RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

PAPER

Dendritic organic-inorganic hybrid polyphenol and branched benzoxazine monomers with low curing temperature

Min Zhang,[a] Zhiwei Tan,[a] Hongxia Ma,[a] Jinjun Qiu,[a] Chengmei Liu*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A novel dendritic organic-inorganic hybrid polyphenol (T2) based on cyclotriphosphazene was synthesized by condensation reaction of T1 and phenol catalysed by phosphotungstic acid. The dendritic polyphenol T2 comprising twelve phenolic hydroxyl groups exhibited excellent solubility in common organic solvents. Three branched benzoxazine monomers with different oxazine ring content were synthesized via Mannich condensation reaction. These branched benzoxazine monomers showed low initial curing temperature. The properties of corresponding polybenzoxazines, such as thermal stabilities, mechanic properties, dielectric properties and gel contents etc. depended significantly on the oxazine ring content of T3. With the increase of the oxazine ring content for T3, these properties could be greatly improved due to their high crosslinking density.

Introduction

Polyphenols extensively distribute in renewable natural resources such as lignin, Chinese lacquer, tannin, et al. and recently become rather unique and intriguing products owing to their diverse range of physicochemical properties and unusual structures.[1-4] Plant polyphenols display a rich and complex spectrum of physical and chemical properties,[5] giving rise to broad chemical versatility including absorption of UV radiation, radical scavenging, and metal ion complexation. In addition, human health has been associated with consumption of foods and beverages rich in plant polyphenols.[6] Tea, chocolate, and wine-inspired polyphenols can act as colorless multifunctional coatings.[7] Except the naturally occurring polyphenols, man-made polyphenol (phenol resins) also developed 100 years ago and they have been used as one kind of engineering materials after curing. For its high reactivity of phenolic hydroxyl groups, polyphenols play as reactive intermediates for many functional polymeric materials. The modification of phenolic hydroxyls can endow them with particular desirable abilities. For example, Ching-Fong Shu and coworkers[8] have reported that the hyperbranched poly(aryl ether oxazole)s with terminal phenolic groups were easily functionalized and the glass transition temperature and the solubility of the hyperbranched poly(aryl ether oxazole)s depended significantly on the nature of the chain ends, which increases with increasing chain-end polarities. Polyphenols are also the amorphous molecular materials used in advanced photoresists because of their excellent solubility in alkali.[9-12] The branched polyphenol-based molecular glass resists had high selectivity to radiation and could form photoresist images as small as 60 nm.[9] However, no reports concerning dendritic polyphenols and their derivatives was published, and only a few studies on branched polyphenols have been reported due to the inherent difficulties in the synthesis and purification.[13,14]

One of the most interesting applications of polyphenols is as the key starting raw materials of polybenzoxazine, which is an ideal alternative of traditional phenol-formaldehyde thermosets.[15-16] Polybenzoxazines are also proved to be an excellent carbon precursor, low-surface-energy and high-thermal-stable material, novel electrolyte material and microelectronic material and so on.[17-19] However, unsatisfied processability and high polymerization temperature limit their application in high-tech fields.[20-22] Feasible structural design of phenols or amines can solve these problems in some extent.[15-16] In order to improve the curing process, active hydrogen containing groups such as carboxylic[23] and phenolic groups[24,25] were incorporated into benzoxazine monomers, which could effectively decrease curing temperature due to their catalytic effect on ring-opening polymerization.

Cyclotriphosphazene (CP) derivatives are typical class of organic-inorganic hybrid compounds [26-28] and incorporation of the CP ring into organic compounds or polymers yields facinating polymermaterials.[29-33] We had a beneficial attempt in this area and preliminarily achieved meaningful results.[34,35] In this article, a novel CP-based dendritic polyphenol T2 was designed and synthesized through a relatively simple two-step reaction. Then, highly branched benzoxazine monomer based on cyclotriphosphazene, T3, was obtained by Mannich reaction of T2, aniline and paraformaldehyde. The representative monomers T3-23.6%, T3-46.6% and T3-75.2%, with oxazine ring content of 23.6%, 46.6% and 75.2%, respectively, were chosen to investigate their polymerization behaviors and corresponding polybenzoxazines' properties.

2. Experimental

2.1. Chemicals

Hexachlorocyclotriphosphazene [$N_3P_3Cl_6$] was recrystallized from dry hexane followed by sublimation (60 °C, 0.05 mmHg) twice before use. 4-hydroxybenzaldehyde (98%), phenol (99%), phosphotungstic acid (99%), thioglycolic acid (99%), paraformaldehyde (95%) and aniline (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Anhydrous potassium carbonate was dried at 140 °C prior to use. Tetrahydrofuran was distilled from sodium under a dry argon atmosphere.

2.2 Synthetic section

Synthesis of T1

T_1 was prepared according to the reported method.[36] Yield: 82%. M.P. = 160-162 °C. ^1H NMR (DMSO-d_6, TMS, ppm):6.74-7.78 (Ar-H, 8H, m), 9.48 (CH=N, 1H, s), 8.52(CH=N, 1H, s).^{13}C NMR (DMSO-d_6, TMS, ppm): 156.8 (C-OH), 156.0 (C=N), 151.8 (C-O), 142.7 (C-N), 134.4 (CH), 131.9 (CH), 129.9 (CH), 123.1 (CH), 121.0(C), 116.1 (CH), 115.5 (CH). ^{31}P NMR (DMSO-d_6, ppm): 8.75.

