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Phosphorus-Containing Polymers from THPS. VII. Synthesis of phosphorus-containing trialkynes and its metal-free 1,3-dipolar cycloaddition reaction with azidated Soybean-oil

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Abstract: A novel hydrolysis-resistant trialkynes, namely tris(prop-2-yn-1-yloxy methyl)phosphane oxide(TPOPO) was prepared from an environmental friendly tetrakis (hydroxymethyl) phosphonium sulfate (THPS). The chemical structure of TPOPO was characterized by FT-IR, NMR (^{1}H, ^{13}C,^{31}P) and MS. The TPOPO underwent metal-free and solvent-free 1,3-dipolar cycloaddition reaction with azidated soybean oil (AzSBO) with different alkyne/azide molar ratio. The gel contents of the cured polymers were higher than 95% and the char yields of polymers at 850℃ were over 16.4%. DMA analysis showed the glass transition temperatures were over 45.9^{o}C. The cured polymers showed high dielectric constant and dielectric loss for their high polarity.

Introduction

As a class of eco-friendly and annually renewable resources, vegetable oils have attracted considerable attention as raw materials for many kinds of polymers which once originated from fossil oil. [1-13]The main driving force for this elaborate effort is mainly related to the renewability, sustainability, availability, cost-effectiveness, nontoxicity and biodegradability of vegetable oil-based polymers. But the vegetable oils can't be used directly as engineering materials for most of them are low molecular weight liquids. Converting the oil feedstock to serviceable solid materials by relatively economic and green method is one of the most important tasks. Though nearly all vegetable oils contain double bands in their structures, only a few of them can be directly polymerized into cross-linked polymers because the naturally occurring double bands in vegetable oil always show low reactivity.[14, 15] Most of vegetable oils often require introducing more reactive functional groups into their structures before polymerization. Many highly reactive oil derivatives have been successfully prepared by introducing different polymerizable groups [1, 2, 4, 6, 7].

Commercially, the inherently safety of polymers is one of the most important issues which should be considered before practical application. One of the merits of vegetable oil based polymers normally is nontoxic, or at least very low toxic. But vegetable oil based materials, like many other organic polymeric materials made from fossil oil, are inherently flammable [5, 6]. Direct utilization of these bio-polymers as engineering materials, construction materials, packing materials and so on, will be confronted with fire threat. The common strategies of overcoming this demerit are using flame retardant additives or copolymerizing with flame retardant monomers in the industry. To meet the application standard, halogen-based organic flame retardants have been used widely in industry to prepare nonflammable polymer materials. However, the flame retardant materials that contain halogens release hydrogen halides and dioxins during combustion, which will cause corrosion and toxicity.[16-20]

The concept of sustainable development requires the development of new green flame retardant polymeric materials. Many attentions have been paid to phosphorus, silicon, nitrogen and boron-containing flame retardant polymers for they generally give off nontoxic combustion products during burning [21-24]. In fact halogen–free fire retardants are increasingly becoming more popular than their halogen counter parts. By now there are some reports concentrated on the preparation and characterization of vegetable oil based fire retardant materials by incorporating with phosphorus and other elements to improve fire standard of resulting biopolymers[25]. Cάdiz [26]reported two different approaches to the creation of phosphorus-containing soybean-oil copolymers. One is the cationic copolymerization of soybean oil with phosphorus-containing comonomer and the other one is the cross-metathesis reaction of soybean oil with functional phosphorus-containing compounds. The resulting thermosets with 1% phosphorus had LOI values about 24.0 and indicated an improvement in the fire-retardant properties of the soybean-oil-based copolymers. Karger-Kocsisc[27] found that acrylated epoxidized soybean oil , which was chemically

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grafted with difunctional flame retardants, could copolymerized with styrene to produce biofoams with high mechanical properties and intrinsic flame resistance. Güngöra[28] prepared Organic–inorganic hybrid UV-curable coating based on methacrylated/phosphorylated epoxidized soybean oil. The coating was applied on polycarbonate substrates and TGA results showed an enhancement in the thermal stability and also flame retardant properties of the coated material. Cάdiz [29] reported that silicon-containing soybean-oil-based copolymers were prepared from soybean oil and p-trimethylsilylstyrene by cationic polymerization using boron trifluoride etherate as initiator. Thermosets with T_g ranging from 50 to 62 °C and LOI values from 22.6 to 29.7 were obtained. They [30, 31]also prepared boron-containing soybean oil based copolymers from soybean oil and 4-vinylphenyl boronic acid by cationic polymerization. Thermosets with T_g ranging from 43 to 60 ^oC and LOI values from 23.7 to 25.6 were obtained. Bromide was also introduced into vegetable oil by Kusefoglu [32] to improve the flame retardancy of bio-polymers. But this method suffers from toxicity problem as mentioned above.

