A high temperature polymer of phthalonitrile-substituted phosphazene with low melting point and good thermal stability

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ABSTRACT: A phthalonitrile-substituted phosphonitrilic monomer has been synthesized from phosphonitrilic chloride trimer and then polymerized with addition of 4-(hydroxylphenoxy)phthalonitrile (HPPN). The chemical structures of the phosphonitrilic monomer and polymer were characterized by Fourier Transform Infrared spectroscopy (FT-IR) and proton Nuclear Magnetic Resonance spectroscopy (^{1}H NMR). Curing behaviors and thermal stabilities of the polymer were investigated through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Analysis showed that the monomer has large processing temperature window and good thermal stability. Apparent activation energy, initial curing temperature (T_i), curing temperature (T_p), and termination curing temperature (T_f) of the phosphonitrilic polymer were explored. Dynamic mechanical analysis (DMA), glass transition temperature (T_g) were studied, and limiting oxygen index (LOI) were estimated from the van Krevelen equation, which indicates the polymer process high modulus and good flame retardance. Micro-scale combustion calorimetry (MCC) was also used for evaluating the flammability of the polymers. Postcuring effects were explored, showing excellent thermal and mechanical properties with postcuring. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42606.

INTRODUCTION

Phthalonitrile resins were originally developed by the Naval Research Laboratory (NRL) more than 30 years ago, which act as a unique class of high-performance thermosetting polymers with a variety of applications in aerospace, marine, and microelectronic areas. Compared to other conventional polymers, the resins possess a number of exceptional properties such as high glass transition temperatures (T_g), outstanding thermal and thermo-oxidative stability, good mechanical properties, good moisture and fire resistance, and high char yield.[1–9] So far, a variety of phthalonitrile-based monomers with structural modifications have been synthesized and their polymers were prepared to enhance the thermal stability, lower the melting point, and increase processing window (the temperature difference between the melting point of the monomer and the exothermic curing temperature) with good processability retained.[10–15]

Phthalonitrile-based monomers can be polymerized thermally; however, neat polymerization is extremely sluggish. The polymer-ization process can be enhanced with the aid of various curing additives, among which the most common ones are aromatic diamines.[10] However, a slowdown of the curing process resulted from volatility of amines has been observed.[4] To solve these problems, two sulfone-containing diamines, bis[4-(3-aminophenoxy)phenyl] sulfone (m-BAPS) and bis[4-(4-aminophenoxy)phenyl] sulfone (p-BAPS), with higher molecular weights and lower volatility and reactivity than those of 1,3-bis(3-aminophenoxy)benzene (m-APB), were chosen as curing agents to improve the processability of phthalonitrile-based resins.[4] Recently, phthalonitrile resins, with different proportions of amino or hydroxy groups in the molecular structure, were found to exhibit self-promoted cure behaviors.[16–19] A variety of self-catalyzed phthalonitrile resins with different main chain structures of aromatic ether, aromatic ether ketone, or aromatic ether imide have been developed.[20,21] More and more attentions have been paid to the self-catalyzed phthalonitrile resins for avoiding addition of catalysts.

On the other hand, polyphosphazene is a class of high molecular-weight polymers consisting of alternating nitrogen and phosphorus

atoms in the backbone of the polymer and the groups in side chains. Since its inorganic and organic parts are close to each other and its main chain is different from typical organic carbon chains, they show outstanding physical and chemical properties compared to those of other polymers.[22–26] The properties of polyphosphazene are influenced by the substitution groups on phosphorus atoms. By introduction of different groups to the phosphorus atoms, the prepared corresponding polymers are expected to possess special performance such as both high and low temperature resistance, excellent flexibility, good reaction active point, good biological compatibility, and biodegradability, etc.[27]

Phosphonitrilic chloride trimer is a kind of phosphazene and acts as an important intermediate material. The planar noncon-jugated 6-membered ring consisting of alternating P- and N-atoms provides high chemical and thermal stability and exhibits two bonding sites for substituents on each P-atom.[28] Several classes of cyclotriphosphazenes have been synthesized from the phosphonitrilic chloride trimer, each exhibiting differ-ent physical and chemical characteristics depending on the type and properties of substituents.[29] The incorporation of cyclotri-phosphazene groups into the polymer backbone is of consider-able interests as a result of their useful thermal and chemical properties. Currently cyclotriphosphazene has been mostly used in areas of flame retardants, thermosetting resin, filling materi-als, and adhesives, etc.[30,31]

The key to the development of high temperature polymers is incorporation of thermally stable structural units such as aro-matic and heteroaromatic rings or units such as silicon, nitrogen, and phosphorus within the backbone of a polymeric system. Many high temperature systems containing aromatic ether phos-phine oxide units within the polymeric structure have been devel-oped over the last 30 years including polyimides,[32] polyethers,[33] and polycyanurates.[34] These systems show enhanced thermal properties and better stability under oxidative conditions. However, little attention has been paid to the modification of phosphonitrile units with phthalonitrile substituents.[35]

In order to solve the problem of volatility of amine initiators and enhance the thermal and processing properties of polymers, we are interested in synthesis of a polymer containing phthalonitrile-substituted phosphonitrilic trimer units with self-promoted cur-ing agents. In this article, we introduced successful synthetic approach to a phosphonitrilic polymer with phthalonitrile sub-stituents, employing self-catalyzed phthalonitrile as the curing agent to initiate polymerization. The obtained polymer exhibits various good properties, such as a low melting point and a broad processing window for easy conversion to crosslinked polymers etc., allowing the resins to compete with other high performance polymeric materials.

EXPERIMENTAL

Materials

Phosphonitrilic chloride trimer (AR, >98.0%) was purchased from Aladdin Industrial Corporation, Shanghai, China and 4-nitrophthalonitrile (AR, >98.0%) was supplied by Jinan Weidu Chemicals, Jinan, China. Potassium carbonate and hydroquinone (AR, >98.0%) were purchased from Tianjin

Fengchuan Chemicals, with triethylamine (TEA, AR, >99.0%) from Tianjin Beilian Fine Chemicals Development Co., Tianjin, China. Acetonitrile (AR), N,N-dimethylformamide (DMF, AR), and anhydrous ethanol (AR, >=99.7%) were supplied by Tianjin Huadong Chemicals, Tianjin, China. All the solvents were used without further purification.