Synthesis of dendritic polyphenol T2

T2 was prepared according to the reported method[37] with a few modifications. A 250 mL three-necked flask was fitted with a magnetic stirring, a thermometer and a Dean-Stark trap. In the flask were placed with T1 (5.0 g, 5.8 mmol), phenol (19.6 g, 208.8 mmol), phosphotungstic acid (1.0 g, 0.35 mmol) and 0.1mL of thioglycolic acid, 80 mL of cyclohexane. The mixture was heated to 100 °C with azeotropic removal of the water formed. Water produced during the reaction was separated out by azeotropic distillation with cyclohexane. The azeotropic distillation was continued until no more water came out. The volatile materials were removed by rotary evaporation and the residue was precipitated in large amount of water, the resulting red solid was filtered off and washed with chloroform and dried in vacuum at 40 °C for 48 h. The crude product was recrystallized from ethyl alcohol/water (1/2). Light yellow powder was collected and dried in vacuum at 50 °C for 48 h. (Scheme 1)
Yield: 78%. ^1H NMR (DMSO-d_6, TMS, ppm): 6.67-6.84 (Ar-H, 12H, m), 5.23 (Ar-CH, 1H, s), 9.29 (Ar-OH, 2H, s). ^{13}C-NMR (DMSO-d_6, TMS, ppm): 56.0 (C-OH), 155.06 (C-O), 148.42 (C), 134.85 (CH), 130.26 (CH), 120.72 (CH), 15.52 (CH), 54.21 (C-CH). ^{31}P NMR (DMSO-d_6, ppm): 8.99.

Synthesis of branched benzoxazine monomers

T3 was prepared according to the reported method[38] with a few modifications. The typical procedure was as follows: A 250 mL three-necked flask was fitted with a magnetic stirring, a thermometer and a Dean-Stark trap. Aniline (6.69 g, 71.93 mmol) and paraformaldehyde (4.32 g, 143.64 mmol) were mixed and stirred in ice bath for 1 h. Then 150 mL toluene, 50 mL DMAc, T2 (15 g, 7.98 mmol) were added into the mixture under stirring. The mixture was gently heated to 110 °C and refluxed for 72 h. Water produced during reaction was separated out by azeotropic distillation with toluene. The samples for different reaction time (3 h, 24 h and 72 h) were sucked with a syringe. After removed the solvents, the residue was collected and dried in vacuum at 50 °C for 48 h. (Scheme 1)

2.3 Measurements

The structure of the compounds were verified by solution-state proton (^1H), 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 phosphorus frequency at room temperature. Chemical shifts are reported in ppm downfield from $SiMe_4$. Thermal transitions were monitored with a differential scanning calorimeter (DSC), Model 204F1 from NETZSCH Instruments, and scan rate of 10 °C/min over a temperature range of 30~300 °C and nitrogen flow rate of 20 mL/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 70 mL/min. A heating rate of 20 °C/min was used and scanning range was from RT to 1000 °C. Infrared spectra were recorded using a Bruker VERTEX 70 Fourier transform infrared spectrometer (FT-IR) under ambient condition. And the potassium bromide disks were prepared by compressing the powder. Mechanical properties were measured using a dynamic mechanical thermal analysis (DMA) apparatus (PerkinElmer, Diamond DMA). Specimens (50×10×1.0 mm) were tested in 3 point bending mode. The thermal transitions were studied in the scope of 20~300 °C at a heating rate of 4° C/min and at a fixed frequency of 1 Hz.

2.4 Preparation of polybenzoxazines

Samples for dynamic mechanical analysis (50×10×1.0 mm), dielectric measurement (20×10×1.0 mm) and humidity absorption test (50×10×1.0 mm) were prepared as follows: Three benzoxazine monomers were added to the tinfoil mold and gently melted at 150 °C under vacuum for 1 h. Later, the samples were heated stepwise and cured in a temperature-controlled oven at 160 °C and 180 °C each for 8 h, then post-cured at 200 °C and 220 °C each for 2 h. Thereafter, samples were allowed to cool slowly to room temperature to prevent cracking. At last, samples were polished to be regularly shaped.

2.5 Gel content of polybenzoxazines

The gel fraction of the samples (50×10×1.0 mm) was determined by standard extraction method[39] using chloroform. The process was involved in continuous extraction with chloroform in a 500 mL round bottom flask for 72 h until constant weight obtained. After the extraction, the samples were dried and the gel content was calculated according to the formula (1) as follows, where m_t and m_0 represented sample weights after and before extraction, respectively.

$$\text{Gel Content (\%)} = \frac{m_t}{m_0} \times 100\% \qquad (1)$$

2.6 Dielectric measurements of polybenzoxazines

Dielectric constant and dielectric loss were measured at room temperature in an air atmosphere by the two parallel plate modes at 125 Hz ~ 18 MHz using Agilent 4294A Precision Impedance Analyzer.[40,41]A sample (about 20 mm×10 mm×2 mm) was placed between the two copper electrodes to form a parallel plate capacitor. Prior to each measurement, the sample was dried under vacuum at 100 °C for 3 h.

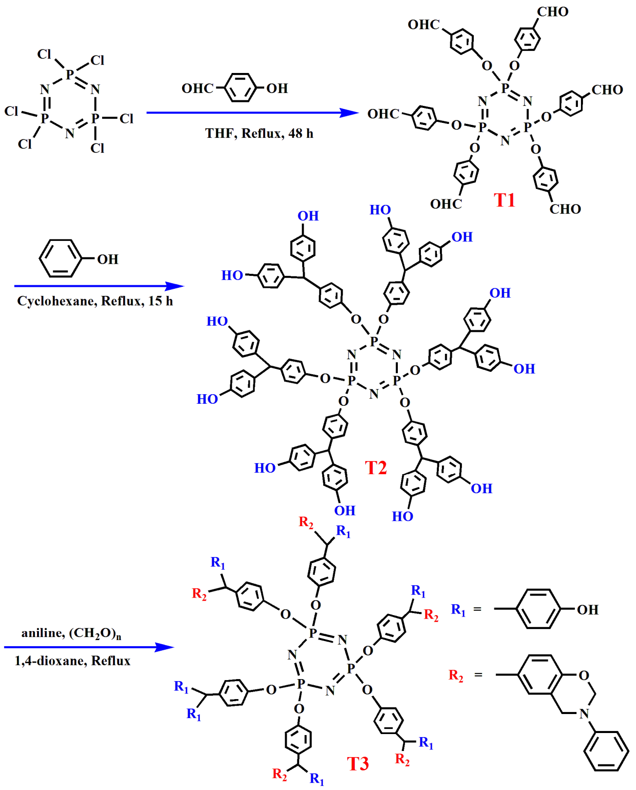
2.7 Humidity absorption

In the humidity absorption measurements, the cured samples were conditioned under vacuum at 90 °C for 20 h before placed in air (75% and 33% RH).[42] All these experiments were conducted at room temperature. Then, the weight percentages of humidity absorption of the cured samples were calculated according to the formula (2) as follows, where the W_t and W_0 represented the sample weights after and before (dry sample) humidity absorption, respectively. Humidity absorption content was measured for 5 samples of each material group and the average values were recorded.

$$\text{Humidity absorption content (\%)} = \frac{W_t - W_0}{W_0} \times 100\%, \qquad (2)$$

3. Results and discussion

3.1 Synthesis and characterization of polyphenol T2



Scheme 1. Synthesis of dendritic polyphenol T2 and branched benzoxazine monomer T3 (R1 and R2 were a random distribution and the sum was 12).