At present, the main method to combine the fire retardant elements with vegetable oil is cationic copolymerization or free radical copolymerization of plant oil with functional comonomers. As we know, the cationic polymerization was always carried out under harsh conditions and these functional comonomers (both for cationic and radical polymerization) can't be easy obtain on a large scale. So efforts must be paid to find out more convenient and efficient method to improve the flame retardancy of vegetable-oil based materials.

Phosphorus-nitrogen synergistic effect [33, 34] is a widely accepted concept in the field of fire retardant. To the best of our knowledge, few reports concerned this topic in the field of vegetable-oil-based biopolymers by now[27]. In fact, both phosphorus[26, 35] and nitrogen elements have been introduced into vegetable oil by chemical bonding separately. The most efficient method of preparing nitrogen-containing soybean oil was to prepare azidated soybean oil (AzSBO) by ring-opening nucleophilic addition of sodium azide to the epoxy soybean oil [34, 36-38]. Then azidated soybean oil can undergo azide–alkyne cycloaddition with various phosphorus-functionalized alkynes to form rigid materials containing both phosphorus and nitrogen elements.

In this paper, a novel phosphorus-containing trialkynes, namely tris(prop-2-yn-1-yloxy methyl)phosphane oxide(TPOPO), was first prepared in our group. The key starting material, tetrakis (hydroxymethyl) phosphonium sulfate (THPS), has been proved that it is an eco-friendly chemical and was awarded the American Green Chemicals Award in 1997[39, 40]. The TPOPO underwent thermal Huisgen cycloaddition reaction[41-46] with AzSBO under catalyst-free and solvent-free environment and obtained both phosphorus-and nitrogen-containing thermosets. Physical properties such as glass-transition temperature (Tg) and decomposition temperatures of these biopolymers are discussed and compared.

Experimental

Materials: Tetrakis (hydroxymethyl) phosphonium sulfate （THPS, 75% solution）was purchased from Hubei Xingfa Chemical Company, China; propargyl bromide, 80% in toluene, stabilized with MgO, were purchased from Alfa Aesar Reagent Co., Ltd; Epoxy soybean oil(ESBO), epoxy value 0.408mol/100g, obtained as gift from Jiangsu Yigete Chemical Co. Ltd, China; Other chemicals and solvent, such as sodiun azide, fluoroboric acid, benzyltriethylammonium chloride, N-methylimidazole, Dimethyl sulfoxide (DMSO), N,N-Dimethylformamide (DMF), ethyl aceteate, chloroform, were all gained from Sinopharm Chemical Reagent Co., Ltd., China.

Characterization and measurements

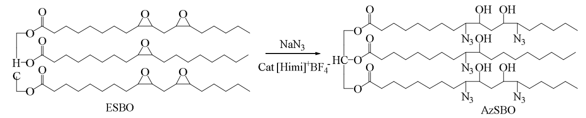
The structures of all compounds were verified by proton (^{1}H), carbon (^{13}C) and phosphorus (^{31}P) nuclear magnetic resonance spectroscopy (NMR) using Bruker AV400NMR spectrometer at proton frequency of 400 MHz as well as the corresponding carbon and phosphorus frequencies at room temperature using deuterated solvents as the solvent. Signals were averaged from 256 transients for ^{1}H NMR and ^{31}P NMR. Fourier transform infrared (FTIR) spectra were recorded with a Bruker Vertex 70 FTIR spectrometer in the region of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. Electrospray ionization mass spectrometric analysis was carried out using an Agilent 1100 Series LC/MSD Trap XCT. Thermal transitions were monitored with a differential scanning calorimeter (DSC), Model 204F1 from NETZSCH Instruments, and scan rate of 2-20℃/min over a temperature range of 30-300°C and nitrogen flow rate of 20mL/min were used in DSC experiments. Thermogravimetric analysis (TGA) was performed with a NETZSCH Instruments' High Resolution STA 409PC thermogravimetric analyzer that was purged with nitrogen at a flow rate of 70mL/min. A heating rate of 20°C/min was used and scanning range was from 40°C to 900°C. Mechanical properties were measured using a dynamic mechanical thermal analysis (DMA) apparatus (PerkinElmer, Diamond DMA). Specimens (50×10×1.0mm) were tested in a 3 point bending mode. The thermal transitions were studied in the scope of 20-200℃ at a heating rate of 4°C/min and at a fixed frequency of 1Hz. The contact angles of the polymer samples after curing were measured at 25 °C using a POWEREACH JC2000C1 contact 15 angle goniometer interfaced with image capture software after injecting a 5-µL liquid drop. To obtain reliable contact data, at least three droplets were measured at different regions of the same piece of sample, with at least two pieces of sample being used. Deionized water was used as a standard when measuring the surface properties. Dielectric constant and dielectric loss were measured at room temperature in an air atmosphere by the two parallel plate modes at 125Hz-1MHz using Agilent 4294A Precision Impedance Analyzer. A sample (about 20mm×10mm×2mm) was placed between two copper electrodes to form a parallel plate capacitor. Prior to each measurement, the sample was dried under vacuum at 100 °C for 3h.