Characterizations

Fourier Transform Infrared (FT-IR) spectra were recorded on a Nicolet Nexus 670 FT-IR spectrometer in KBr pellets between 4000 and 400 cm^{-1} in air. proton Nuclear Magnetic Resonance spectroscopy (^{1}H NMR) spectra were obtained using a Bruker AV400 Nuclear Magnetic Resonance (NMR) spectrometer at a proton frequency of 400 MHz with DMSO-d$_6$ as the solvent. Dif-ferential Scanning Calorimetric (DSC) study was performed on a TA Instruments 2920 DSC from 50 to 350°C at a heating rate of 5, 10, 15, and 20°C/min with a nitrogen flow rate of 20 mL/min. Thermogravimetric analysis (TGA) was performed using a TA Instruments Q50 thermogravimetric analyzer at a heating rate of 10°C/min and from room temperature to 1000°C under nitrogen and air atmosphere with a flow rate of 100 mL/min, respectively. The micro-scale combustion calorimetry (MCC) measurement was conducted using a FTT0001 micro-scale combustion calorim-eter produced by British. The sample, approximately 3 mg, was heated to 700°C using a linear heating rate (1°C/s) in a stream of nitrogen flowing at 80 cm^3/min flow rate. The thermal degrada-tion products of the sample in nitrogen were mixed with a 20 cm^3/min stream of oxygen prior to entering the 900°C combustion furnace. Dynamic mechanical analysis (DMA) was recorded using a Tritec 2000 dynamic mechanical analyzer (British Triton Instruments) at a frequency of 1 Hz with a heating rate of 3°C/min from 30 to 380°C (the upper temperature limit of analyzer). Molecular weight and polydispersity of polymers were determined on a gel permeation chromatography (GPC) equipped with two liner Mixed-B columns (Polymer Lab Corpo-ration, PL-CPC220, column size 300×7.5 mm) and a refractive index detector at 40°C. The elution phase was THF (elution rate 1 mL/min) and polystyrene was used as the calibration standard.

Synthesis of Phthalonitrile Monomers

Synthesis of 4-(hydroxylphenoxy)phthalonitrile (HPPN). To a three-necked flask were added hydroquinone (9.6097 g, 87.27 mmol), potassium carbonate (6.0168 g, 43.53 mmol), and 40 mL of DMF. The mixture was stirred at room temperature for 1 h and 4-nitrophthalonitrile (7.5554 g, 43.62 mmol) was added. The mixture was continuously stirred at room tempera-ture for 24 h. Then the mixture was poured into 400 mL of dilute hydrochloric acid solution (0.1 mol/L). The precipitated gray solid was collected by suction filtration and washed with plenty of distilled water. After recrystallized from ethanol/water (the ratio of ethanol to water is 4 : 1), the product was dried at 80°C in vacuum oven for 24 h, yield: 76%. ^{1}H NMR (400 MHz, DMSO-d$_6$) [ppm]: δ 9.64 (s, 1H), 8.06 (d, ^3J=8.8 Hz, 1H), 7.68 (d, ^4J=2.4 Hz, 1H), 7.28 (dd, ^3J=8.8 Hz, ^4J=2.4 Hz, 1H), 7.02 (d, ^3J=8.8 Hz, 2H), 6.86 (d, ^3J=9.2 Hz, 2H).

Synthesis of [4-(3,4)-cyanophenoxy]-Phenoxy Cyclotriphosphazene (CPCP). Phosphonitrilic chloride trimer (HCCP, 0.7492 g, 2.15 mmol), acetonitrile (35 mL), triethylamine (2 mL), and HPPN

(3.0541 g, 12.93 mmol) were put in a three-necked flask. The mixture was heated with stirring at 65°C for 48 h and allowed to stand until crystals appeared and then filtered and collected the filtrate. Thereafter, the filtrate was concentrated and lyophilized in the refrigerator and the CPCP monomer was obtained, yield: 73%. IR (KBr, cm^{-1}): 2231(–CN), 1248(C–O), 1169 (P–O), 884(P–N), ^{1}H NMR (400 MHz, DMSO-d$_6$) [ppm]: δ 8.09–8.05 (m, 6H), 7.77–7.68 (m, 6H), 7.36–7.16 (m, 30H).

Preparation of Phosphonitrilic Polymer (CPCP Polymer). Phosphonitrilic polymer (CPCP polymer) was prepared from the synthesized CPCP monomer with the addition of 4-(hydroxylphenoxy)phthalonitrile (HPPN) at elevated temperatures. Firstly, 5 wt % of HPPN was added into CPCP monomer with vigorous stirring. Then the mixture was moved into a mold and melted at 90°C. Prepolymer was obtained through quenching the melted mixture to room temperature. Polymer was prepared in a muffle furnace, and the curing procedure was described as follows: 280°C, 2 h; 300°C, 2 h; 320°C, 2 h; 340°C, 2 h; 360°C, 2 h, and 380°C, 2 h. The prepared polymer was machined into rectangular specimens (35 mm×10 mm×2 mm) for DMA experiments, and a small amount of the phosphonitrilic polymer were used for TGA experiments.

Water Uptake Experiment
A sample of the polymer cured with 5 wt % HPPN up to 380°C was immersed into distilled water at room temperature for 480 h. The sample was removed from water, then blotted the sample surface water off with a tissue, and weighed every 24 h to determine the amount of water absorbed.

RESULTS AND DISCUSSION

Structural Characterization of HPPN and CPCP Monomer
The procedures of synthesis of CPCP phosphonitrilic monomer are presented in Scheme 1. As shown in Scheme 1, 4-(hydroxylphenoxy)phthalonitrile (HPPN) was synthesized as the intermediate material via substitution reaction of 4-nitrophthalonitrile and hydroquinone in the presence of K$_2$CO$_3$ in DMF. At the very beginning of the polycondensation, HPPN reacted with HCCP with hydrogen chloride generated, which was then absorbed by trimethylamine (TEA) to afford TEA·HCl. The reaction of HCl and TEA spontaneously accelerated the nucleophilic replacement reaction between the terminal hydroxy group and P–Cl. Thus, six chlorine atoms in phosphonitrilic chloride trimer could be substituted when heated in the presence of TEA.

The chemical structures of the as-prepared HPPN and CPCP monomer were characterized by FT-IR and ^{1}H NMR analyses.

In infrared (IR) spectrum of the CPCP monomer (Figure 1), the peak at 884 cm^{-1} is attributed to the P–N characteristic absorption of cyclotriphosphazene. A strong peak ascribed to P=N stretching vibration can be seen at 1169 cm^{-1},[35] with the absorption signals at 1248 cm^{-1} and 2231 cm^{-1} corresponding to stretching of C–O and the nitrile groups (–CN), respectively. At the same time, the absorption peak of P–O–Ph can be seen at 954 cm^{-1}, which proves the successful reaction of HCCP and HPPN. Proton NMR spectra of HPPN and CPCP monomer were exhibited in Figures 2 and 3, respectively, which are in line with the IR data.

In order to further demonstrate that the six chlorine atoms in phosphonitrilic chloride trimer could be substituted during the reaction, gel permeation chromatography (GPC) was used to characterize the molecular weight (Figure 4). Based on the GPC spectrum of CPCP monomer, the molecular weight distribution index is 1.08 and the number average molecular weight (Mn) is 1575, while theoretical calculated molar mass (M) is 1546, which confirmed the substitution of six chlorine atoms in phosphonitrilic chloride trimer. The small peak labelled 370 might be the residual material of HCCP.

Generally, most of the phthalonotrile monomers are bis-phthalonitrile.[2,3,36] Here, we prepared a CPCP monomer with six phthalonitrile substituted cyclotriphosphazene structure, which expands the family of phthalonitrile-based polymers.