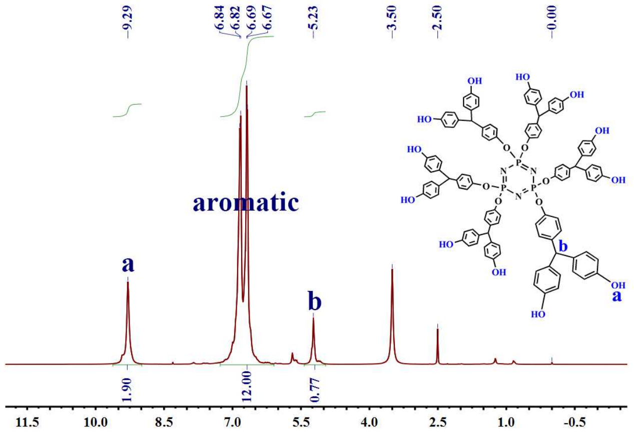


Fig. 1 ^{1}H NMR spectrum of T2 (solvent: DMSO-d_6)

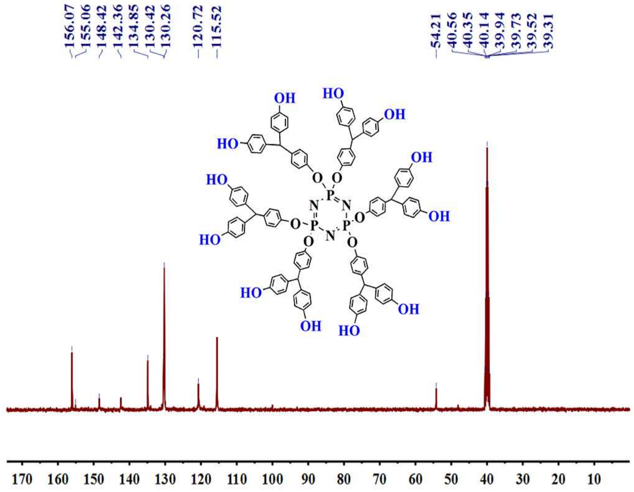


Fig. 2 ^{13}C NMR spectrum of T2 (solvent: DMSO-d_6)

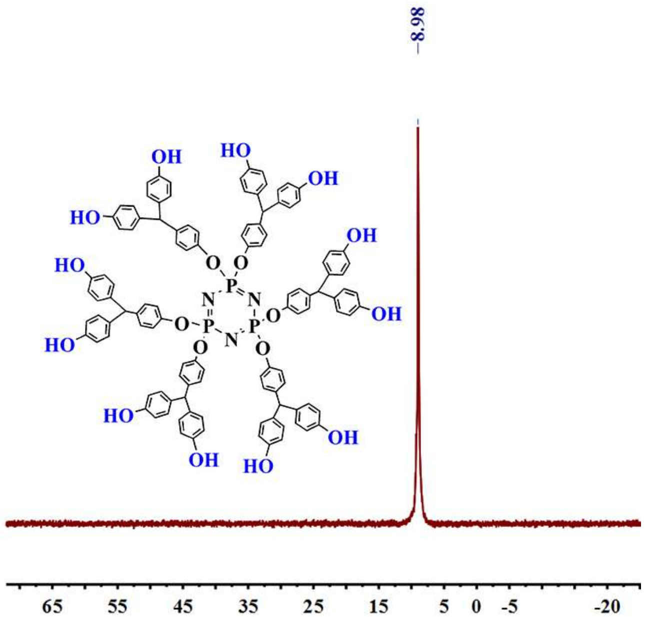


Fig. 3 ^{31}P NMR spectrum of T2 (solvent: DMSO-d_6)

Branched polyphenol T2 was facilely prepared via the condensation of T1 with phenol catalyzed by phosphotungstic acid and thioglycolic acid (Scheme 1). Initially, we performed the reaction in the solvent of toluene, but ^{1}H NMR analysis showed the purity of the product was poor due to the high azeotropic temperature in toluene-water system. To reduce side reactions, which might result from the oxidation of phenolic hydroxyls and the deactivation of catalysts, cyclohexane was used in the reaction. Main impurities (phenol and catalysts) in the crude product were easy to remove through repeated dissolution in ethanol and precipitation in water. T2 with high purity were obtained by recrystallized from ethyl alcohol/water. The dendritic polyphenol exhibited excellent solubility in common organic solvents such as methanol, ethanol, acetone, 1,4-dioxane, THF, ethyl acetate, DMSO and DMF, etc..

Fig. 1 showed the ^{1}H NMR spectra of T2. Peaks at 9.29 ppm (Ar-OH) and 5.23 ppm (Ar-CH) verified the successful introduction of phenol to T1 structure. Signals at 6.67-6.84 ppm for Ar-H were also observed. In the corresponding ^{13}C NMR spectrum in Fig. 2, resonance appearing at 54.21 ppm was assigned to the methyne carbon of Ar-CH. Other chemical shifts (ppm) were assigned to the aromatic carbon resonances: 156.0 (C-OH), 155.06 (C-O), 148.42(C), 134.85 (CH), 130.26 (CH), 120.72 (CH), 115.52 (CH). The ^{31}P NMR was shown in Fig. 3, and a single peak appeared at 8.98 ppm, which indicated that the substituted reaction of phenol onto T1 was complete.

