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Structure and thermal properties of phosphorus-containing polyol synthesized from cardanol

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P-containing cardanol polyol (PCP), a novel cardanol derivative, was synthesized. Its structure was confirmed by Fourier transform infrared spectrometry (FT-IR) and ¹H nuclear magnetic resonance (¹H NMR). Its flame retardancy and thermal stability were assessed by limiting oxygen index (LOI) and thermogravimetric analysis (TGA). TGA showed the degradation occurred in two stages with varying mass rate losses of PCP. The PCP showed higher initial decomposition temperature (Ti), final degradation temperature (Tf), and maximum degradation temperature (Tmax) than cardanol diol (CD) of the same class, and also had higher mass residual than CD (6.77% vs. 0.02%). To study the flame retardancy of PCP, we prepared a series of polyurethane foams (PUFs) with different contents of PCP. LOI increased continuously with the increasing content of PCP added into PUF. The thermal degradation of PCP was disclosed by TGA-FTIR and TGA-MS. During degradation, PCP continued to release PO free radicals and o-phenylphenoxy free radical, which acted as scavengers of H• and OH• during two degradation stages at 200 °C. Moreover, the phosphaphenanthrene group may create a char residue acting as a barrier for the polymer matrix.

Key words: Cardanol; phosphorus; polyol; thermal properties

Introduction

In recent years, bio resources have attracted much attention in preparation of value-added products because they would replace scarce resources and contribute to global sustainability. These renewable materials are sometimes cheaper than petrochemicals.¹ Renewable resources refer to any material having recent biological origin, such as wood, agricultural crops, municipal solid waste, and even animal manure.²⁻³ The most widely used renewable resource is vegetable oils owing to their availability, versatility, and technical feasibility.⁴⁻⁵ Among all vegetable oils, cardanol is an agricultural by-product abundantly obtained from the complete distillation of cashew nut shell liquid (CNSL), and stands out for preparing cost effective materials.⁶⁻⁹ Cardanol is a promising, renewable and abundant resource for preparation of chemicals, mainly because it does not threaten food application. Cardanol is

unique since it contains a phenolic moiety with an unsaturated 15-carbon side chain having 1 to 3 double bonds. The long chain in the cardanol imparts flexibility due to internal plasticizing and the reactivity of the hydroxyl phenyl group of cardanol can be taken advantage of to develop a variety of structurally diverse functional molecules.¹⁰ Cardanol and its derivatives are mainly applied as thermosetting resins, plasticizers, coatings, and biocomposites.¹¹⁻¹⁴

In recent years, there are many studies about the chemical modification of cardanol to diol or polyol compounds. For instance, the phenoxy group of cardanol by reacted with epichlorohydrin to form glycidyl ether, which was hydrolysed by the catalyst heteropolyacid to form the corresponding diol, and then polyurethanes (PUs) with good coating properties were synthesized.¹⁵ The phenoxy group of the cardanol reacted with 3-chloropropane-1,2-diol to form the corresponding diol under the catalysis of sodium hydroxide, and then a telechelic urethane-methacrylate UV curable crosslinkers was synthesized and its crosslink density was enhanced by incorporation of double bonds at cardanol side chains during a polymerization.¹⁰ With the same approach, Sakulsaknimitr *et al.*¹⁶ started to adapt the diol to create thermally and oxidatively stable Pus due to the cardanol side chains.

Moreover, a series of polyols were prepared from cardanol to study the structure-property relationship, and

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cardanol-based polyols could yield tough rigid polyurethanes, PU based on diol was semirigid.¹⁷

Suresh also prepared rigid foams using cardanol-developed polyols, and the epoxy intermediate reacted with excessive organic acid to form a formoxy-hydroxy ester.¹⁸ The half ester formed during saponification gave the polyols, which were successfully to prepare rigid polyurethane foams with good physiochemical properties.

To improve the thermal stability of materials, many researchers have studied the chemical modification of cardanol. Calò *et al.*¹⁹ used a novel cardanol-derived benzoxazine prepolymer to synthesize phenolic resins with good thermal properties and flame retardant characteristics. Ravichandran *et al.*²⁰ synthesized polycardanol in aqueous media with significantly high thermal stability and low heat release capacity.

Despite such studies on the synthesis or chemical modification, there is rare research on synthesis of P-containing polyol from cardanol based on unsaturated side chain as far as we know.

As reported, phosphorylated CNSL prepolymer and phosphorylated cardanol prepolymer were synthesized from CNSL and cardanol, respectively, and synthetic mechanisms involving this type of additive were investigated.²¹⁻²⁴ Moreover, natural rubber modified with phosphorylated CNSL prepolymer has higher flame retardancy and resistance to thermo-oxidative decomposition, compared to that containing similar dosages of 2-ethyl hexyl diphenyl phosphate.²⁵ Also appropriate addition of phosphorylated cardanol was used to improve the thermal stability of ethylene propylene diene rubber.²⁶

However, such studies have consolidated a research program based on phenolic moiety, not on unsaturated side chain.

The objective of the present work was to develop a novel P-containing polyols (PCP) from cardanol. The structure of PCP was investigated by Fourier transform infrared spectra (FT-IR) and ¹H nuclear magnetic resonance (¹H NMR). Its thermal properties including flame retardancy and thermal stability were assessed by limiting oxygen index (LOI) and thermogravimetric analysis (TGA). Its thermal degradation was disclosed by TGA-FTIR and TGA coupled with mass spectrometry (TGA-MS).

Experimental

Materials

The main materials included cardanol (purity about 95 %, Shanghai Meidong Biomaterials Co., Ltd., China); 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO, 97 %) and triphenylphosphine (Ph₃P, > 99 %) (both Aladdin Co., Inc., USA). Epichlorohydrin (≥ 99 %), H₂SO₄ (95.0 %-98.0 %), anhydrous ZnCl₂ (98 %), formic acid (88 %), and H₂O₂ (≥ 30 %) (all from Nanjing Chemical Co. Ltd., Nanjing, China) were of reagent grade. Polyether polyol 4110 (hydroxyl value: 430-410 mg KOH/g, viscosity at 25 °C: 3600 mPaS⁻¹) was obtained from Jiangsu Qianglin Bio-energy Co., Ltd. 4,4'-Diphenyl-

methane-diisocyanate (MDI) 35 NCO % was obtained from Yantai Wanhua Polyurethane Co. Ltd. (Yantai, China). The catalyst and surfactant were obtained from commercial sources and used as received. All other chemicals used in this study were of reagent grade and used without further purification.