Polymerization of HPPN and CPCP Monomer
Differential Scanning Calorimetric (DSC) analysis was carried out to examine the polymerization reaction of CPCP monomer with 5 wt % HPPN and the results are shown in Figure 5. Samples were heated from 50°C to 350°C at 10°C/min under nitrogen atmosphere. The endothermic transition appears at 159.2°C [Figure 5(a)], which corresponds to the melting point of HPPN, and the exothermic peak at about 283.1°C stands for the self-polymerization process. Figure 5(b) shows the DSC curve of CPCP monomer with 5 wt % HPPN. The CPCP monomer exhibits a low melting point at 87.4°C, and the melting point of HPPN was moved to 140.2°C, while the exothermic peak at 306.7°C proves the occurrence of polymerization reaction.

Thus, it can be seen that HPPN participated in the polymerization reaction [Figure 5(b)] and acted as a curing agent at the same time, solving the problem of volatility of curing agents. This demonstrates that HPPN can not only be polymerized by self-polymerization but also can be used as the curing agent for polymerization of the CPCP monomer. The large processing window (219.3°C) between the melting point (87.4°C) and the curing exothermic peak (306.7°C) implies that the CPCP monomer has fine processability.

Comparison of the FTIR spectra of the CPCP monomer and its corresponding polymer was presented in Figure 1. In the spectrum of the CPCP polymer, the absorption peak of –CN shifts to 2224 cm^{-1}, with the intensity much weaker than that of 2231 cm^{-1} for the monomer. The characteristic absorption peak at 1526 cm^{-1} and 1357 cm^{-1} due to triazine ring structure was exhibited,[37] with the absence of resonances at 1708 cm^{-1}, 1591 cm^{-1} as well as 1563 cm^{-1}, which are found in the IR spectrum of the monomer. This indicates that the curing reaction has occurred and the nitrile groups have participated in curing reaction. However, no evidence of phthalocyanine and polyindoline formation is observed.

Based on above analyses, presumably, the CPCP polymer is of triazine ring structure and the possible two frameworks were described in Figure 6. Other possible structures were not given. If the triazine ring was formed by three CPCP monomers, the polymer structure was as shown in Figure 6(a). If HPPN was embedded in the structure, it was as shown in Figure 6(b).
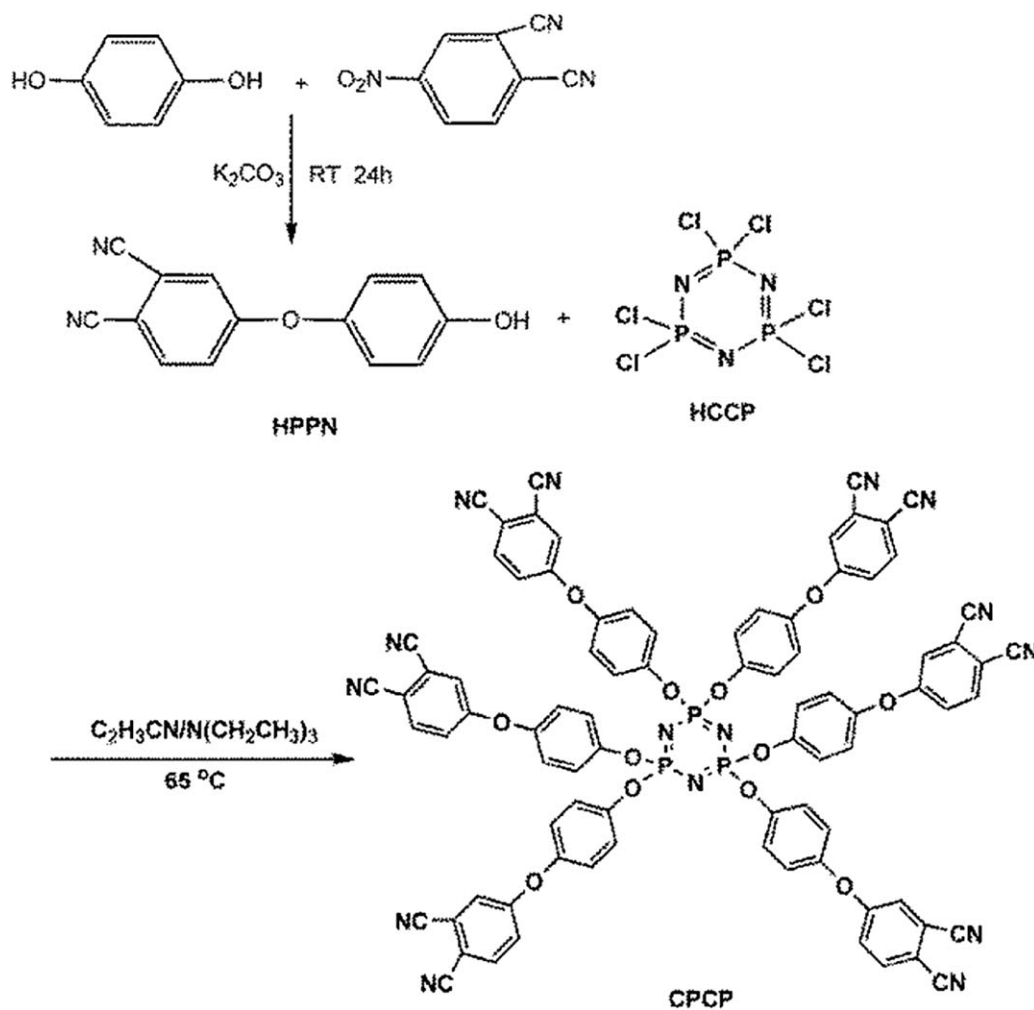
Scheme 1. Synthesis of CPCP monomer.

Thermal and Mechanical Properties

TGA curves of the CPCP polymer under nitrogen and air atmosphere are shown in Figure 7 and the thermal parameters are collected in Table I. As seen, $T_{d,5\%}$ is 490°C, and 527°C, T_{max} is 500°C and 530°C, and the char yield at 800°C is 78% and 83% under nitrogen atmosphere for the polymer cured up

