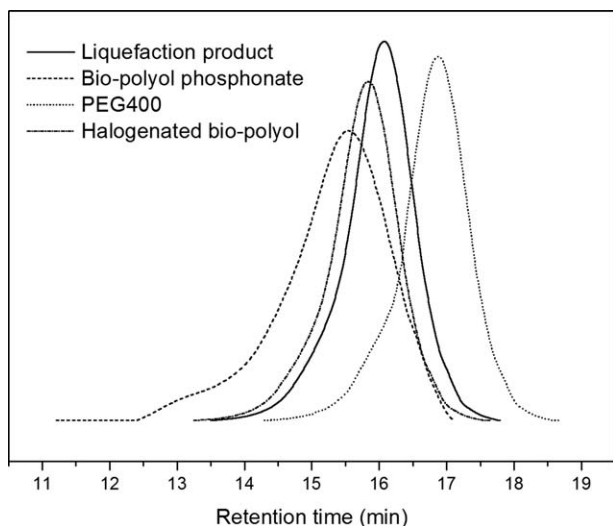


Figure 3. Gel permeation chromatograms of the liquefying reagent, the liquefaction product and the bio-polyol phosphonate.

phosphonate > halogenated liquefaction product > liquefaction product > liquefying reagent. The \overline{M}_n and the \overline{M}_w of these substances are listed in Table II. At the beginning of the liquefaction, the plant fibrous components had not been dissolved into the liquefying reagent, so that the average molecular weight of the liquefaction product was actually the molecular weight of the liquefying reagent. During the liquefaction procedure, the dissolution of the components in plant fiber into the liquefying reagent resulted in the variation of the average molecular weight of the liquefaction products. The increase in the average molecular weight of the liquefaction product after the reaction with trimethyl phosphate can be attributed to the introduction of phosphonate.

Properties of the Bio-polyol Phosphonate. This polyol phosphonate prepared in this work is expected to be used as a polyol component to prepare polyurethane foams. The phosphorus content, the viscosity and the hydroxyl number of the bio-polyol phosphonate are listed in Table III where BPP1 through BPP5 represent the bio-polyol phosphonates prepared with different trimethylphosphate-to-hydroxy molar ratios. The phosphorus content was calculated based on the weights of the converted trimethylphosphate and the obtained bio-polyol phosphonate.

As shown in Table III, the phosphorus content of bio-polyol phosphonate increased with the increase in the trimethylphosphate-to-hydroxy molar ratio. The viscosity of

Table II. Average Molecular Weights of Liquefaction Product and Its Derivatives

Sample	\overline{M}_n	\overline{M}_w	$d = \overline{M}_w / \overline{M}_n$
PEG 400	364	445	1.22
Liquefaction product	625	781	1.25
Halogenated liquefaction product	685	915	1.34
Biopolyol phosphonate	966	1622	1.68

liquefaction product was 165 mPa·s while that of bio-polyol phosphonate increased to 448–553 mPa s⁻¹. The viscosity of bio-polyol phosphonate increased with the increasing of phosphorus content. A reasonable explanation to the increase in the viscosity is that the liquefaction product and epichlorohydrin crosslinked during the modification procedure.

The hydroxyl number had no significant change when the phosphorus content increased from 0 to 4.03%. The number of hydroxyl groups and molecular weight had effects on the hydroxyl number. As shown in Figure 1, the total number of hydroxyl groups did not change. However, the molecular weight of bio-polyol phosphonate, shown in Figure 3, increased. These two factors resulted in the slight increase of hydroxyl number.

Effect of Phosphorus Content on the Thermal Stability of the Polyurethane Foam

The TGA and DTG curves of polyurethane foams with different phosphorus contents are shown in Figures 4 and 5, respectively. With regard to the phosphorus-free polyurethane sample, the degradation at 200–400°C could be attributed to depolycondensation reaction. The rate of degradation was reduced at enhanced temperature until the sample was degraded completely at about 700°C. There existed only one peak in the DTG curve of this sample. Differently, two major peaks were observed in the DTG curves of phosphorus-containing polyurethane foam, which was similar to what Price et al.¹³ reported. As shown in Figures 4 and 5, both phosphorus-containing and phosphorus-free polyurethane foams decompose in the similar manner except at temperature of ~320°C, indicating onset of the fire-retardant action. It was reported that phosphorus-containing compounds usually start to decompose at relatively low temperature, and a protective phosphorus-carbon layer which acts as an insulating layer to retard the heat transfer from flame to polymer is thus formed.¹⁴ The flame retardancy was thus improved.¹⁵ The final residue yield had only a slight

Table III. Properties of the Bio-polyol Phosphonates

Sample	Trimethylphosphate-to-hydroxy molar ratio	Phosphorus content (%)	Conversion of trimethylphosphate (%)	Viscosity (mPa s ⁻¹)	hydroxyl number (mg KOH ⁻¹ g ⁻¹)
BPP1	0.00	0.00	0	165	243
BPP2	0.25	0.75	30	448	233
BPP3	0.50	1.45	36	509	241
BPP4	0.75	2.54	45	531	231
BPP5	1.00	4.03	56	553	234