3.2 Synthesis of branched benzoxazine monomers

T3 was synthesized using phenol (T2), aniline, and formaldehyde according to Scheme 1. As shown in Scheme 1, the benzoxazine and phenol groups were randomly distributed as branches of benzoxazine monomer T3. The exact position and numbers of the benzoxazine and phenol groups in T3 molecule were time-dependent and could not be determined. But the sum of the benzoxazine and phenol groups in T3 molecule was 12. As the reaction proceeds, the phenol groups would be gradually turned into the benzoxazine groups through Mannich reaction. The formation of oxazine rings was monitored by ^{1}H NMR and the results were presented in Fig. 4. Resonances appearing at 4.50 ppm and 5.27 ppm are assigned to the methylene protons of O-CH_2-N of the benzoxazine ring, respectively. The multiplets at 6.66-6.80 ppm are assigned to the aromatic protons. The singlet peak at 9.28 ppm is assigned to the unreacted phenolic hydroxy proton. The single peak at 5.73 ppm is assigned to the methine proton connected with three phenyl rings.

The oxazine ring content for benzoxazine monomers at given time interval was determined from ^{1}H NMR spectra using the equation (3) as follows.

$$C(\%)=\frac{3R}{1-2R}\times 100\% \qquad (3)$$

where C is the oxazine ring content at given time interval, R the ratio of integral area of methylene protons for O-CH_2-N and the integral area of all aromatic protons. The equation was established in the condition of not considering the opening of oxazine ring. Different oxazine ring content for all monomers at given time interval was listed in Table S1. The estimated oxazine ring content after 3 h, 24 h and 72 h was 23.6%, 46.6% and 75.2%, respectively. The peak assigned to the phenolic hydroxyl still exists after 72 h, so it is not necessary to prolong the reaction time.

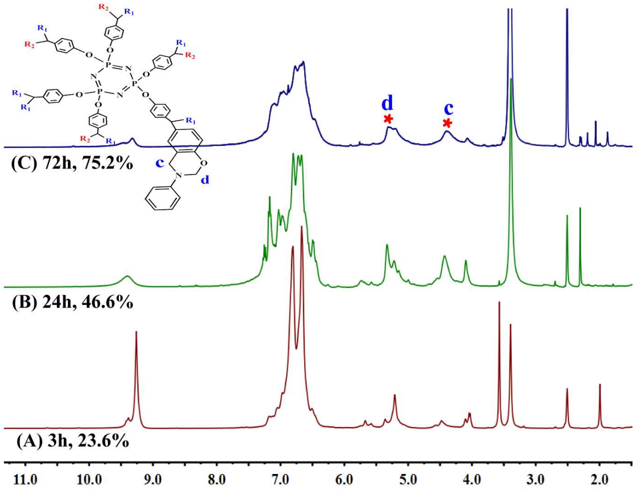


Fig. 4 ^{1}H NMR spectra of branched benzoxazine monomers (solvent: DMSO-d_6). The different oxazine ring contents at given time interval were marked in the spectra.

3.3 DSC studying the curing behavior of branched benzoxazine monomers

It is known that the high polymerization temperature is a major drawback that limits the application of polybenzoxazine. The polymerization temperature of the three hydroxyl-containing benzoxazine monomers was examined by DSC and the results were shown in Fig. 5 and summarized in Table 1. A wide exothermic peak corresponding to the ring-opening polymerization was observed for T3-23.6 % in which the onset and maximum temperatures of the exotherm were 97.2 °C and 201.5 °C, respectively. With the increase of oxazine ring content, the exothermic peaks changed obviously from the DSC results. For T3-46.6 %, the onset and maximum temperatures of the exotherm were increased to 169.7 °C and 222.4 °C, respectively; for T3-75.2%, the onset and maximum temperatures of the exotherm were separately increased to 170.8 °C and 206.4 °C, respectively. Comparing to T3-46.6% and T3-75.2%, the polymerization temperature for T3-23.6% was obviously reduced. The results indicated that hydroxyl groups could reduce the onset polymerization temperature of benzoxazine monomers, which was in accordance with other report.[24] Nevertheless, the maximum temperature of the exotherm gave the ascending order of T3-23.6 %, T3-75.2% and T3-46.6 %. The reason for the higher maximum temperature of T3-46.6% than T3-75.2% may be due to the different oxazine ring distribution in T3-46.6 % and T3-75.2 %. It was reported that the side groups of the CP derivatives were arranged approximately perpendicular to the CP ring, forming parallel triplets pointing upward and downward to give a calamitic superstructure capable of being organized in a nematic phase.[43,44] It meant that the oxazine rings and hydroxyl groups were distributed separately in the top and bottom faces of the CP plane. In addition, the position of hydroxyl group relative to benzoxazine structure played a significant role in accelerating the polymerization.[45] For T3-46.6 %, the oxazine ring content was close to 50%, and the oxazine rings and hydroxyl groups were nearly distributed at far intervals as the branches of T3-46.6 %. While for T3-75.2 % with far more oxazine ring content than that of T3-46.6 %, the high concentration of oxazine rings were closer to the hydroxyl groups, which benefited the catalytic efficiency of the hydroxyl groups.

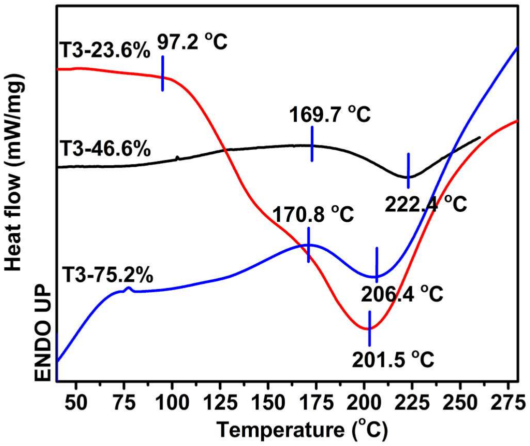


Fig. 5 DSC curves of polybenzoxazines by curing monomers T3-23.6%, T3-46.6% and T3-75.2%.