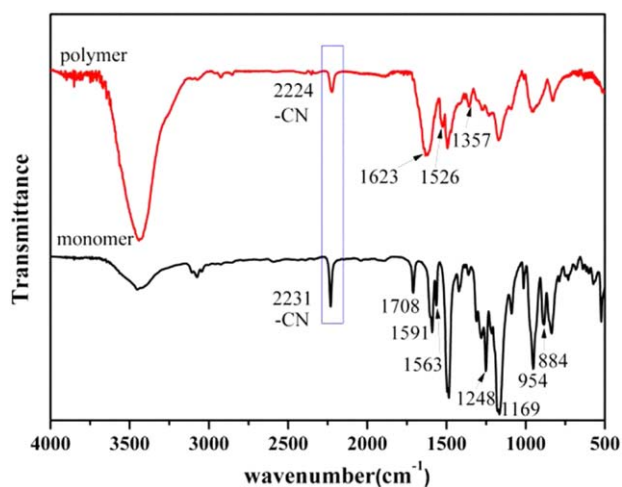**Figure 1.** FT-IR spectra of CPCP monomer and polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
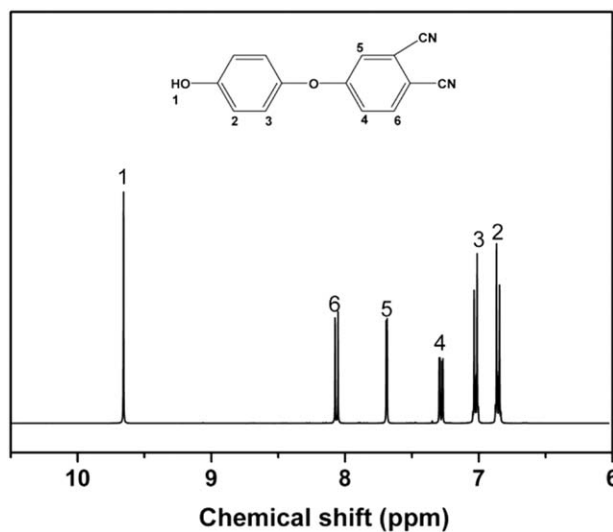
Figure 2. ^{1}H NMR spectrum of HPPN.
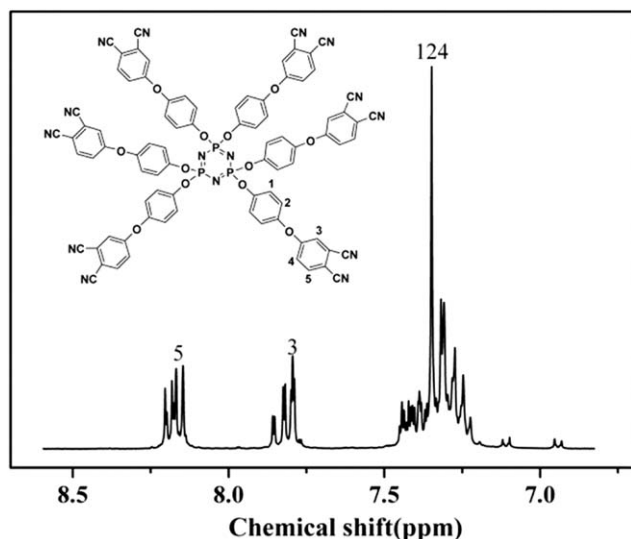
Figure 3. ^{1}H NMR spectrum of CPCP monomer.

to 360°C and 380°C, respectively, demonstrating high thermal stabilities. Under air atmosphere, excellent thermo-oxidative properties were exhibited with high $T_{d,5\%}$, being 489°C and 510°C for the polymers cured up to 360°C and 380°C, respectively. The maximum loss rates for both appeared at 510°C, which may be due to the decomposition of HPPN small molecules formed the triazine ring structure. Presumably, aromatic ring structures combined with P, N-heterocyclic rings in the polymer backbones lead to the outstanding thermal stabilities for the prepared polymers. Postcuring effects showed that more excellent thermal properties can be achieved.

According to Van Krevelen,[38] there is a linear relationship between limiting oxygen index (LOI) and char residue (CR) for halogen-free polymers, namely,

$$LOI = 17.5 + 0.4[CR]$$

where LOI is defined as the minimum fraction of oxygen in an oxygen–nitrogen mixture just sufficient to sustain combustion of the specimen after ignition[39] and CR is the char residue in weight percent in nitrogen. According to the char yield at
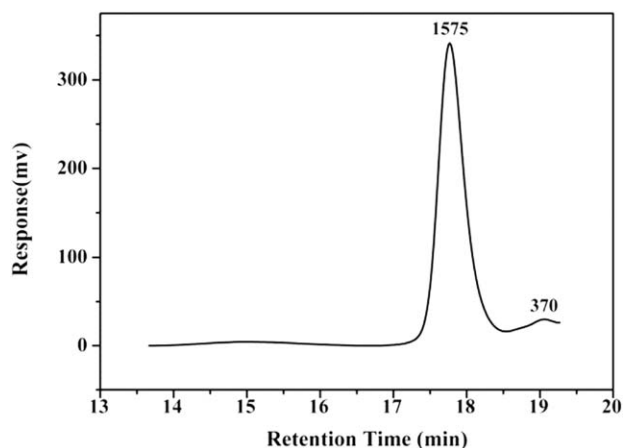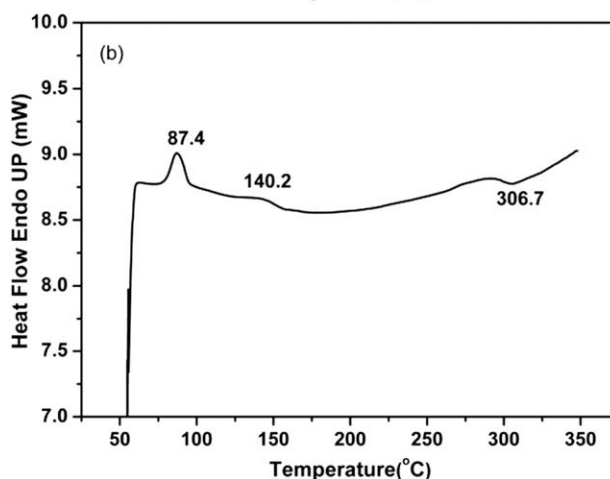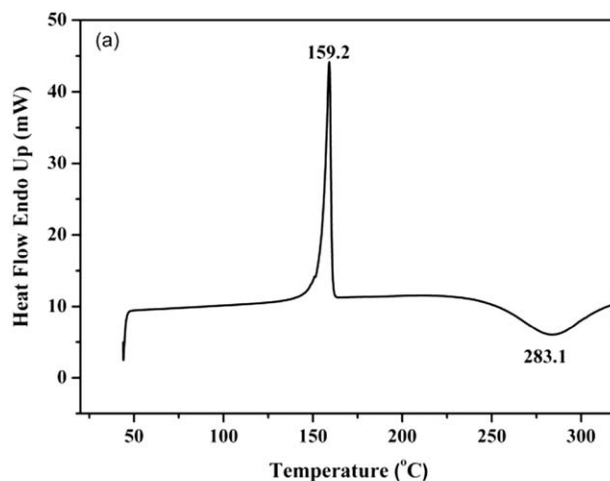

Figure 4. GPC spectrum of CPCP monomer.

Figure 5. DSC curves of (a) HPPN and (b) CPCP monomer/5 wt % HPPN blends.

800°C in nitrogen (cured at 380°C), the calculated value of LOI is 50.7. The LOI value of 26 or higher is rated as a flame-retardant material.[40] Therefore, the prepared CPCP polymer can be regarded as an excellent flame retardant material.