Preparation of cardanol diol (CD)

The route for preparation of CD is illustrated in Scheme 1. In the first step, cardanol reacted with epichlorohydrin under alkaline conditions to form monoglycidyl ether (epicard).¹⁷ In a typical experiment, 150 g (0.5 mol) of cardanol was put into a 500-mL round-bottom flask equipped with a mechanical stirrer, followed by addition of 0.15 g (~ 0.1 %) of anhydrous ZnCl₂. Under mechanic stirring, the mixture was heated to 95 °C in an oil bath. The required amount of epichlorohydrin (74.02 g, 0.8 mol) was then added dropwise while the temperature was maintained. After all epichlorohydrin was added (starting time), the reaction proceeded for 2 h. Then a stoichiometric amount of NaOH (32 g/150 mL water) was added dropwise. The reaction system was heated to 100 °C and kept there for 3 h. The product was separated and washed with excessive water to remove the byproduct NaCl and other unreacted materials. It was then dried over anhydrous Na₂SO₄. The epoxy value of epicard was 0.187 mol·100 g⁻¹. The epoxide ring was then opened under acidic conditions to give the glycol. Typically, epicard (106.8 g, 0.3 mol) was mixed with twice its weight of 10 % H₂SO₄ (213.6 g) in a 1000-ml three-neck round-bottom flask, fitted with a mechanical stirrer. The reaction mixture was heated to 105 °C and kept there for 14 h under stirring. Water would reflux at 105 °C. The product was extracted in ether, washed with water until turning neutral to litmus, and dried over anhydrous Na₂SO₄. The yield of the isolated product was 90 %. The hydroxyl value of the diol was 144 mg KOH/g.¹⁷

Preparation of PCP

Scheme 1 shows the schematic of PCP synthesis. In the first step, the CD as-prepared (56.10 g, 0.15 mol) was cooled to 0 °C, followed by addition of 6.90 g of formic acid (0.15 mol). Then 34 g of 30 % H₂O₂ (0.3 mol) was then added dropwise to the mixture while the temperature was maintained for 24 h. The product was extracted in ethyl acetate, washed with water until reaching neutral to litmus, and dried over anhydrous Na₂SO₄. The solvent was removed through an evaporator to form epoxide-containing cardanol diol (ECD), with a yield of 83 %.

ECD (60 g) and DOPO (10.81 g) were charged into a 250 ml three-necked round-bottomed flask equipped with a magnetic stirrer, a thermometer and a nitrogen inlet. The mixture was heated in an oil bath to 125 °C under nitrogen gas to form a transparent solution, followed by addition of 0.6 g of Ph₃P as a catalyst. The new mixture was slowly heated in an oil bath to 140 °C and maintained there for 6 h. Finally, yellow PCP with hydroxyl number of 287 mg KOH/g was obtained.

Determination and Characterization

Determination of hydroxyl numbers of CD and PCP

The hydroxyl numbers of CD and PCP were determined according to *Plastics-Polyether Polyols- Part3: Determination of Hydroxyl Number (GB/T12008.3-2009)* developed for polyether polyols probably with steric hindrance. Briefly, an acetylation reagent solution was prepared freshly everyday from 116 g of phthalic anhydride, 700 mL of dry pyridine and 16 g of imidazole (catalyst). CD (PCP) and blank samples were each refluxed at 115 ± 2 °C in flasks containing 25 mL of the acetylation reagent solution. Then after the flasks were left to cool down to room temperature, the excessive phthalic anhydride was hydrolyzed with distilled water. The resulting phthalic acid in each sample was titrated with 0.5 M NaOH in an automatic titrator (ZDJ-4A, China). The hydroxyl number of each sample (mg KOH/g) was calculated as follows:

$$\text{Hydroxyl number (mgKOH/g)} = \frac{(B-A)M \times 56.1}{w} + \text{Acid value} \quad (1)$$

where *A* is the volume of the NaOH solution used to titrate a CD (PCP) sample (mL); *B* is the volume of the blank solution (mL); *M* is the normality of the NaOH solution (mol/L) and *w* is the weight of CD (PCP) (g).

Determination of epoxy values of epicard and ECD

The epoxy value was determined by the HCl–acetone method. A HCl–acetone solution was prepared from 1 mL : 40 mL of HCl : acetone and used immediately. About 0.5 g of a sample was dissolved in 20 mL of the HCl–acetone solution. After 30 min, the excessive HCl was titrated by 0.5 M NaOH in the automatic titrator. The epoxy value (mol·100 g⁻¹) of each sample was calculated as follows:

$$\text{Epoxy value (mol} \cdot 100 \text{ g}^{-1}) = \frac{(B-A) \times M}{10w} \quad (2)$$

where *A* is the volume of the NaOH solution used to titrate an epicard (ECD) sample (mL); *B* is the volume of the blank solution (mL); *M* is the normality of the NaOH solution (mol/L) and *w* is the weight of epicard (ECD) (g).

FT-IR spectra were recorded with a Nicolet iS10 FTIR meter (Nicolet Instrument Corp., USA) by the attenuated total reflection (ATR) method, in the optical range of 525–4000 cm⁻¹ and with 16 scans on average at a resolution of 4 cm⁻¹.

¹H NMR spectra were recorded with a Bruker AV-300 Advance spectrometer (Bruker, Germany) at a frequency of 300 MHz. The chemical shifts were expressed in parts per million (δ scale) and with tetramethylsilane (TMS) as a reference. Acetone-d was selected as the solvent. The parameters were set as follows: dummy scans, 4; acquisition time, 2.2720 s; delay time, 1.0 s; number of scans, 16; spectral width, 7211 Hz.

TGA was carried out on an STA 409 PC/PG analyzer (Netzsch, Germany). Specifically, a small amount of a sample was placed in an Al₂O₃ pan, which was put in a furnace. Then

the furnace was heated at 20 °C/min from 35 to 800 °C under a nitrogen atmosphere.