3.4 Gel contents of the polybenzoxazines

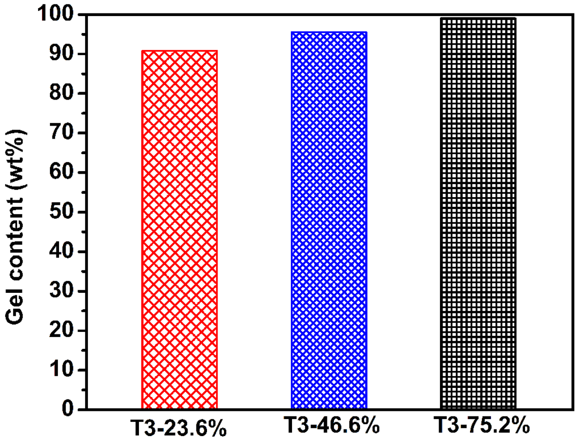


Fig. 6 Gel contents of the polybenzoxazines PT3-23.6%, PT3-46.6% and PT3-75.2%.

The gel contents of the polybenzoxazines cured by monomers T3-23.6%, T3-46.6% and T3-75.2% were determined using the methodology described in the experimental part, and the results were shown in Fig. 6. The gel contents of PT3-23.6%, PT3-46.6% and PT3-75.2% were 90.8%, 95.5% and 99%, respectively. The results indicated that the gel contents of all polybenzoxazines depended on different oxazine ring content of the monomers. The increase of the oxazine ring content in the monomer would bring high gel content and high crosslinking density. For the polybenzoxazine PT3-23.6% cured by monomer T3-23.6%, in which the oxazine ring content was 23.6%, the gel content reached 90.8%, which was the lowest among the three monomers. It meant that even small amount of benzoxazine units attached on the middle molecular weight polyphenol T2 (mol. W_t = 1882 g/mol) could act as effective crosslinkers to form thermosets with high crosslinking density. When the oxazine ring content exceeded 50%, the gel content of the corresponding polybenzoxazine was above 95%.

3.5 Thermal properties of cured polymers

Thermal stability of the three polybenzoxazines was investigated by TGA. The TGA profiles were shown in Fig. 7, and the details were shown in Table 1. The 5% and 10% weight loss temperatures ($T_{5\%}$ and $T_{10\%}$) for the polybenzoxazine PT3-23.6% were 375 and 407 °C, respectively. While for PT3-46.6% and PT3-75.2%, the $T_{5\%}$ and $T_{10\%}$ were all higher than that of 23.6%: for PT3-46.6%, they were 408 and 437 °C, respectively; for PT3-75.2%, they were 427 and 474 °C, respectively. Similarly, the maximum weight loss temperature (T_{max}) of the polybenzoxazine PT3-75.2% was also lower than those of PT3-23.6% and PT3-46.6%. The Y_c of PT3-75.2% was as high as 56.2%, and PT3-23.6% and PT3-46.6% were much lower than that of PT3-75.2%, the PT3-23.6% sample held the lowest yield, only 46.8%.

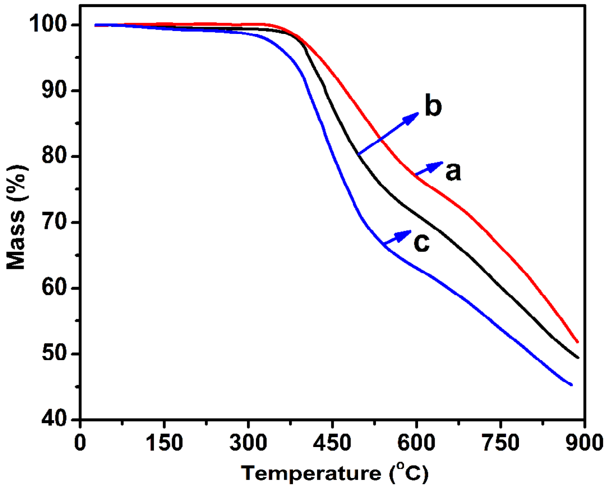


Fig. 7 TG curves of polybenzoxazines. a. PT3-75.2%, b. PT3-46.6%, c. PT3-23.6 %.

From the TGA results, we could deduce that the organic-inorganic hybrid polybenzoxazines, by curing the above monomers T3-23.6%, T3-46.6% and T3-75.2%, showed outstanding thermal stability. It was considered that the rigid inorganic CP ring enhanced the thermal stability of the polybenzoxazines which provide thermally stable sites comparing to the traditional main-chain type polybenzoxazine such as bisphenol-based polybenzoxazines.[23] Furthermore, the number of benzoxazine moieties on CP ring also played an important role in the thermal stability of polybenzoxazines by improving cross-linked density and minimizing dangling side groups. Hence, the higher the oxazine ring content, the better the thermal stability of the polybenzoxazine was.

Table 1 Thermal stability of polybenzoxazines by curing T3-23.6%, T3-46.6% and T3-75.2%

Samples	T_o [a] (°C)	T_{max} [b] (°C)	$T_{5\%}$ [c] (°C)	$T_{10\%}$ [d] (°C)	$T_{max.}$ [e] (°C)	Y_c [f] (%)
T3-23.6%	97.2	201.5	375	407	403	46.8
T3-46.6%	169.7	222.4	408	437	435	51.9
T3-75.2%	170.8	206.4	427	474	498	56.2

[a] Onset temperature of exothermic peak .

[b] Maximum of the polymerization exotherm.
[c] The temperature for 5% weight loss
[d] The temperature for 10% weight loss.
[e] Maximum weight loss temperature.
[f] Char yields at 850 °C.

3.6 Mechanic properties of polybenzoxazines

The dynamic mechanical properties of the CP-based polybenzoxazines PT3-23.6%, PT3-46.6% and PT3-75.2% were measured from room temperature to the rubbery plateau of each material. The storage moduli (E') of these polybenzoxazines were presented in Fig. 8(A). The E' value of PT3-23.6% at room temperature was 0.319 GPa, while they were 1.03 GPa and 2.16 GPa for PT3-46.6% and PT3-75.2%, respectively. The E' value of the polybenzoxazine were influenced by the number of the benzoxazine moieties, which led to more spatial crosslinking sites. Hence, the high oxazine ring content was greatly in favor of the increase of the E' value for the corresponding polybenzoxazine.