Micro-scale combustion calorimetry (MCC) test is another typical technique to evaluate the flame retardancy and simulate the real fire of a material, which is a pyrolysis combustion flow calorimetry with dynamic capability to measure heat releases rate (HRR) and other related parameters of polymers using samples of a few milligrams.[41] The temperature, corresponding to the peak heat release rate (PHRR), was defined as ignition temperature (IT).[41,42] Figure 8 shows the heat release rate (HRR) change as the temperature increasing. The data of peak heat release rate (PHRR), ignition temperature (IT), total heat release (THR), and heat release capacity (HRC) were listed in Table II. As shown in Figure 8, the two plots of the polymers contain a sharp peak as well as a broad and asymmetrical peak, which may be the part of the materials degradation and carbon layer formation process. With the increase of curing temperature, PHRR, THR, and HRC of the polymer cured up to 380°C are all lower than that of the polymer cured up to 360°C, indicating that increasing the curing temperature can improve the flame retardant performance. As shown in Table II, the PHRR and THR of CPCP polymer-380°C
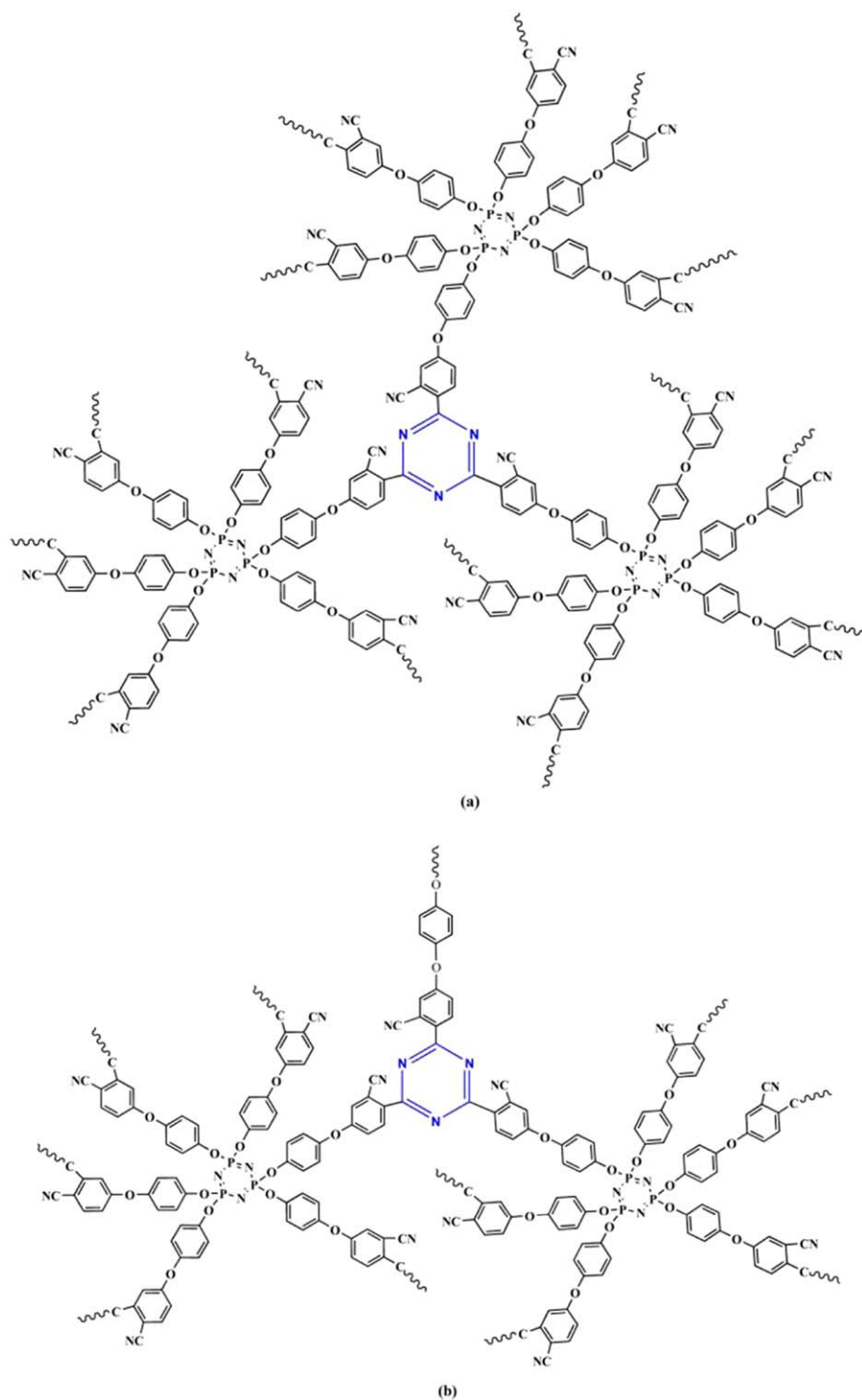
Figure 6. The possible triazine ring structures of CPCP polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

are only just 22.8 w/g and 0.1 kJ/g, respectively, which are all lower than that in the literature.[43] The results indicating that high strength and thermal stability of carbon layer were formed in the process of test, which covered on the surface of the material, prevented the transfer of heat and oxygen and inhibited further degradation of the inner material. According to above analysis, the CPCP polymer has excellent flame retardancy.

Dynamic mechanical analysis (DMA) was performed to investigate the mechanical properties of the CPCP polymer, and Figure 9 shows the plots of storage modulus (E'), loss modulus, and loss tangent (tan δ) versus temperature between 30°C and 380°C. As seen, the storage modulus of the CPCP polymer is about 2.7 GPa at 30°C, which is lower than that of alkyl-center-trisphenolic-based phthalonitrile polymer,[44] and this may be
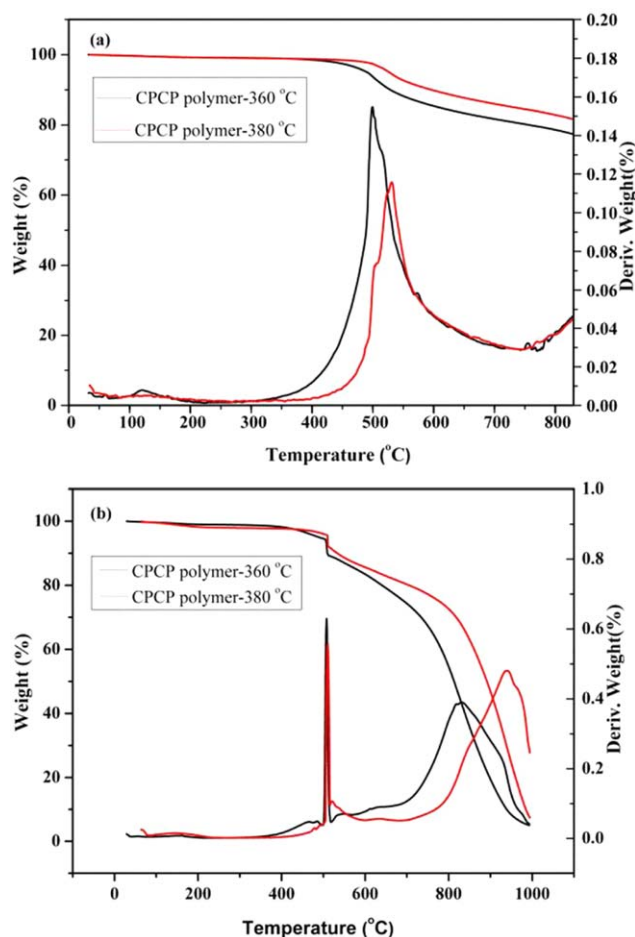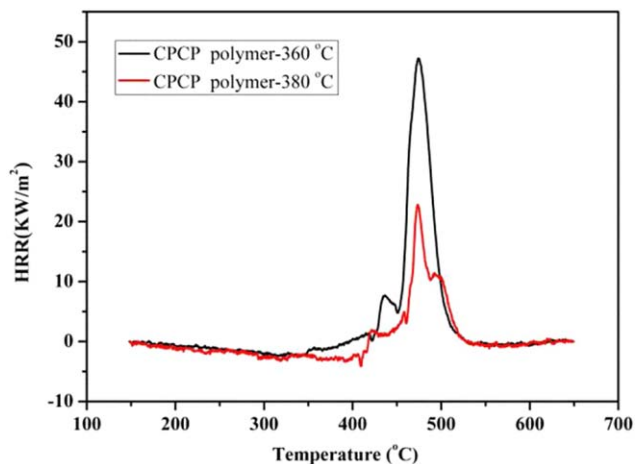
Figure 8. HRR curves of the CPCP polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The thermo-oxidative stability experiment for the polymer was carried out over an extended period at elevated temperatures. Figure 10 presents oxidative aging plots for the polymer when heated at elevated temperatures in air for 17 h. The values of weight residue are listed in Table III, which illustrates the percentages of total cumulative weight residue for each stage. After aged at 100, 200, and 250°C in air for a total of 8 h, the CPCP polymer retains 98.43% of its initial weight. At 400°C, the polymer shows less than 3% of weight loss. The total weight loss after heating at 400°C is about 2.06%. The above results reveal superior thermo-oxidative properties of the phthalonitrile-based phosphonitrile polymer.