TGA–FTIR spectra were measured on a 409PC/PG thermal analyzer (Netzsch, Germany) coupled with the Nicolet iS10 FT-IR device. A small amount of each sample was heated at 20 °C/min from 40 to 800 °C under N₂ atmosphere. The scanning range was 4000–600 cm⁻¹ at a resolution of 4 cm⁻¹.

TGA–MS spectra were recorded on the 409PC/PG thermal analyzer coupled with a QMS403C instrument (Netzsch, Germany). A small amount of each sample was heated at 20 °C/min from 40 to 800 °C under N₂ atmosphere. The scanning range was m/v 2–200.

LOI was determined at room temperature on a JF-3 oxygen index instrument (Jiangning Analysis Instrument Factory, China) according to *Plastics-Determination of Burning Behavior by Oxygen Index (GB/T 2406.1-2008)*. Each sample was 130 × 10 × 10 mm³ in size.

Results and discussion

FT-IR

Figure 1 shows the FT-IR spectra of cardanol, CD, ECD, and PCP. The spectrum of CD shows new sharp bands at 1047 and 1123 cm⁻¹, confirming the presence of primary and secondary alcohols, respectively.¹⁵

The spectrum of ECD shows the characteristic peaks of epoxide at 848 and 916 cm⁻¹, indicating the occurrence of epoxidation reaction. Compared with CD, the peak at 3009 cm⁻¹ disappears for ECD, meaning the double band on side chain was transformed to epoxy groups.²⁷ The spectrum of PCP shows peaks at 916 and 1477 cm⁻¹, which are attributed to the P–O–Ph deformation vibration and the P–Ph group, respectively. The spectrum of PCP does not show the absorbance of epoxy group in ECD at 848 cm⁻¹, or the stretching vibration at 2385 cm⁻¹ for P–H in DOPO, implying the reaction of P–H of DOPO with ECD (Fig. S1 in ESI).

¹H NMR

¹H NMR was also employed to investigate the structures of CD and PCP (Fig. 2). Compared with cardanol (Fig. 2a) and CD (Fig. 2b), the peak at δ 8.0 (peak 11 in Fig. 2) of CD corresponding to the proton of –OH disappears, indicating the conversion of phenolic hydroxyl group. The new peaks at δ 3.69, 3.97 and 3.99–4.21 indicate the presence of primary and secondary alcohols.¹⁶

On the ¹H NMR spectrum of ECD, the peaks at δ 5.79 (peak 5), 5.39 (peak 10) and 5.09–4.95 (peak 6) ascribed to the proton of –CH=CH– almost disappear, indicating the conversion of the unsaturated double bonds of the side chain. New peaks 10' and 10'' at δ 2.93 and 2.85 ascribed to the methane protons of the oxirane ring appear (Fig. 2c), indicating the occurrence of epoxidation. Furthermore, the neighboring methylene protons (peaks 7 and 8 in Fig. 2) appear to down shift by the oxidation (peaks 7' and 8' in Fig. 2), meaning the reaction of the unsaturated groups.¹

On the ¹H NMR spectrum of PCP (Fig. 2d), the characteristic peaks at δ 7.0–8.2 correspond to the proton on

the phosphaphenanthrene groups (peak12 in Fig. 2d). The peaks 10' and 10'' at δ 2.93 and 2.85 disappear, indicating the conversion of oxirane ring. The spectrum of PCP does not show the peak at δ 9.00 (Fig. S2 in ESI), which is associated with the P-H of DOPO.²⁸ All results indicate the reaction of DOPO with the epoxy groups in ECD, and support the successful preparation of PCP.

TGA of CD and PCP

The thermal stabilities of CD and PCP were investigated by TGA and derivative thermogravimetry (DTG). Results are summarized in Table 1 and Figure 3. The thermograms clearly show the degradation occurs in two stages with varying mass rate losses for CD and PCP. The first stage occurs within 320-420 °C and is due to the dehydration of hydroxyl and formation of ether compounds. The second stage occurs within 420-795 °C where the aromatic rings are continuously dehydrated to form the thickening rings as a part of char residue.²⁹

The parameters of interest are initial decomposition temperature (T_i), final degradation temperature (T_f), maximum degradation temperature (T_{max}), and char yield. At the first stage, T_i , T_f , and T_{max} of PCP are 341.7, 419.7 and 385.5 °C, respectively; at the second stage, T_i and T_{max} of PCP are 434.5, and 466.7 °C, which are higher compared with CD. All these data indicate that PCP is thermally more stable than CD.

Another important property of PCP is its contribution to the increased yield of mass residue. PCP has a higher mass residue than CD (6.77% vs. 0.02%), which suggests the low flammability and high thermal stability of PCP. The very small char yield of CD may be attributed to its raw material cardanol, whose long aliphatic hydrocarbons side chain allows CD to burn easily. After incorporation of DOPO, not only the potential of DOPO structure for phosphorus released then worked in the gas phase, but also the decomposition products of PCP might react to form volatile or solid products depending on the chemical surroundings in the pyrolysis zone.³⁰

TGA-FTIR of CD and PCP

Figure 4 shows the 3D TGA-FTIR spectra of gas products in the thermal degradation of CD and PCP.

Figure 4 shows peaks around 3500-3800, 2900-3100, 2100-2400, 1100-1300, and 600-1100 cm^{-1} .

Figure 5 shows the FT-IR spectra of pyrolysis products of CD at different time points. The main products are -OH-containing compounds (3500-3800 cm^{-1}), saturated hydrocarbons (3050-2800 cm^{-1}), CO_2 (2353 and 669 cm^{-1}), CO (2178 cm^{-1}), and aromatic derivatives (1000-700 cm^{-1}).³¹⁻³³ The peak at about 1725 cm^{-1} indicates the presence of carbonyl group (C=O). The peak at about 1105 cm^{-1} indicates the presence of ether group,²⁹ while the ether group also disappears with the temperature rise, confirming that new forming ether group will continue to degrade.