The glass transition temperature (T_g) is also an important property of the polybenzoxazines, which could be deduced from the corresponding peak temperature of tan δ value in Fig. 8(B). The T_g of PT3-23.6% was 173.3 °C, while they were 175.1 °C and 179.2 °C for PT3-46.6% and PT3-75.2%, respectively. The highest cross-linked degree for PT3-75.2% could constrain the move of the cross-linked chains under heat and let them start to move at higher temperature. Thus, the T_g of PT3-75.2% was higher than that of PT3-23.6% and PT3-46.6%. Besides, the PT3-75.2% sample produced a broader glass transition than PT3-23.6% and PT3-46.6%, which meant that the composition distribution in PT3-75.2% was not so narrow as that in PT3-23.6% and PT3-46.6%.

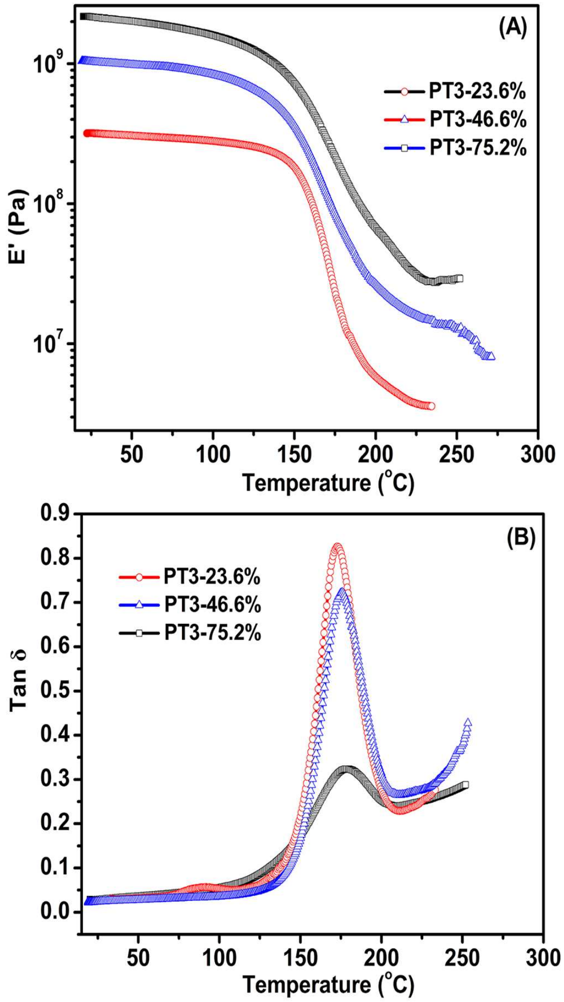


Fig. 8 Storage moduli (A) and Tan δ (B) of polybenzoxazines PT3-23.6%, PT3-46.6% and PT3-75.2%.

3.7 Dielectric analysis of polybenzoxazines

Dielectric property of polymers is one of the key characters for its application in microelectronic devices.[40] The dependence of the dielectric constant and dielectric loss of the three polybenzoxazine samples PT3-23.6%, PT3-46.6% and PT3-75.2% were studied in the frequency range of 125 Hz ~ 10^6 Hz at room temperature. Fig. 9 showed that both the dielectric constant (ε) and the dielectric loss (tan δ) depended largely on the oxazine ring content. For the dielectric constant and dielectric loss was directly related to the polarizability of material and could be increased by increasing the polarizability. Therefore, the dielectric constant and dielectric loss were strongly dependent on its chemical structure.[41] Dielectric constants of the polybenzoxazine PT3-23.6% at 125 Hz was about 5.74, for PT3-46.6% and PT3-75.2%, the value changed to 4.57 and 4.45, respectively. In the frequency range of 125 Hz to 10^6 Hz, the dielectric constant for each sample showed a little decrease. When the frequency of applied field increased to 10^6 Hz, the dielectric constants of PT3-23.6%, PT3-46.6% and PT3-75.2% declined to 4.85, 4.09 and 3.75, respectively. It was because that PT3-75.2% was highly cross-linked polymer and most components linked together by chemical bonds, so it showed lowest polarizability. While for PT3-23.6% and PT3-46.6%, cured by the monomers with the oxazine ring content of 23.6% and 46.6%, respectively, the uncrosslinked groups acted as polar pendant groups linked to the network by chemical bond and increased the polarizability. The dielectric loss of PT3-23.6%, PT3-46.6% and PT3-75.2% at 125 Hz were 0.061, 0.042 and 0.040, respectively. These values showed little changes in the frequency range of 125 Hz ~ 10^6 Hz. The reason for such changes was the same as that of the dielectric constant.

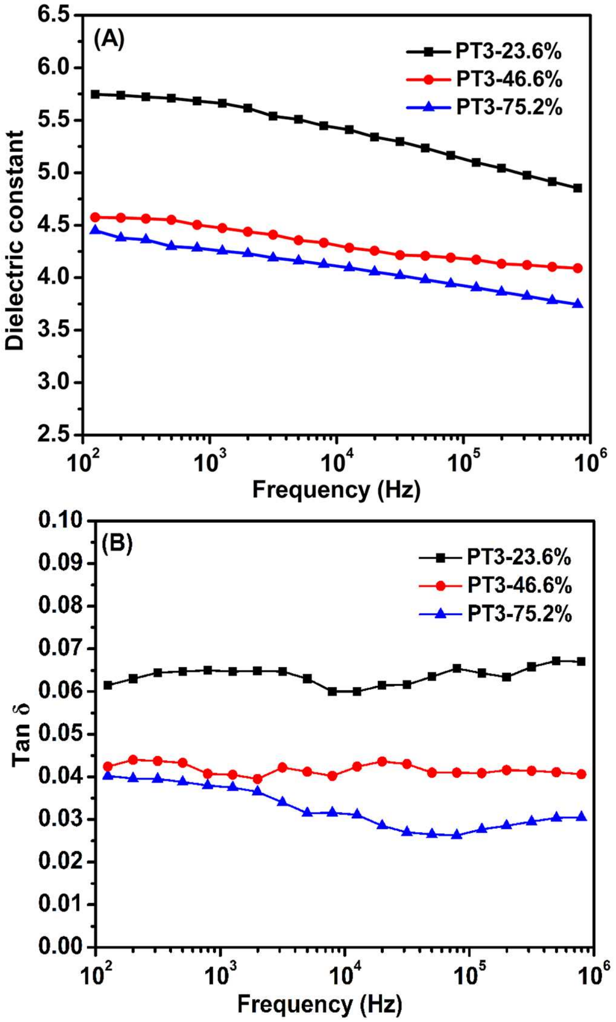


Fig. 9 Frequency dependence of the dielectric constant (A) and dielectric loss (B) of the polybenzoxazines PT3-23.6%, PT3-46.6% and PT3-75.2%.