Study of Curing Reaction Kinetic Parameters
Analysis of Apparent Activation Energy. Figure 11 shows the DSC curves of curing reactions at different heating rates of 5, 10, 15, and 20°C/min with a nitrogen flow rate of 20 mL/min, with exothermic peaks appearing at 300.6°C, 306.7°C, 314.9°C, and 316.4°C, respectively. This is may be due to the system has enough time to react with each other at low heating rates, so reaction was started at low temperatures. However, when the heating rate speeds up, the resin system response is slow, making its characteristic temperatures higher than those at low heating rates. Apparent activation energy of the resin is obvious reflection of the reaction degree. Here, Kissinger method was used to calculate the apparent activation energy. Kissinger equation[45] is as following:

Figure 7. TGA curves of the CPCP polymer in (a) N$_2$ and (b) air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

due to the lower crosslinking degree caused by steric hindrance. When the temperature increases up to 380°C, the storage modulus gradually decreases and it still remains 500 MPa at 380°C, which may be due to the incompletely curing. There is no apparent increase in tan δ with the temperature increasing up to 380°C, indicating a high glass transition temperature (>380°C). It is known that the high glass transition temperature is particularly important for high temperature polymers as T_g determines the upper limit of application temperature, with high modulus and high T_g necessary for high temperature resins as well.

Table I. Thermal Parameters of the CPCP Polymers

Polymer	N$_2$				Air		
	$T_{d,5\%}$[a] (°C)	T_{max}[b] (°C)	Char yield[c] (800°C, %)	LOI[d]	$T_{d,5\%}$[a] (°C)	T_{max}[b] (°C)	Char yield[c] (800°C, %)
360°C	490	500	78	48.7	489	510,827	55
380°C	527	530	83	50.7	510	510,941	73

[a] Temperature at which 5% weight loss were recorded by TGA at heating rate of 10°C/min in air or nitrogen, respectively.
[b] Temperature at which maximum loss rate was recorded by TGA at heating rate of 10°C/min in air or nitrogen.
[c] Residual weight retention at 800°C in nitrogen or air.
[d] Limiting oxygen index.

Table II. MCC Analysis Results of CPCP Polymer

Sample	PHRR (w/g)	IT (°C)	THR (kJ/g)	HRC (J/g K)
CPCP polymer-360°C	47.2	476.3	1.2	47
CPCP polymer-380°C	22.8	481.4	0.1	23
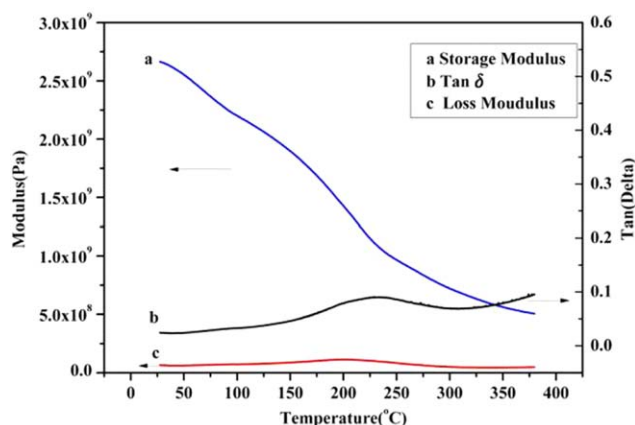
Figure 9. DMA curves of the CPCP polymer cured with 5 wt % of HPPN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$-\ln \frac{\beta}{T_p^2} = \frac{E_a}{RT_p} - \ln \frac{A'R}{E_a}$$

where β is the heating rate (°C/min); T_p is the peak temperature of curing reaction (K); R is the gas constant; and E_a is the reaction activation energy.

Data of $\ln(\beta/T_p^2)$ and $1/T_p$ at different heating rates were exhibited in Table IV, with linear relationship of $\ln(\beta/T_p^2)$ versus $1/T_p$ shown in Figure 12. Based on the straight slope (-2.58×10^4), the value of reaction activation energy was calculated to be 214.5 kJ/mol.
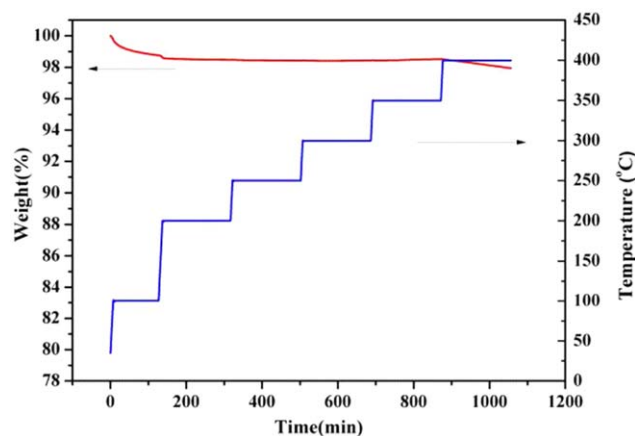
Figure 10. Weight loss of the CPCP polymer in air at elevated temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Parameters for the Oxidative Aging of the CPCP Polymer