As shown in Figure 6, the evolved gas analysis for PCP at different time points exhibits characteristic bands of -OH

(3500-3800 cm^{-1}), saturated hydrocarbons (3050-2800 cm^{-1}), CO_2 (2357 and 669 cm^{-1}), and CO (2178 cm^{-1}), which are similar to the results of CD. Unlike CD, the new absorption band at 1105 cm^{-1} is sharper and stronger. With the temperature rise up to 623 °C (29.179 min), the peak at 1105 cm^{-1} is also rather obvious. Therefore, we deduce the phosphaphenanthrene group degrades at the same time, which was considered as the absorption of PO free radicals.²⁹ Other P-containing components such as P-Ph and P-H were not found, implying most of the decomposition products of phosphaphenanthrene group remain in the condensed phase and improve the residual char yield.³⁴

TGA-MS of PCP

To further disclose the degradation route, we performed TGA-MS to investigate the exact composition of the pyrolysis fragments. The volatilization profiles of the fragments originating from the thermal degradation of PCP components are shown in Figure 7. The signals at m/z 44 and m/z 28 are attributed to CO_2 and CO, respectively, which are released since low temperature. The fragments with m/z 65, 66, 77 and 78 can be assigned to aromatic components, which are released at high temperature. Other fragments with m/z 47, 63 and 64 can be assigned to OP^+ , O_2P^+ , and HO_2P^+ , respectively, produced from degradation of DOPO in PCP.³⁵ During degradation, PCP continues to release PO free radicals during two degradation stages since 200 °C, which agrees well with the TGA-FTIR data. The fragments are m/z 168, 169 and 170. For the existence of DOPO group, we deduce m/z 170 is from *o*-phenylphenol, and m/z 168 and 169 are dibenzofuran and *o*-phenylphenoxyl free radical, respectively. Moreover, *o*-phenylphenoxyl free radicals are also released during two degradation stages.

Given the pyrolysis products discussed above, we conclude that P-based flame retardant is able to act in both the vapor phase and condensed phase. In the vapor phase, volatile radicals such as $\text{OP}\cdot$, $\text{O}_2\text{P}\cdot$, and $\text{HO}_2\text{P}\cdot$ act as scavengers of $\text{H}\cdot$ and $\text{OH}\cdot$. In the condensed phase, they may create a char residue acting as a barrier for the polymer matrix, which corresponds well with other literatures.³⁶⁻³⁸

Determination of LOI

LOI reflects the minimum oxygen concentration (in an oxygen-nitrogen flowing mixture) required to support downward flame combustion, and can be used to indicate the flame retardancy of polymers.³⁹⁻⁴⁰

To study the flame retardancy of PCP, we prepared a series of PUFs added with different contents of PCP by a one-pot free-rise method. Table 2 shows the flammability of pure PUF and flame retardant PUFs by their LOI. As expected, the addition of PCP into PUF leads to the increase of LOI, which rises in a dosage-dependent way.

Compared with PUF-1# to PUF-3#, the LOIs of PUFs added with 30, 50 and 70 php PCP are 19.3 %, 20.4 % and 22.0 % respectively, Compared to pure PUF. The PUFs added with PCP have higher LOIs compared with those added with CD at the

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same dosage. This phenomenon might be attributed to the P-containing group in PUFs.⁴¹

Conclusions

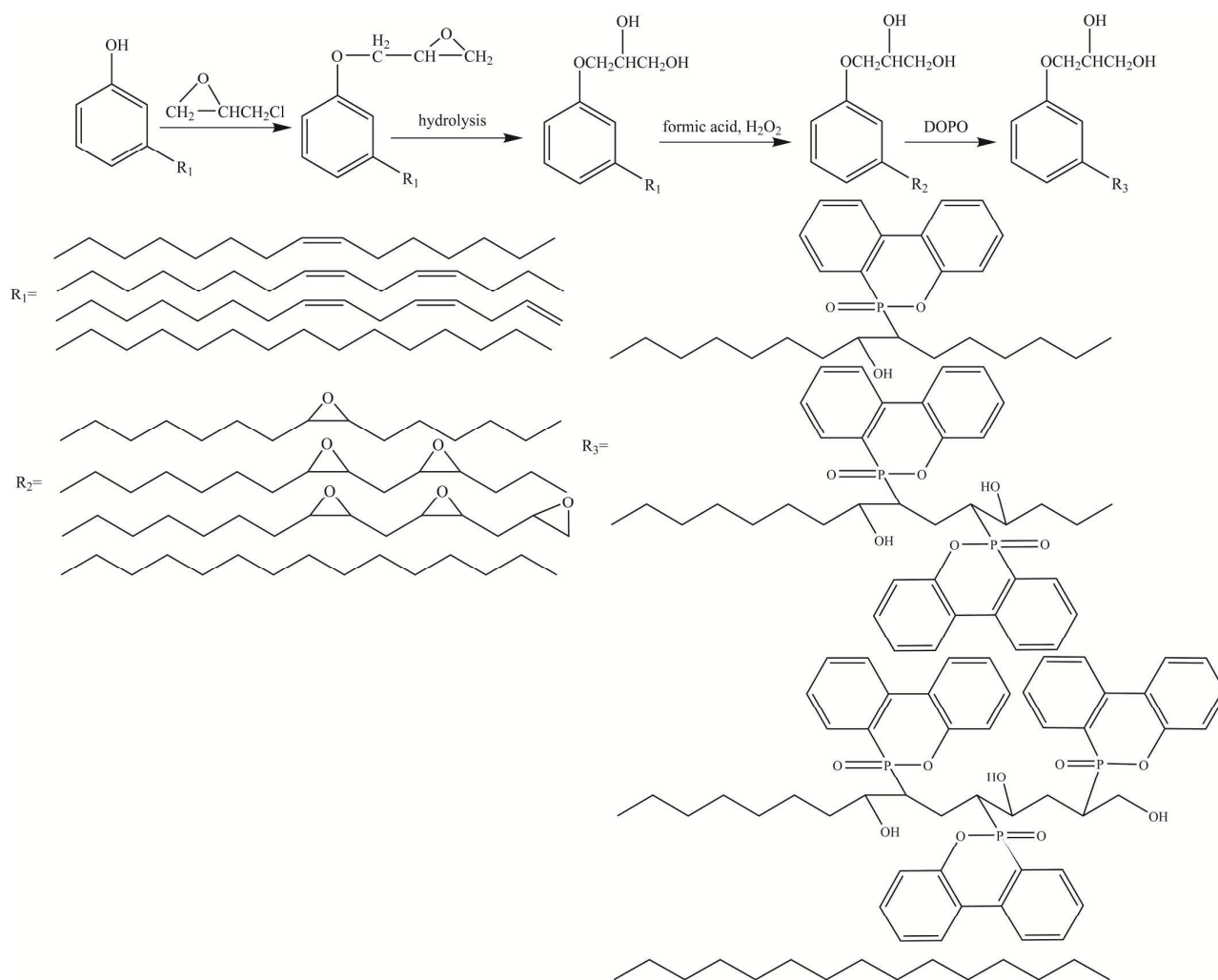
PCP, a novel cardanol derivative, was synthesized. Its structure was confirmed by FT-IR and ¹H NMR. Its flame retardancy and thermal stability were assessed by LOI and TGA. The degradation occurred in two stages with varying mass rate losses for PCP. The PCP had higher T_i, T_f, and T_{max} than CD of the same class. PCP also had higher mass residue than CD (6.77% vs. 0.02%) and higher thermal stability. LOI increased in a dosage-dependent way after addition of PCP into PUF. During thermal degradation of PCP disclosed by TGA-FTIR and TGA-MS, PCP continued to release PO free radicals and *o*-phenylphenoxyl free radical acting as scavengers of H• and OH• since 200 °C. The phosphaphenanthrene group may create a char residue acting as a barrier for the polymer matrix. This study provides scientific data for production of value-added products from cardanol.