Preparation of tris(prop-2-yn-1-yloxy methyl)phosphane oxide(TPOPO)

7g (0.05mol) THPO(tris(hydroxymethyl)phosphine oxide) and 0.7g benzyltriethylammonium chloride (10% weight percent of THPO) were added into a four-neck flask equipped with condenser, dropping funnel, mechanic stirrer and thermometer. 20mL of 30% NaOH aqueous solution was dropped into the flask at such speed that the temperature of reaction mixture was below 35^{o}C under mechanical stirring. After finishing addition of NaOH solution, the temperature of mixture was cooled to 0℃ by ice-water bath. 29.0g (80wt% in toluene, 0.195mol) propagyl bromide was added dropwise under stirring in 2h and the temperature was controlled below 5℃ during addition. After all propagyl bromide was added to the flask, the temperature was raised up to 50℃ and kept at this temperature for 10h under rapid stirring. The reaction mixture was cooled to room temperature and suitable amount of water was added in order to dissolve the NaBr. Then the mixture was transferred into separation funnel and the organic layer was washed with water for several times until no Br^- ion being detected by $AgNO_3$ solution. The organic layer was dried with anhydrous Na_2SO_4. After filtration, the remaining propagyl bromide was distilled out at 90-95℃ under normal pressure. Finally, the remaining organic liquid was placed in high vacuum to remove all volatiles. 7.94g brown viscous liquid was obtained. The yield based on THPO was 62.9%. MS: m/z$[M+Na]^+$= 277.05947.

Synthesis of Azidated Soybean Oil (AzSBO)

Azidated soybean oil-based (AzSBO) was synthesized via a ring-opening reaction of epoxy groups of ESBO with sodium azide using 1-methylimidazolium tetrafluoroborate($[Hmim]^+BF_4^-$) as the catalyst according to the previously reported procedure[38]. ESBO (183.8 g, 750 mmol epoxy), NaN_3 (73.9 g, 1.125mol), $[Hmim]^+BF_4^-$ (27.8 g , 15.1wt%), and DMF (170 g) were added into a 500 mL one-neck round bottom flask equipped with a condenser, mechanic stirrer, and oil bath. The reaction mixture was stirred at 95 °C for 60 h. At the end of reaction (60 h), the reaction mixture was allowed to cool to room temperature, dissolved in ethyl acetate (800mL), and transferred to a separatory funnel. The solution was successively washed with saturated sodium chloride solution (100 mL*5) and distilled water (100 mL*5) to remove the catalyst and unreacted sodium azide. The organic layer was dried over magnesium sulfate and the solvent was removed under vacuum at 40°C. AzSBO was obtained as a dark-brown and viscous liquid with 81.3% yield. The nitrogen content of the AzSBO was determined by elemental analysis.



Scheme 1 Reaction of ESBO with NaN_3 to prepare azidated soybean Oil (AzSBO)

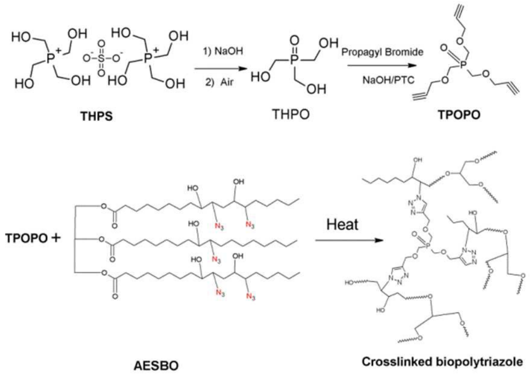
Preparation of cross-linked biopolymer by catalyst-free thermal cycloaddition reaction

Three cross-linked biopolymers were prepared in this research with different alkyne/azide ratios. The general procedure was as following. Weighted amount of AzSBO and TPOPO(15.0g in total) were mixed in a round–bottomed flask equipped with magnetic stirrer, 10mL chloroform was added into it to dilute the mixture. The mixture was stirred at room temperature for 0.5h to get a well-mixed solution. Then the solvent was stripped off by rotatory evaporator under vacuum. The mixture was transferred to aluminum mould (50mm*10mm*1mm), and the air was removed at 60 °C and 80 °C each for 2 h under vacuum, The step curing was achieved in an oven at 100 °C for 12 h, then at 130 °C , 160^{o}C and 190 °C each for 2 h. The sample was cooled down to room temperature slowly and kept at this temperature at least 48h before next measurements.