3.8 Humidity absorption of the polybenzoxazines

The humidity absorption of the three polybenzoxazine samples PT3-23.6%, PT3-46.6% and PT3-75.2% were measured at different relative humidity (RH = 75% & 33%) at room temperature. As shown in Fig. 10, all the polybenzoxazine samples exhibited a low water uptake value (< 1.0 wt%) at room temperature after 10 days regardless of the RH value of the air was high or low duo to the complete hydrogen-bond network formed between phenolic OH and nitrogen atoms which hinder the water absorption and transportation.[42] Meanwhile, the water uptake ability of the samples changed regularly with the increase of the oxazine ring content. The final water absorption values of the three polybenzoxazines decreased in the order of PT3-23.6%, PT3-46.6% and PT3-75.2%. The value of PT3-23.6% was about 0.95 wt%, and the value decreased to about 0.79 wt% and 0.66 wt% for PT3-46.6% and PT3-75.2%, respectively. The lower water uptake ability of PT3-75.2% was attributed to the higher crosslinking density in the network.

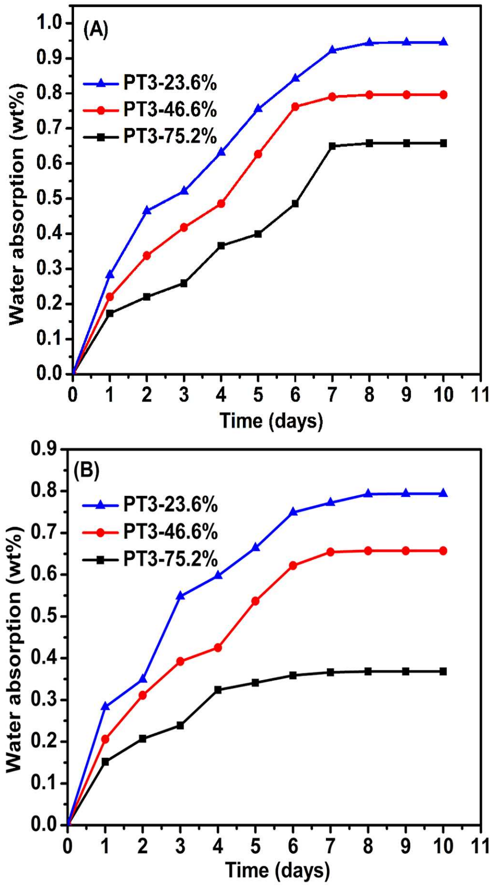


Fig. 10 Humidity adsorption of the polybenzoxazines PT3-23.6%, PT3-46.6% and PT3-75.2% at different relative humidity (RH) at room temperature. a. RH=75%; b. RH=33%.

4. Conclusions

We synthesized a novel dendritic organic-inorganic hybrid polyphenol (T2) based on cyclotriphosphazene. The dendritic polyphenol possessed good solubility in common solvents. Based on the dendritic phenol, three branched benzoxazine monomers T3-23.6%, T3-46.6% and T3-75.2% with different content of phenolic hydroxyl groups were synthesized via Mannich condensation reaction. The polymerization behaviors of the monomers and properties of the polybenzoxazines depended largely on the oxazine ring content of corresponding monomers. These monomers T3-23.6%, T3-46.6% and T3-75.2% showed low initial polymerization temperature due to the catalytic effect of their phenolic hydroxyl groups. The more phenolic hydroxyl groups the monomer had, the easier it started to ring-opening polymerization under heat. The thermal stability, mechanic property, dielectric property and humidity absorption of the polybenzoxazines relied on the oxazine ring content in corresponding monomers. The char yields at 850 °C were near to

60%, T_g were all higher than 170 °C, and dielectric constants were about 4 at 1 MHz, and corresponding humidity absorptions of them were below 1.0 wt% (the lowest one was about 0.66 wt%). Combined with the excellent performances of polybenzoxazines, we believe that the facile synthesis and versatility of dendritic polyphenol are attractive potentials that will lead to many additional applications beyond the one we have described.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 21274049), the Opening Project of Key Laboratory of Optoelectronic Chemical Materials and Devices of Ministry of Education, Jianghan University (No. JDGD-2013-06) and the Fundamental Research Fund for Central Universities (2013QN159). All authors give sincerely thanks to Analysis and Testing Center of HUST for NMR and DMA test.

Notes and references

[a] *School of Chemistry and Chemical Engineering, Key Laboratory for Large-Format Battery Materials and System, Ministry of Education, Huazhong University of Science and Technology, Wuhan, 430074, P.R. China*
* *Author to whom correspondence should be addressed. Tel: +86-27-87559627; Fax: +86-27-87559627; E-mail: liukui@mail.hust.edu.cn*