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Scheme1 The synthetic route for preparation of CD and PCP

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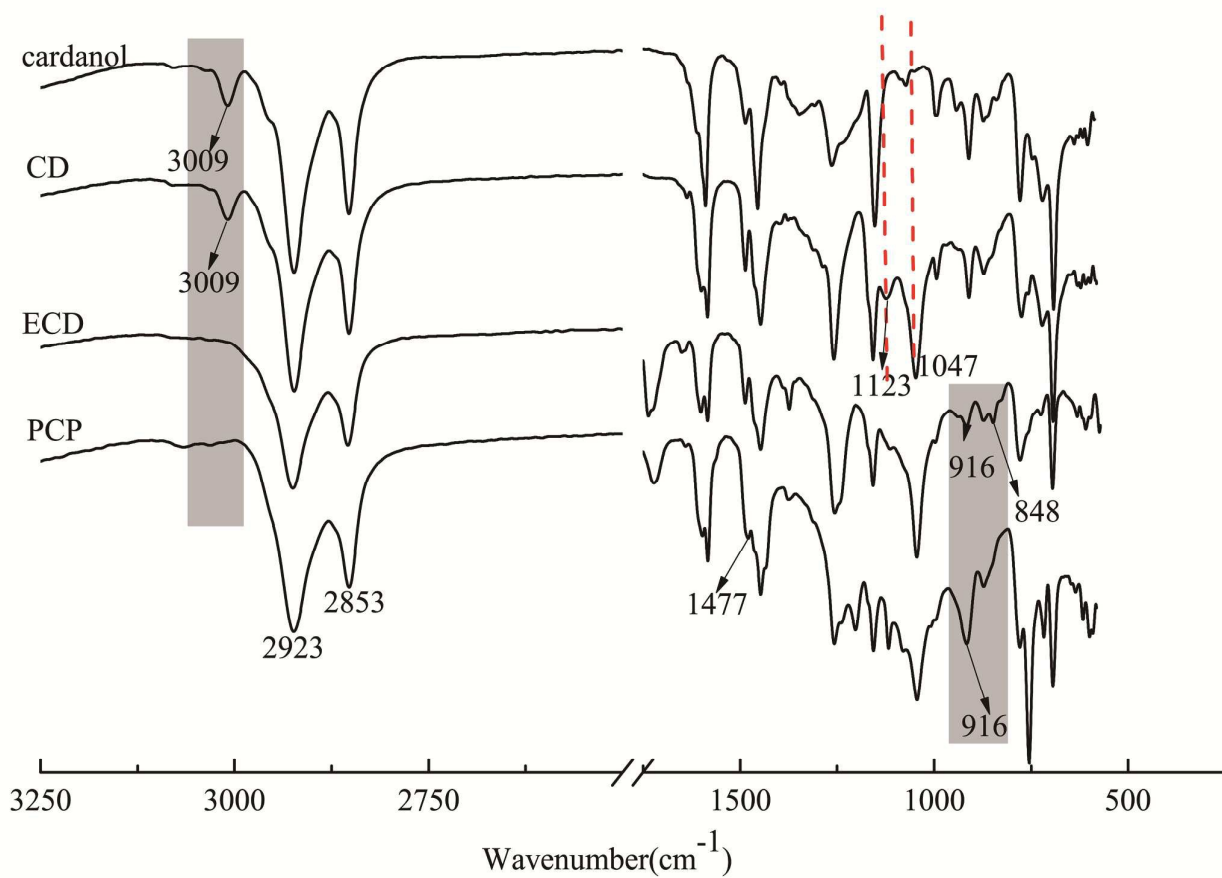