Results and discussion

Synthesis and characterization of starting chemicals

The multiple-alkyne compounds are key starting materials in dipolar cycloaddition reaction. Though many kinds of alkynes have been used in click chemistry, phosphorus-containing multiple-alkynes were seldom reported in literatures according to the best of our knowledge. Tripropargyl phosphate and analogous compounds [47-49] are readily obtained phosphorus-containing compound, but its hydrolysis-sensitivity and strong acidity after hydrolysis will impose negative effect on final materials. So a novel hydrolysis-resistant phosphorus-containing trialkynes, namely tris[(prop-2-yn-1-yloxy)methyl]phosphane oxide(TPOPO), was first designed and synthesized in our group according to Scheme 2.



Scheme 2 Synthesis of TPOPO and its thermal cycloaddition reaction with AzSBO

The starting tetrakis(hydroxymethyl) phosphonium sulfate (THPS), is an eco-friendly water-soluble chemical which can be obtained at industrial scale in China as main co-product during sodium hypophosphite production. THPS was originally used as a biocide in industrial cooling systems, oil field operations, and the paper-making industry and it is readily biodegradable and has no potential to bioaccumulation. Meanwhile THPS is rapidly oxidized in the environment to THPO (trishydroxymethylphosphine oxide) which has a very low aquatic toxicity and is not considered to present an environmental hazard. So, THPS passed an environmental attestation in America and was awarded the American Green Chemicals Award in 1997 [39].

The THPS was nearly quantitatively transferred to THPO under basic condition and air was used as the oxidant. TPOPO was prepared by standard Willamson method with the aid of phase transfer catalyst (PTC)[40]. That is, transformation of hydroxyl group into sodium alkoxide with sodium hydroxide and successive treatment with propagyl bromide. The TPOPO was obtained as brown viscous liquid and the yield of TPOPO was over 60% based on THPO. The concentration of NaOH was in the range of 25-30% (w/w) for higher concentration of NaOH would result in highly viscous reaction mixture which hider the reaction going smoothly. On the contrary, lower concentration of NaOH would lower the reaction rate and product yield.

The FT-IR spectrum of TPOPO is shown in Fig.1.The characteristic peaks of -C≡C- stretch vibration appears at 2114.1cm^{-1}, and the vibration absorption of ≡C-H locates at 3288.4cm^{-1}, 3213.3cm^{-1} and 641.5cm^{-1}. The typical peak for P=O appears at 1180.3cm^{-1} and the peak for C-O-C at 1092.7cm^{-1}. The peaks appearing at 2895.8cm^{-1}、2858.8cm^{-1} are due to -CH_2-vibration.

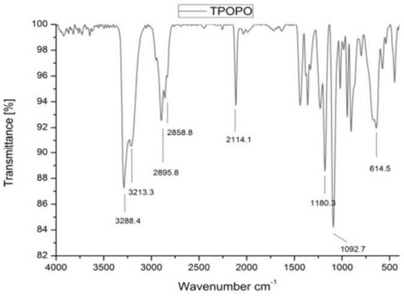


Fig. 1 FT-IR spectrum of TPOPO

The ^{31}P NMR spectrum of TPOPO is showed in Fig 2. It is very clear that only one peak appears at 39.29ppm. This result is exactly consistent with the theoretic structure of TPOPO.

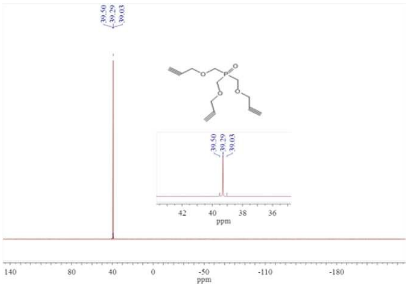


Fig. 2 ^{31}P NMR spectrum of TPOPO

^1H NMR spectrum of TPOPO is shown in Fig.3. The peak locates at 4.30ppm originated from the two protons in ≡C-CH_2-；The peak appears at 4.08ppm are attributed to protons of P-CH_2-O-; peak centered at 2.53ppm are assigned to protons of -C≡CH. The integral peak area ratio of three kinds of protons is 2:2:1, exactly equals to theoretic value.