1 B. Lochab, S. Shukla and I. K. Varma, *RSC Advances*, 2014, **4**, 21712 21752.
2 W. Jiang, K. Lai, K. Liu, R. Xia, F. Gao, Y. Wu and Z. Gu, *Nanoscale*, 2014, **6**, 1305-1310.
3 D. G. Barrett, T. S. Sileika and P. B. Messersmith, *Chem. Commun.* 2014.
4 J. A. Nichols and S. K. Katiyar, *ARCH. DERMATOL. RES.*, 2010, **302**, 71-83.
5 E. Haslam, *Practical polyphenolics: from structure to molecular recognition and physiological action*, Cambridge University Press, 1998;
6. V. R. Preedy, *Tea in health and disease prevention*, Elsevier, London, 2013
7 T. S. Sileika, D. G. Barrett, R. Zhang, K. H. A. Lau and P. B. Messersmith, *Angew. Chem. Int. Ed.*, 2013, **52**, 10766-10770.
8 Z. H. Gong, C. M. Leu, F. I. Wu and C. F. Shu, *Macromolecules*, 2000, **33**, 8527-8533.
9 D. Bratton, R. Ayothi, H. Deng, H. B. Cao and C. K. Ober, *Chem. Mater.*, 2007, **19**, 3780-3786.
10 A. D. Silva, L. K. Sundberg, H. Ito, R. Sooriyakumaran, R. D. Allen and C. K. Ober, *Chem. Mater.*, 2008, **20**, 7292-7300.
11 T. Nakayama and M. Ueda, *J. Mater. Chem.*, 1999, **9**, 697-702.
12 J. Liu, Y. Qiao, Z. Liu and L. Wang, *RSC Advances*, 2014, **4**, 21093-21100.
13 J. Zhang, H. Wang and X. Li, *Polymer*, 2006, **47**, 1511-1518.
14 H. Wu, X. Huang, M. Gao, X. Liao and B. Shi, *Green Chem.*, 2011, **13**, 651-658.
15 N. Ghosh, B. Kiskan and Y. Yagci, *Prog. Polym. Sci.*, 2007, **32**, 1344-1391.
16 Y. Yagci, B. Kiskan and N. N. Ghosh, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 5565-5576.
17 C. F. Wang, Y. C. Su, S. W. Kuo, C. F. Huang, Y. C. Sheen and F. C. Chang, *Angew. Chem. Int. Ed.*, 2006, **45**, 2248-2251.
18 C. H. Lin, S. L. Chang, T. Y. Shen, Y. S. Shih, H. T. Lin and C. F. Wang, *Polym. Chem.*, 2012, **3**, 935-945.
19 S. K. Kim, T. Ko, K. Kim, S. W. Choi, J. O. Park, K. H. Kim, C. Pak, H. Chang and J. C. Lee, *Macromolecular Research*, 2012, **20**, 1181-1190.
20 P. Yang, X. Wang, H. Fan and Y. Gu, *Phys. Chem. Chem. Phys.*, 2013, **15**, 15333-15338.
21. T. Agag and T. Takeichi, *Polymer*, 2000, **41**, 7083-7090.
22. W. C. Chu, J. G. Li and S. W. Kuo, *RSC Advances*, 2013, **3**, 6485-6498.
23. W. H. Hu, K. W. Huang and S. W. Kuo, *Polym. Chem.*, 2012, **3**, 1546-1554.
24. R. Andreu, J. Reina and J. Ronda, *J. Polym. Sci., Part A: Polym. Chem.*,2008, **46**, 6091-6101.
25. W. Men, Z. Lu and Z. Zhan, *J. Appl. Polym. Sci.*, 2008, **109**, 2219-2223.
26 H. R. Allcock, *Wiley-Interscience*, 2003.
27 S. Sudhakar and A. Sellinger, *Macromol. Rapid Commun.*, 2006, **27**, 247-254.
28 J. Y. Chang, H. J. Ji, M. J. Han, S. B. Rhee, S. Cheong and M. Yoon, *Macromolecules*, 1994, **27**, 1376-1380.
29 P. Mohanty, L. D. Kull and K. Landskron, *Nat Commun*, 2011, **2**, 401.
30 C. Y. Yuan, S. Y. Chen, C. H. Tsai, Y. S. Chiu and Y. W. Chen-Yang, *Polym. Adv. Technol.*, 2005, **16**, 393-399.
31 M. Harmjanz, B. L. Scott and C. J. Burns, *Chem. Commun.*, 2002, 1386-1387.
32 Y. W. Cho, J.R. Lee and S.C. Song, *Bioconjugate Chem.*, 2005, **16**, 1529-1535.
33 P. Jia, J. Xu, J. Ma and X. Lu, *Eur. Polym. J. nal*, 2009, **45**, 772-778.
34 X. Wu, S. Z. Liu, D. T. Tian, J. J. Qiu and C. M. Liu, *Polymer*, 2011, **52**, 4235-4245.
35 X. Wu, Y. Zhou, S. Z. Liu, Y. N. Guo, J. J. Qiu and C. M. Liu, *Polymer*, 2011, **52**, 1004-1012.
36 G. A. Carriedo, L. Ferńndez‐Catuxo, F. J. G. Alonso, P. G. Elipe, P. A. Gonźlez and G. Śnchez, *J. Appl. Polym. Sci.*, 1996, **59**, 1879-1885.
37 J.-z. Xu, N.-z. Jiang, J. Zhang and R.-s. Jiang, *CHEM . RES. CHINESE U.*, 2005, **21**, 65-68.
38 S. W. Choi, H. Y. Sun, M. J. Lee and W. S. Jeon, *EUROPEAN PATENT*, 1760110 A1, 2006.
39 M. Claudino, J. M. Mathevet, M. Jonsson and M. Johansson, *Polym. Chem.*, 2014, **5**, 3245.
40 H. C. Chang, H. T. Lin and C. H. Lin, *Polym. Chem.*, 2012, **3**, 970-978.
41 K. D. Demir, B. Kiskan, S. S. Latthe, A. L. Demirel and Y. Yagci, *Polym. Chem.*, 2013, **4**, 2106-2114.
42. J. Sundberg, G. Toriz and P. Gatenholm, *Polymer,* 2013, **54**, 6555-6560.
43. K. Moriya, T. Suzuki, S. Yano and S. Miyajima, *J. Phys. Chem. B*, 2001, **105**, 7920-7927.
44. J. Barbera, M. Bardaji, J. Jimenez, A. Laguna, M. P. Martinez, L. Oriol, J. L. Serrano and I. Zaragozano, *J. Am. Chem. Soc.*, 2005, **127**, 8994-9002.
45. M. Baqar, T. Agag, R. Z. Huang, J. Maia, S. Qutubuddin and H. Ishida, *Macromolecules*, 2012, **45**, 8119-8125.