Fig. 1 The FT-IR spectra of cardanol, CD, ECD and PCP

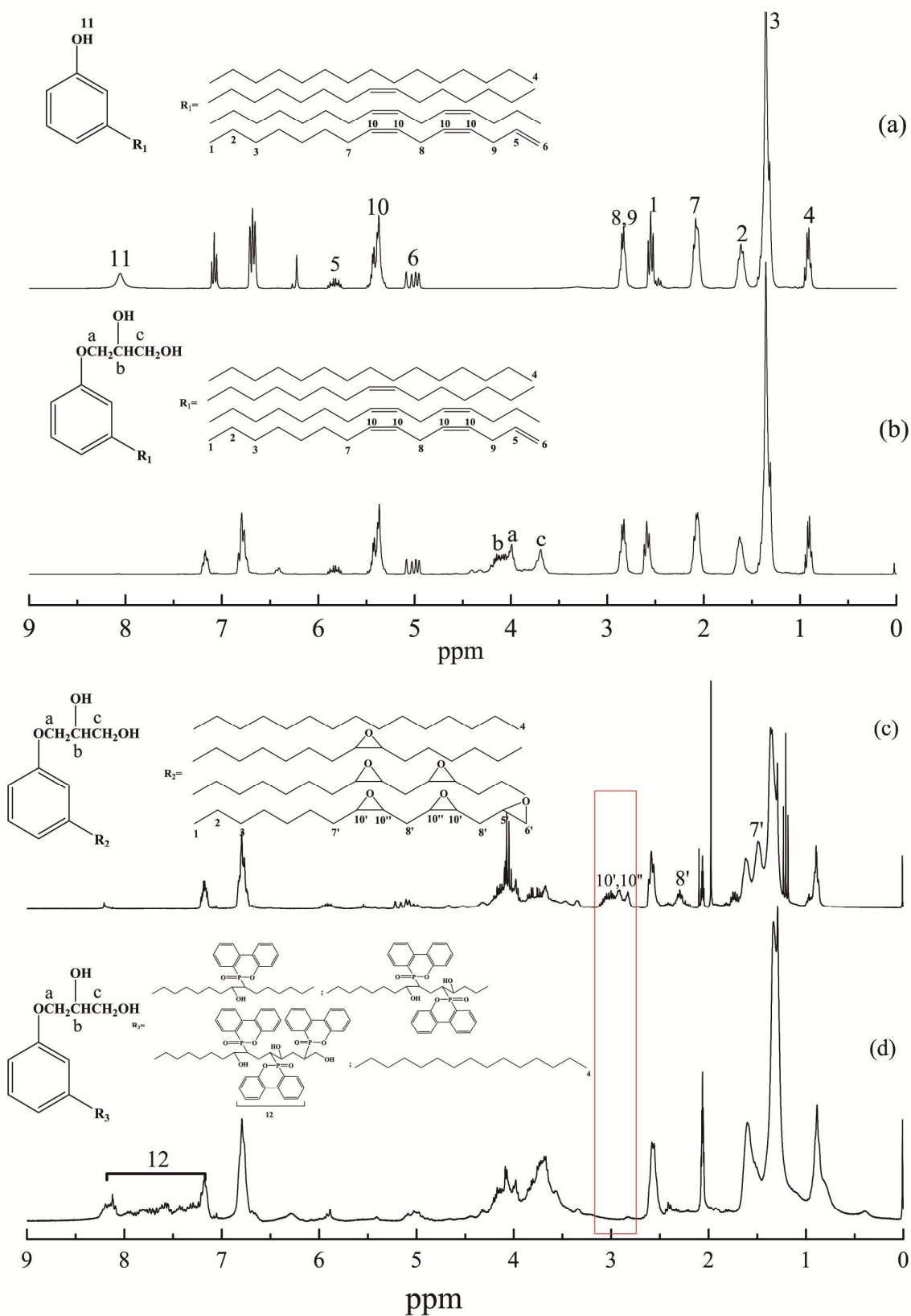
Fig. 2 The ^1H NMR spectra of cardanol, CD, ECD and PCP

Table 1 TGA data of CD and PCP

Samples	Degradation step(no.)	Degradation temperature (°C)			Mass loss(%)	Residual mass(%)
		T _i	T _f	T _{max}		
CD	I	322.8	398.9	369.8	35.1	0.02
	II	412.1	795.2	454.7	64.88	
PCP	I	341.7	419.7	385.5	44.2	6.77
	II	434.5	795.2	466.7	49.03	

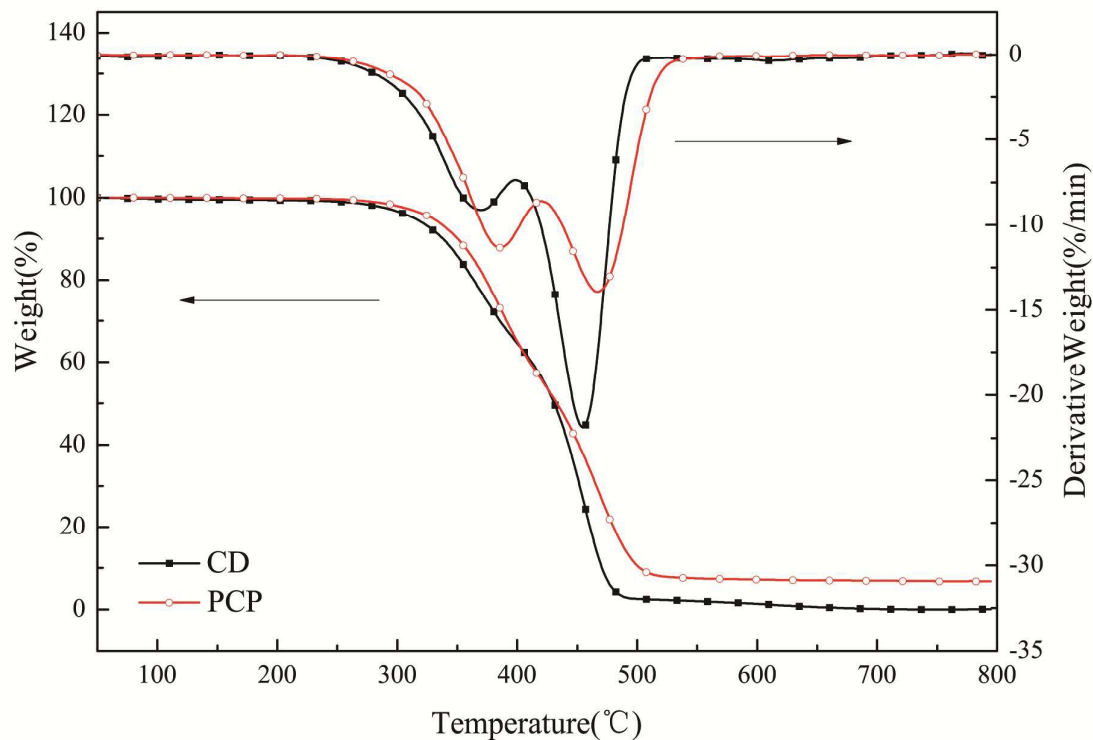


Fig. 3 TGA and DTG curves of CD and PCP

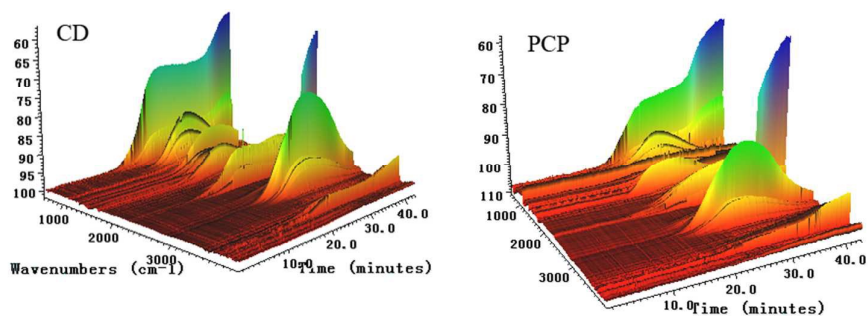


Fig. 4 The 3D TGA-FTIR spectra of gas phase in the thermal degradation of CD and PCP