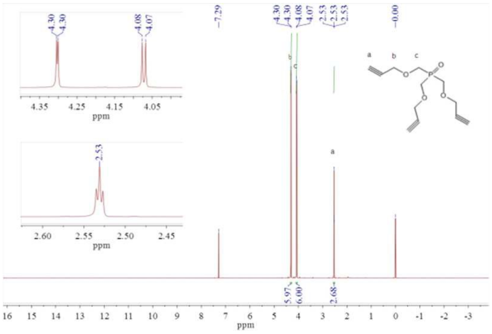


Fig. 3 ^1H NMR spectrum of TPOPO

^{13}C NMR spectrum of TPOPO is shown in Fig.4. The signal at 78.23ppm originated from the carbon of -C≡CH and at 76.19ppm generated from the carbon of -C≡CH. The peaks at 63.28ppm~64.27pm are attributed to the methylene carbon connecting to phosphorus atom (P-CH_2-O), the signals at 60.71ppm~60.59ppm are due to the methylene carbon atom of -CH_2-C≡CH .The peaks located in the range of 77.54ppm~ 76.90ppm are assigned to solvent.

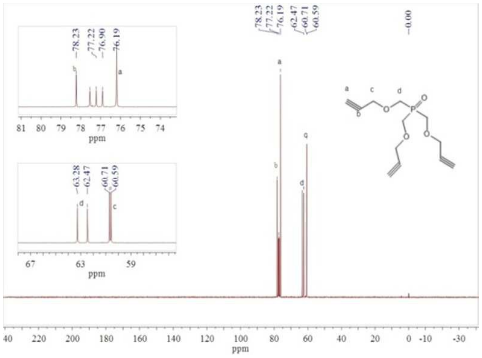


Fig. 4 ^{13}C NMR spectrum of TPOPO

AzSBO was prepared according to reported method [38]. The FT-IR spectra of ESBO and AzSBO are depicted in Fig.5. Obviously two new peaks appears at 3376.3 cm^{-1}(OH)，and 2103.9 cm^{-1}(-N_3). The former peak is attributed to hydroxyl groups originated from the ring-opening reaction of epoxy group, the next one from the azide groups. The characteristic peaks for epoxy group at 825.5cm^{-1} disappeared completely. The nitrogen content of the AzSBO was determined by elemental analysis and the data listed in Table 1.The average nitrogen content is 11.03% and it means that the per -N_3 group equals 382.1g of AzSBO. The sulfur came from the sulfonated product of soybean oil. For concentrated H_2SO_4 was the catalyst for preparing the ESBO.

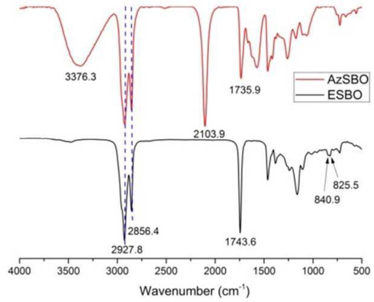


Fig. 5 FT-IR spectra of ESBO and AzSBO

Table 1 The result of elemental analysis for AzSBO

Number	Weight[mg]	N[%]	C[%]	H[%]	S[%]
1	2.4250	11.04	62.04	9.263	0.441
2	2.6850	11.01	62.04	9.485	0.352
average		11.03	62.04	9.374	0.397

Thermal Huisgen reaction studied by DSC

Three crosslinked polymers with different alkyne/azide ratios were prepared according to Table 2. Before curing reaction, the thermal Huisgen cycloaddition reaction was studied by differential scanning calorimetry (DSC) at different heating rate (P1 as example). The results of DSC study are shown in Fig. 6 and the corresponding data are collected in table 3. With increasing the heating rates，the initiation temperatures(T_o) of cycloaddition reaction increased from 94.9°C to 125.8°C, the peak temperatures(T_p) of exothermal process of reaction shifted from 126.8°C to 172.5°C and the termination temperature of reaction varied from 163.5°C to 206.5°C.

Table 2 Formulas for crosslinked polymers and related properties

Polymer	**P1**	**P2**	**P3**
AzSBO/TPOPO Weight(g)	12.28/2.73	12.03/2.97	11.75/3.26
AzSBO/TPOPO (Weight ratio)	4.50	4.05	3.60
Alkyne/azide (molar ratio)	1:1	1:0.9	1:0.8
Phosphorus Content (%,wt)	2.22	2.42	2.65
Nitrogen content (%, wt)	9.02	8.84	8.63
Gel Content(%)	95.0	96.0	95.0
Contact angel(°)	80.6°	83.4°	87.4°

To better understand the curing processes, the curing kinetics was investigated using non-isothermal differential scanning calorimetry (DSC) at different heating rate (Fig. 6). Kissinger, Ozawa, and Flynn–Wall–Ozawa methods [50-52] were used to determine the kinetic parameters and built the kinetic models. The activation energy for preparing P1 is 69.0 KJmol^{-1} (Kissinger method), 72.3 KJ mol^{-1}(Ozawa method), 74.5 KJ mol^{-1}(Flynn–Wall–Ozawa method), respectively. The reaction is a typical self-catalyzed reaction and the calculated curing parameter at heating tare 0k/min is 92.65 °C(T_o), 127.00 °C(T_p), 164.18°C(T_t), respectively. So the curing procedure for preparing sample was: 100 °C curing for 12 h, then at 130 °C, 160°C and 190 °C each for 2 h. The post treatment at high temperature can improve the percent conversion of alkyne and azide.