Stage	Temperature (°C)* Time (min)	Remaining weight (%)
A	100*120	98.76
B	200*180	98.47
C	250*180	98.43
D	300*180	98.43
E	350*180	98.40
F	400*180	97.94
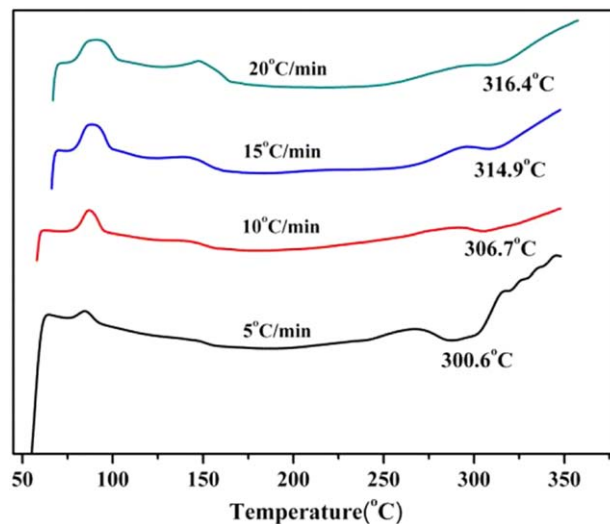
Figure 11. The DSC curves of curing reaction at different heating rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Analysis of Curing Temperature. At different heating rates, different peak temperatures of curing appear in DSC curves, which make the actual curing temperature of thermosetting materials difficult to be determined. Therefore, T-β figures (Figure 13) are used to calculate approximate curing temperatures, that is, make the T-β curves extrapolate to 0°C/min, and which are initial curing temperature, curing exothermic peak temperature, and curing complete temperature. These three temperatures are defined as gel temperature (T_{gel}), curing temperature (T_{cure}), and the post processing temperature (T_{treat}), respectively.

The initial curing temperatures, curing temperatures, and termination curing temperatures at different heating rates are marked as T_i, T_p, and T_f, respectively, and listed in Table V. The T_i-β,

Table IV. $\ln(\beta/T_p^2)$ and $1/T_p$ at Different Heating Rates

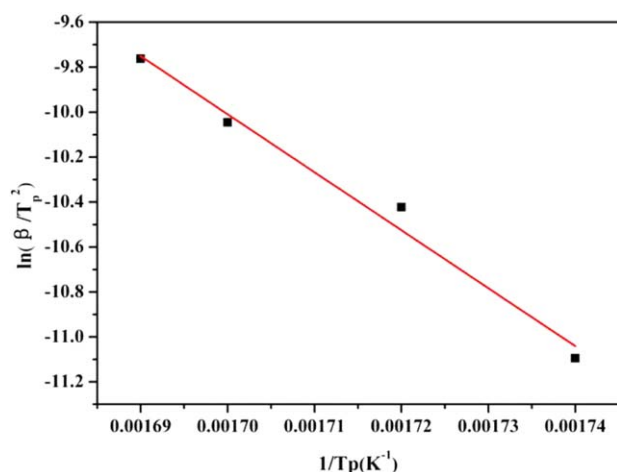| β (°C/min)	T_p (K)	$\ln(\beta/T_p^2)$	$1/T_p$ ($\times10^{-3}$ K^{-1})
5	573.75	−11.09	1.74
10	579.85	−10.42	1.72
15	588.05	−10.04	1.70
20	589.55	−9.76	1.69

Figure 12. The relationship of $\ln(\beta/T_p^2)$ and $1/T_p$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

T_p-β, and T_f-β curves were presented in Figure 13 to obtain T_{gel}, T_{cure}, and T_{treat}, which are about 284.4°C, 295.7°C, 307.1°C, respectively. Above data provided important information for polymer processing.

Water Uptake

The water uptake was calculated using the following equation:

$$\text{Water uptake } (\%) = (M_2-M_1)/M_1 \times 100$$

where M_1 and M_2 are the weights of the CPCP polymer at dry state and after immersion in distilled water, respectively.

The water uptake increases rapidly during the first stage as shown in Figure 14, and it appears to level off after approximately 264 h depending on the experimental temperature. It reaches about 3.0% after 480 h of immersion in distilled water at room temperature, analogous to those of alkyl-center-trisphenolic-based phthalonitrile polymer and naphthyl-based phthalonitrile polymer (2.9%, 3.0%).[44,46] The low water uptake of the CPCP polymer may be ascribed to the low contents of hydrophilic groups in polymer chains. The low water uptake is

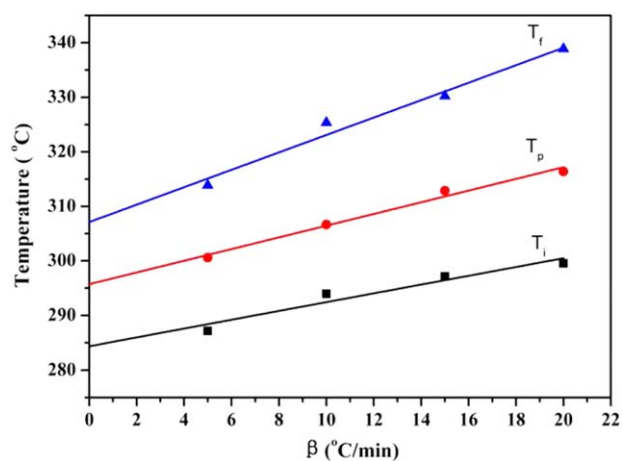**Table V.** Parameters for β and T_i, T_p, and T_f at Different Heating Rates

β (°C/min)	T_i (°C)	T_p (°C)	T_f (°C)
5	287.2	300.6	313.9
10	293.9	306.7	325.4
15	297.1	314.9	330.2
20	299.5	316.4	338.9

a significant advantage for high temperature polymers when used in a highly humid or aqueous environment.

CONCLUSIONS

A phthalonitrile-substituted phosphonitrilic monomer and its corresponding polymer were developed, and their chemical structures were characterized by FT-IR and ^{1}H NMR analyses. The polymer generated during polymerization was investigated to be of triazine ring structures. Curing behaviors were recorded by DSC analysis, and TGA data revealed that the polymer of phthalonitrile-based phosphazene possesses outstanding thermal stability. Apparent activation energy of the phosphonitrilic polymer is 214.5 kJ/mol, with initial curing temperature (T_i), curing temperature (T_p), and termination curing temperature (T_f) being about 284.4°C, 295.7°C, and 307.1°C, respectively. Dynamic mechanical analysis (DMA) showed that the storage modulus (E') is 2.7 GPa at 30°C and the glass transition temperature (T_g) is higher than 380°C. Limiting oxygen index (LOI) was estimated to be 50.7 according the van Krevelen equation, and MCC analysis indicates that the polymer has good flame retardancy. Postcuring effects were explored, which show that more excellent thermal and mechanical properties can be achieved with postcuring.