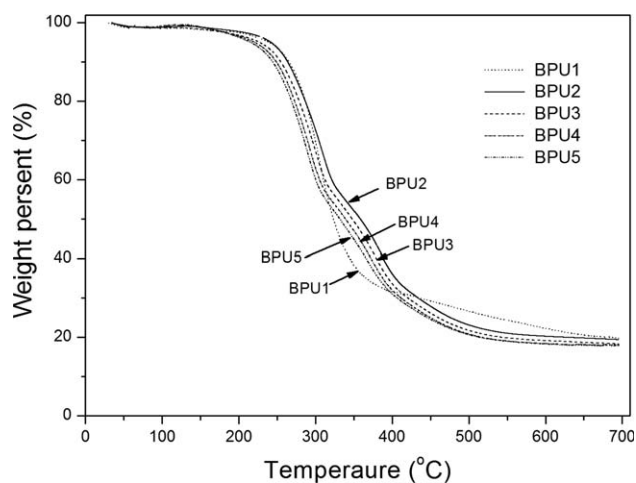


Figure 4. TGA curves of Polyurethane foams with different phosphorus contents.

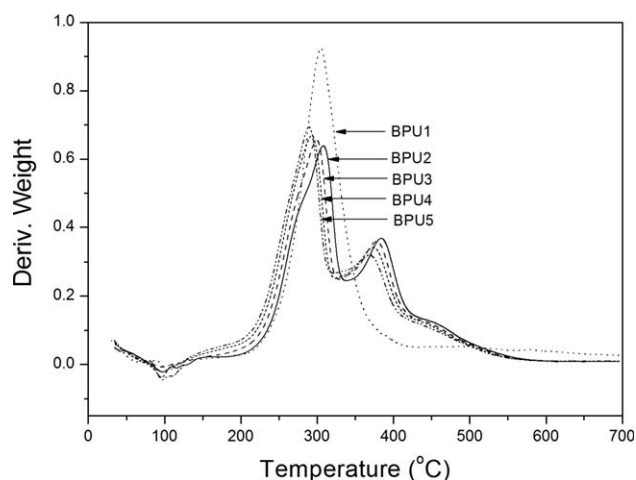


Figure 5. DTG curves of Polyurethane foams with different phosphorus contents.

difference when the dosage of polyol phosphonate varied, indicating that the final results of thermal decomposition were similar although the decomposition experienced different stages. It was also found from Figure 4 that the initial decomposition temperature of polyurethane foam had a slight reduction when bio-polyol phosphonate was introduced. The initial decomposition temperature of polyurethane foams containing 4.03% of phosphorus was 234°C while that of phosphorus-free polyurethane was 240°C. The reduction of the initial decomposition temperature is due to the difference in the stability of P–C and P–O bonds. As we have known, the P–C bond was less stable than the C–C bond and the P–O bond. Based on the data of bond energy of P–C, P–O, and C–C,^{16,17} it can be estimated that the P–C bond breaks prior to other two bonds during thermal degradation. The decomposition of phosphorus-containing substances (polyol phosphonate) favors the thermal stability of the polyurethane.

Effect of Phosphorus Content on the Flame Retardant of the Polyurethane Foam

Polyurethane foams prepared from BPP1 through BPP5 were named by BPU1 through BPU5, respectively. The data of LOI,

Table IV. Limiting Oxygen Index, Density, and Compressive Strength of Polyurethane Foams

Polyurethane foam	LOI (%)	Density (kg m ⁻³)	Compressive strength (kPa)
BPU1	23.4	48	129
BPU2	24.5	59	225
BPU3	26.3	62	273
BPU4	27.0	63	246
BPU5	27.1	56	186

an important index to evaluate the combustion behavior of the polyurethane foam, are shown in Table IV. As shown in Table IV, LOI values increased when the bio-polyol phosphonate was used as polyols component to prepare the polyurethane. The phosphorus–carbon layer retarded heat and mass transfer between the gas and the condensed phases.¹⁸ As a result, when the fire retardant was introduced, the flammability of polyurethane foams decreased and LOI value increased greatly. The LOI of polyurethane foams had the sequence BPU1 < BPU2 < BPU3 < BPU4 < BPU5. This sequence agreed well with the phosphorous contents in bio-polyol phosphonate. It demonstrates that the flame retardancy was improved with the increase in phosphorous contents.

Mechanical Properties of the Polyurethane Foam

The compressive strength of the polyurethane prepared from polyol phosphonate in this study, as shown in Table IV, could meet the standard requirements for rigid polyurethane foam for insulation (Type II) according to Chinese National Standard GB 50404-2007.

CONCLUSIONS

Phosphorous-containing bio-polyol was successfully synthesized from halogenated bio-polyol and trimethylphosphite via the Michaelis–Arbuzov rearrangement. This kind of phosphorous-containing bio-polyol was an effective flame retardant for preparing the polyurethane. Increasing the addition of phosphorous-containing bio-polyol favors the improvement of the flame retardancy of polyurethane. The flame retardancy of polyurethane foam was improved greatly when the phosphorous-containing bio-polyol was used as polyols component to prepare polyurethane.

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