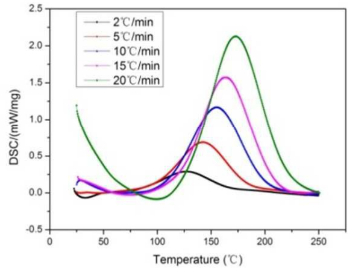


Fig. 6 DSC thermograms of TPOPO with AzSBO with different heating rate

Table 3: The date of T_o, T_p and T_t for polymer P1 at the different heating rate

Heating rate K(°C)/min	T_o K (°C)	T_p K(°C)	T_t K (°C)
2	368.05(94.90)	399.95(126.80）	436.65(163.50）
5	375.25(102.10)	415.35(42.20）	454.75(181.60）
10	383.65(110.50）	428.25(155.10）	470.25(197.10）
15	397.45(124.30）	436.55(163.40）	479.65(206.50）
20	398.95(125.80）	445.65(172.50）	488.95(215.80)
0 (Calculated)	365.80(92.65）	400.15(127.00）	437.33(164.18)

Thermal Huisgen reaction studied by FT-IR

The curing reaction of AzSBO and TPOPO was also monitored by FT-IR and the spectra are shown in Fig.7. At room temperature, the strong absorption peaks at 2106.2cm^{-1} originated from both azide group and triple bond. After curing at 100°C for 12h, the peak at 2106.2cm^{-1} disappeared almost completely. Further heat treatment has no notable effect on peak intensity. It indicated that the newly prepared trialkyne could react with AzSBO smoothly. The peaks at 3310.9cm^{-1} and 648.1cm^{-1} (due to triple bond) also weakened with heat treatment. The characteristic vibration peak for triazole group appeared at 3153.4cm^{-1} after curing reaction. During the thermal Huisgen cycloaddition reaction, the typical peaks of C=O (1737.7cm^{-1}) and P=O(1093.9cm^{-1}) kept unchanged and indicated the high thermal stability of cured polymer.

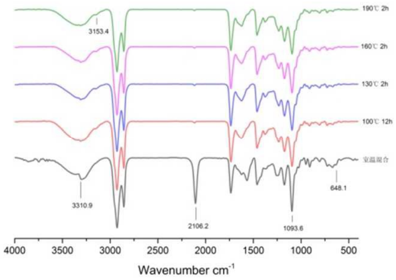


Fig. 7 FT-IR spectra of TPOPO with AzSBO under various curing condition

Thermal stability of crosslinked polymers

According to presetting curing procedure, three crosslinked polymers were prepared for property study. All crosslinked polymers show dark red appearances (Fig. 8) and can be bent to some extent. The DSC curves of cured polymers are depicted in Fig. 9 and it is found that there is no extra endothermal or exothermal peak appearing, which means that the cycloaddition reaction between alkyne and azide nearly completed. Though unreacted alkyne groups may remain in P2 and P3, but the total amount of remaining alkynes was small and the polymerization enthalpy of remaining alkyne was too weak to be recorded by DSC instrument.

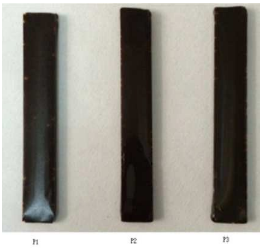


Fig. 8 Digital Photographs of P1,P2 ,P3

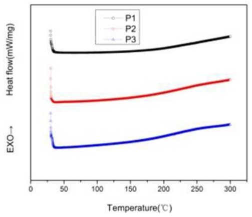


Fig. 9 DSC curves of three crosslinked polymers

The thermal stability of three crosslinked polymers was measured by thermogravimetric analysis. Both TG and DTG curves are shown in Fig 10 and corresponding data are collected in Table 4. From TG curves, we can find that three polymers showed high thermal stability below 300°C and weight loss is less than 10%. The rapid weight loss of three polymers appears in the temperature range of 300°C to 520°C, the first maximum weight loss temperature locates at 375°C and the second one appears at about 450°C as DTG curves show. Between 600°C to 900°C, the weight loss rate becomes gentle indicating the formation of thermal stable char. The fire-retardant property of polymer can be estimated from limited oxygen index (LOT) which can be calculated according to the empirical formula[40]:

$$LOI=17.5+0.4Y_{c,}$$

where Y_c is the char yield of polymer at 850°C in nitrogen atmosphere.