Based on above analysis, it could be concluded that the phosphonitrilic polymer with phthalonitrile substituents is a very promising candidate material for high performance materials and expands the phthalonitrile-based polymer family.
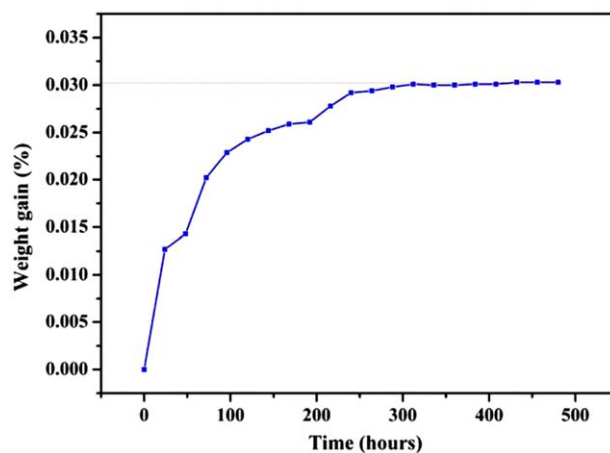

Figure 13. The relationship of temperature and β. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 14. Water uptake of CPCP polymer after 480 h of immersion in distilled water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

REFERENCES

1. Keller, T. M. *J. Polym. Sci. Part A: Polym. Chem.* **1988**, *26*, 3199.

2. Keller, T. M. *Polymer* **1993**, *34*, 952.

3. Keller, T. M. *Chem. Mater.* **1994**, *6*, 302.

4. Sastri, S. B.; Keller, T. M. *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36*, 1885.

5. Sastri, S. B.; Keller, T. M. *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 2105.

6. Dominguez, D. D.; Jones, H. N.; Keller, T. M. *Polym. Compos.* **2004**, *25*, 554.

7. Keller, T. M.; Dominguez, D. D. *Polymer* **2005**, *46*, 4614.

8. Laskoski, M.; Dominguez, D. D.; Keller, T. M. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 4136.

9. Dominguez, D. D.; Jones, H. N.; Keller, T. M. *High Perform. Polym.* **2006**, *18*, 283.

10. Amir, B.; Michael, R. K.; Zhou, H.; Aurangzeb, H. *Polym. Int.* **2014**, *63*, 465.

11. Liu, T.; Yang, Y.; Wang, T.; Wang, H.; Zhang, H.; Su, Y.; Jiang, Z. *Polym. Eng. Sci.* **2014**, *54*, 1695.

12. Laskoski, M.; Neal, A.; Keller, T. M.; Dominguez, D. D.; Klug, C. A.; Saab, A. P. *J. Polym. Sci. Part A: Polym. Chem.* **2014**, *52*, 1662.

13. Zou, X.; Xu, M.; Jia, K.; Liu, X. *J. Appl. Polym. Sci.* **2014**, *131*, 41203.

14. Selvakumar, P.; Sarojadevi, M.; Sundararajan, P. *Mater. Sci. Eng. B* **2010**, *168*, 214.

15. Sumner, M. J.; Weyers, R. Y.; Rosario, A. C.; Riffle, J. S.; Sorathia, U. *Polymer* **2004**, *45*, 5199.

16. Zhou, S. H.; Hong, H. B.; Zeng, K.; Miao, P. K.; Zhou, H. F.; Wang, Y. P.; Liu, T.; Zhao, C. E.; Xu, G. L.; Yang, G. *Polym. Bull.* **2009**, *62*, 581.

17. Zeng, K.; Zhou, K.; Zhou, S. H.; Hong, H. B.; Zhou, H. F.; Wang, Y. P.; Miao, P. K.; Yang, G. *Eur. Polym. J.* **2009**, *45*, 1328.

18. Guo, H.; Chen, Z. R.; Zhang, J. D.; Yang, X. L.; Zhao, R.; Liu, X. B. *J. Polym. Res.* **2012**, *19*, 9918.

19. Amir, B.; Zhou, H.; Liu, F.; Aurangzeb, H. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 5916.

20. Zhang, Z.; Li, Z.; Zhou, H.; Lin, X.; Zhao, T.; Zhang, M.; Xu, C. *J. Appl. Polym. Sci.* **2014**, *131*, 40919.

21. Amir, B.; Michael, R. K.; Zhou, H.; Javid, H. Z.; Shahid, H.; Aurangzeb, H. *Polym. Chem.* **2013**, *4*, 3617.

22. Allcock, H. R.; Gebura, M.; Kwon, S.; Neenan, T. X. *Biomaterials* **1988**, *9*, 500.

23. Jader, R. D.; Gleria, M. *Prog. Polym. Sci.* **1998**, *23*, 179.

24. Young, S. G.; Kojima, M.; Magill, J. H.; Lin, F. T. *Polymer* **1992**, *33*, 3215.

25. Thomas, A. A.; David, J. S. U.S. Patent 4,357,458, Akron, November 2, **1982**.

26. Allcock, H. R. *Science* **1992**, *255*, 1106.

27. Allcock, H. R. *Appl. Organomet. Chem.* **1998**, *12*, 659.

28. Schrogel, P.; Hoping, M.; Kowalsky, W.; Hunze, A.; Wagenblast, G.; Lennartz, C.; Strohriegl, P. *Chem. Mater.* **2011**, *23*, 4947.

29. Gleria, M.; Jaeger, R. De. *J. Inorg. Organomet. Polym.* **2001**, *11*, 1.

30. Mathew, D.; Nair, C. P. R.; Ninan, K. N. *Polym. Int.* **2000**, *49*, 48.

31. Zhang, T.; Cai, Q.; Wu, D. Z.; Jin, R. G. *J. Appl. Polym. Sci.* **2005**, *95*, 880.

32. Hergenrother, P. M.; Havens, S. J. *J. Polym. Sci Part A: Polym. Chem.* **1989**, *27*, 1161.

33. Smith, C. D.; Grubbs, H.; Webster, H. F.; Gungör, A.; Wightman, J. P.; McGrath, J. E. *High Perform. Polym.* **1991**, *3*, 211.

34. Abed, J. C.; Mercier, R.; McGrath, J. E. *J. Polym. Sci. Part A: Polym. Chem.* **1997**, *35*, 977.

35. Allcock, H. R.; Neenan, T. X. *Macromolecules* **1986**, *19*, 1495.

36. Laskoski, M.; Dominguez, D. D.; Keller, T. M. *Polymer* **2007**, *48*, 6234.

37. Snow, A. W.; Griffith, J. R.; Marullo, N. P. *Macromolecules* **1984**, *17*, 1614.

38. Van Krevelen, D. W. *Polymer* **1975**, *16*, 615.

39. Lin, C. H.; Wang, C. S. *Polymer* **2001**, *42*, 1869.

40. Wenthold, R. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6401.

41. Lyon, R. E.; Walters, R. N. *J. Anal. Appl. Pyrol.* **2004**, *71*, 27.

42. Hergenrother, P. M.; Thompson, C. M.; Smith, J. G.; Connell, J. W.; Hinkley, J. A.; Lyon, R. E.; Moulton, R. *Polymer* **2005**, *27*, 5012.

43. Jin, W. Q.; Yuan, L.; Liang, G. Z.; Gu, A. *J. ACS Appl. Mater. Interfaces* **2014**, *6*, 14931.

44. Sheng, H. T.; Peng, X. G.; Guo, H.; Yu, X. Y.; Tang, C. C.; Qu, X. W.; Zhang, Q. X. *Mater. Chem. Phys.* **2013**, *142*, 740.

45. Kissinger, H. E. *Anal. Chem.* **1957**, *29*, 1702.

46. Zhao, F. H.; Liu, R. J.; Kang, C.; Yu, X.; Naito, K.; Qu, X. W.; Zhang, Q. X. *RSC Adv.* **2014**, *4*, 8383.