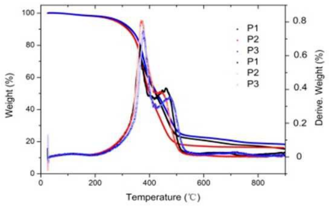


Fig. 10 TGA curves of polymers under Nitrogen

The char yields of three polymers are 16.4%, 16.4% and 18.6%, respectively. The calculated LOI values are 24.1, 24.1 and 24.9, respectively. Obviously the flame retardancy of soybean oil-based polymers improves dramatically by introducing phosphorus and nitrogen elements. Comparing with previous reports[34, 36, 37], the char yield of most AzSBO-based polytriazole was lower than 15% at 600°C and no data was given at 850°C, this research provides a convenient and effective method to improve the fire-rertardancy of soybean oil-based thermosets.

Table 4 Thermal properties of three cured polymers

Polymers	$T_{5\%}$ (℃)	$T_{10\%}$ (℃)	T_{max1} (℃)	T_{max2} (℃)	Y_c (%)	LOI
P1	**278.4**	**321.1**	**366.8**	**461.7**	**16.4**	**24.1**
P2	**276.1**	**319.2**	**370.4**	**440.9**	**16.4**	**24.1**
P3	**289.1**	**332.3**	**376.9**	**477.3**	**18.6**	**24.9**

$T_{5\%}$: Temperature of 5% weight loss.
$T_{10\%}$: Temperature of 5% weight loss.
T_{max}: Temperature at Maximum decomposition rate.
Y_c: Char yield at 850°C under nitrogen.
LOI: Limit Oxygen Index.

It is also noticed that the molar ratio of Alkyne/azide has some effect on thermal properties of three polymers. Analyzing the data listed in Table 4, it seems that the P3 shows a little better thermal stability than that of P1 and P2.The possible explanation is the excess alkyne will provide extra crosslinking sites at high temperature, resulting in improvement of thermal stability. Meanwhile the phosphorus content of P3 is slightly higher than that of P1 and P2. It is well known that phosphorus can promote the formation of carbon layer[22, 23].

The dynamic mechanical properties of the step cured polymers were obtained as a function of the temperature beginning in the glassy state of each sample to the rubbery plateau of each material. The T_g, storage moduli and cross-linking density of the three polymers can be deduced from the corresponding curves (Fig. 11) and all data are listed in Table 5.

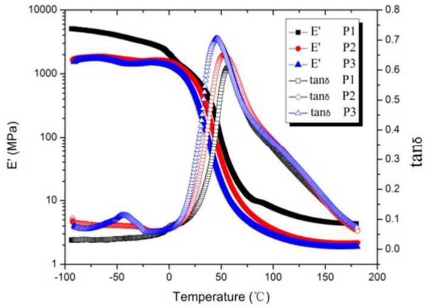


Fig. 11 DMA curves of polymers

It is found that the T_gs of the three polymers are 57.0°C, 53.0°C, 45.9°C, respectively. With increasing of alkyne/azide molar ratio, the T_g of corresponding polymer declines slowly. For at high molar ratio of functional group, the unreacted alkyne component can act as plasticizer to lower the glass transition temperature of polymer. The storage modulus of three polymers show same changing trend as T_gs. At room temperature, the storage moduli of P1 is 1.02 GPa, however, it is 0.97GPa for P2 and 0.70GPa for P3, respectively. Normally T_g and mechanic properties of crosslinked polymers mainly depend on crosslinking density, high crosslinking density normally results in more stiff polymer. The cross-linking density (υ_e) is the number of moles of network chains per unit volume of the cured polymers and it can be estimated from the rubbery plateau modulus using an equation from the statistical theory of rubber elasticity theory[34, 53]:

$$\upsilon_e = E'/3RT$$

where, E′ is tensile storage modulus obtained in the rubbery plateau, T is temperature in °K corresponding to the storage modulus value, and R is the gas constant.

Though the equation is strictly valid only for lightly cross-linked materials, it can also be used to compare qualitatively the level of cross-linking among structure-likely polymers. The calculated crosslinking-density of three polymers is shown in Table 5, they are 0.39mol/m^3(P1), 0.19 mol/m^3(P2), 0.17mol/m^3(P3), respectively. Among the three polymers, P3 shows the lowest crosslinking density and possess more free volume to let the chain segment move freely at low temperature, so its T_g value is the smallest one.

Table 5 Mechanical and dielectric Properties of Polymers

Polymer	T_g (℃)	E_1' (GPa)	E_2' (GPa)	E_3' (MPa)	υ_{e1} (10^3mol/m^3)	ε	Tanδ
P1	**57.0**	**4.31**	**1.02**	**4.35**	**0.39**	**9.4**	**0.25**
P2	**53.0**	**1.87**	**0.97**	**2.16**	**0.19**	**8.9**	**0.10**
P3	**45.9**	**1.67**	**0.70**	**1.87**	**0.17**	**10.0**	**0.08**

T_g: The glass transition temperature.
E_1': the storage modulus at -60°C of glassy states.
E_2': the storage modulus at room temperature.
E_3': the storage modulus at 175°C of rubbery states.
υ_{e1}: the crosslinking density at 175°C.
ε : dielectric constant at 1MHz at room temperature.
Tanδ: dielectric loss at 1MHz at room temperature.

Surface properties

The surface properties of three polymers were studied by measuring the water contact angle (Table 2) .The contact angles are 80.6°(P1), 83.4°(P2), and 87.4°(P3), respectively. Comparing with reported results [54-57], the present three polymers show a little stronger hydrophilicity. This result is attributed to the fact that phosphorus is a high electronegative element and P=O bond has a strong tendency to form hydrogen bond with water. Meanwhile the surface property also relates to chain segment movement. For Polymer P3, it possesses largest contact angle among three polymers, the reason is that the chain movement of P3 is easier than that of other two polymers for its low crosslinking density. As we know, the long alkyl chains in soybean oil are typical hydrophobic. At low crosslinking density, some of them can move to the sample top and form a hydrophobic surface. But in polymer with high crosslinking density, the chain movement is restricted to some extent for lack of enough free volume, such as in P1.

Dielectric properties of cured polymers

Dielectric property of polymers is very sensitive to its polarity, additives and impurity remaining during production[58]. The dependence of the dielectric constant and dielectric loss of all samples in the frequency range of 400Hz~1MHz were studied at room temperature (Fig. 12 and Table 5). Comparing with previous researches [59, 60], both the dielectric constant (ε) and the dielectric loss (tan δ) of present three polymers are bigger than that of polytriazoles from soybean oil source. This result is assigned to following reasons. First, as we mentioned above, P=O bond is a high polarizable group, introducing phosphorus into polymer network will increase the polarity of final polymer. Meanwhile, AzSBO contains many hydroxyl groups and azide groups after ring-opening reaction of epoxy with azide, and they are both polarized easily to result in high polar product. Moreover, some impurity and byproduct, such as sulfonated soybean oil, also remain in polymer and the sulfonic acid groups also have contribution to high dielectric constant of crosslinked polymer. The elemental analysis results indicate the presence of sulfur. The electric loss values of three

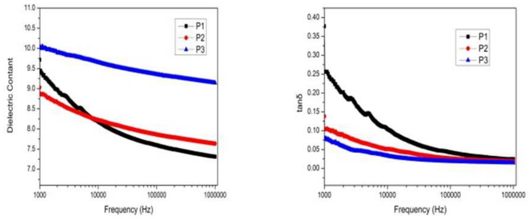


Fig. 12 Dielectric constant and Dielectric loss vs frequency of polymers

polymers are much higher than that of normal polytriazoles. One of the main factors affect the electric loss is the concentration of charge carrier in polymer matrix[58]. For AzSBO/TPOPO based polytriazole, though TPOPO has high purity according to structure analysis experiment, the AzSBO contains many hydroxyl, sulfonic and other polar groups and these groups will act as charge carrier when voltage is applied to sample, so it will show high dielectric loss. This result indicates clearly that purity of starting materials is one of the key factors to prepare low dielectric loss polymer.

Conclusions

Tetrakis (hydroxymethyl) phosphonium sulfate (THPS) is an eco-friendly starting materials for the preparation of phosphorus-containing functional compounds. The novel trialkyns, TPOPO was successfully prepared from THPS through two step reaction. TPOPO can act as an effective crosslinker to azidated soybean oil (AzSBO) though metal-free 1,3-dipolar cycloaddition. Three crosslinked polymers with different functional group ratios of alkyne (C≡C) to azide (N_3) were prepared and their gel contents were higher than 95%. TGA showed that the 5% weight loss temperatures of the three polymers were 278.4℃, 276.1℃ and 289.1℃ , respectively, and the char yields of polymers at 850℃ are 16.4%, 16.4% and 18.6%. Limiting oxygen index(LOI) calculated by TGA results were 24.1%(P1), 24.1%(P2), and 24.9%(P3), respectively. DMA analysis shows that storage modulus at the room temperature are 1.02GPa(P), 0.97GPa(P2) and 0.70GPa(P3), and the glass transition temperature are 57.0℃, 53.0℃, and 45.9℃, respectively. Three polymers all show a little stronger hydrophilicity than traditional soybean oil-based biopolymer, this will benefit to further biodegradation reaction. Three polymers exhibited relatively high dielectric constant and dielectric loss for the polarizable groups, such as hydroxyl, P=O and unreacted functional groups, which will increase the polarity of polymer and charge carrier concentration.

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Graphical Abstract