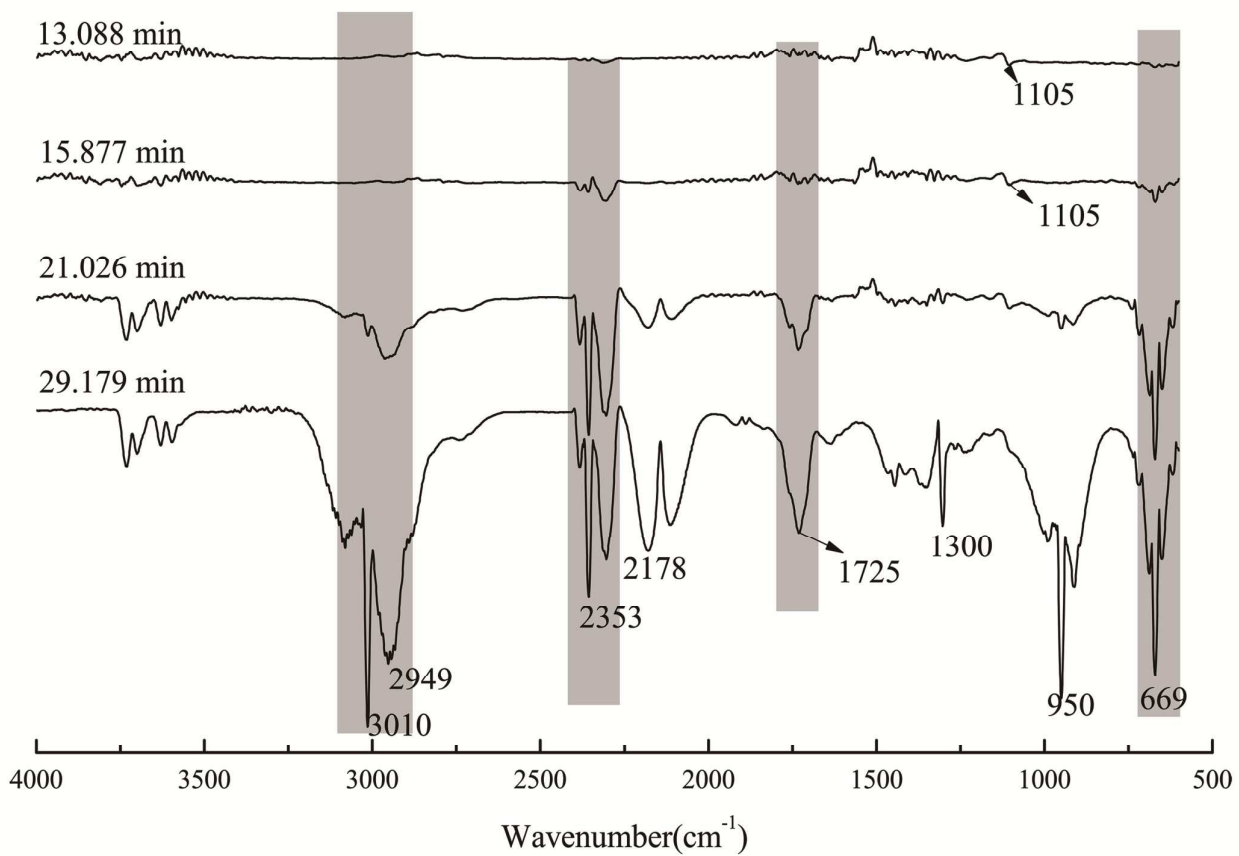


Fig. 5 FT-IR spectra of pyrolysis products of CD at different time

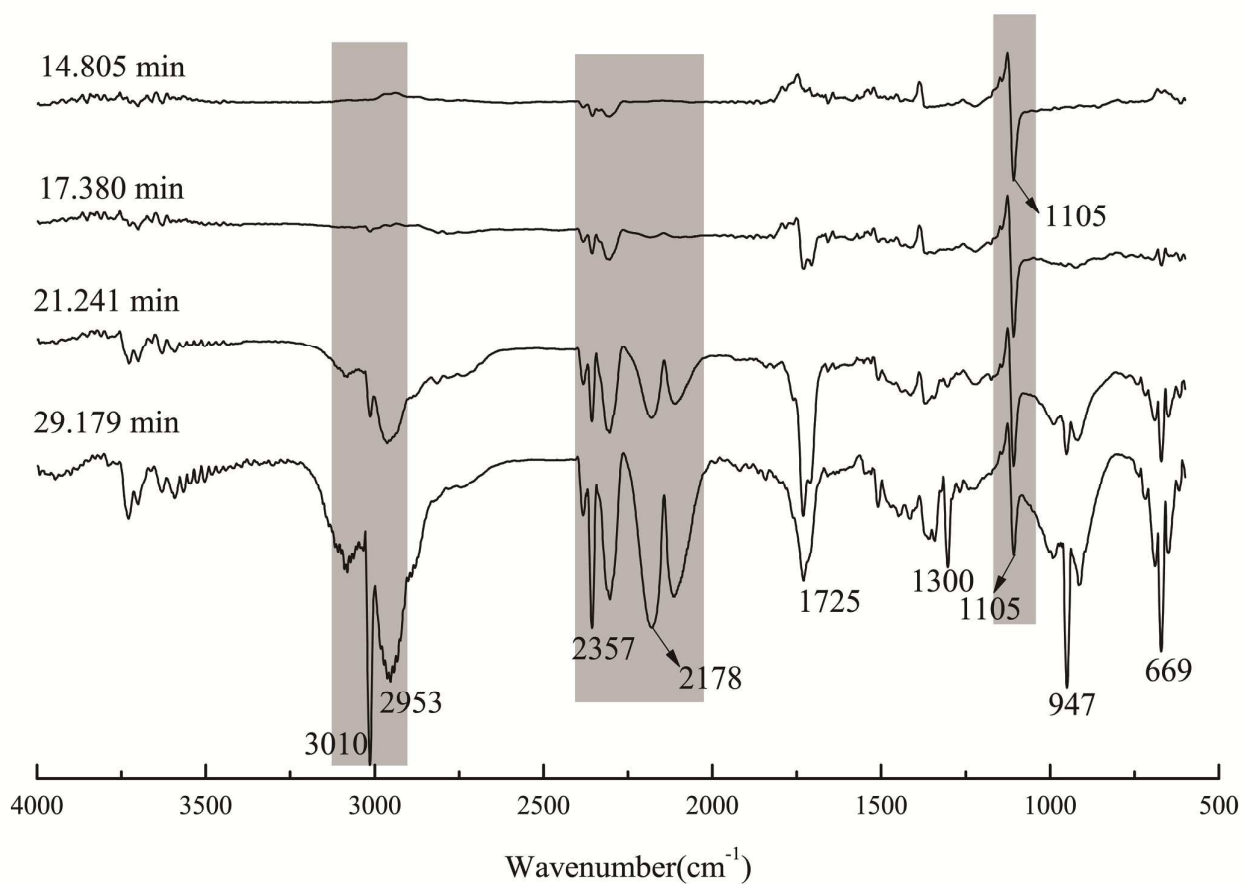


Fig. 6 FT-IR spectra of pyrolysis products of PCP at different time

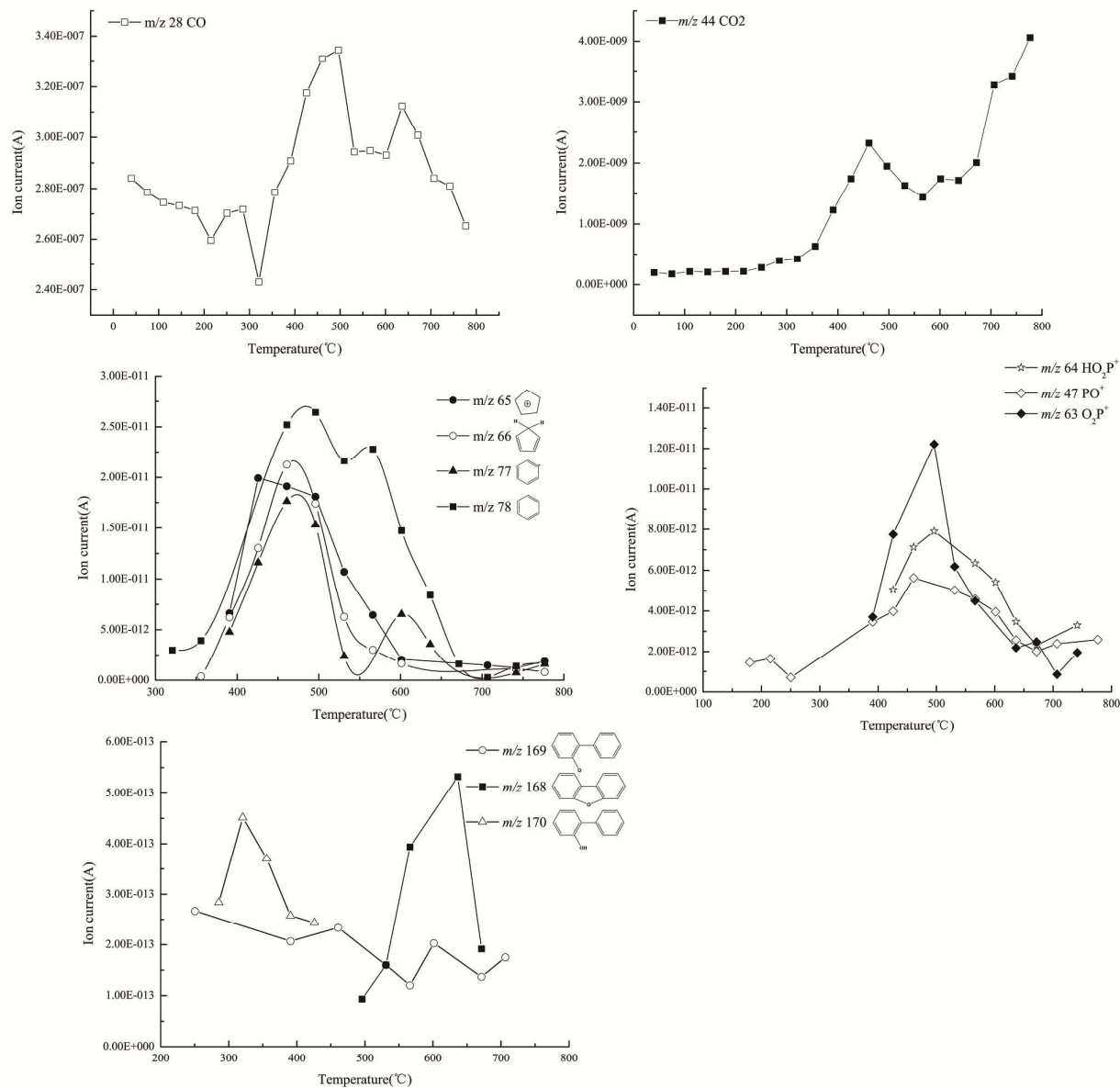


Fig. 7 Ion current curves for species produced from degradation of PCP

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Table 2 Formulations and LOIs of PUFs added with different contents of PCP or CD

Samples	polyether polyol 4110	PCP	CD	MDI	Catalyst	Surfactant	Blowing agent	LOI (%)
Neat PUF	100	—	—	130	1	2.5	20	18.2
PUF-1#	70	30	—	130	1	2.5	20	19.3
PUF-2#	50	50	—	130	1	2.5	20	20.4
PUF-3#	30	70	—	130	1	2.5	20	22.0
PUF-4#	70	—	30	130	1	2.5	20	18.5
PUF-5#	50	—	50	130	1	2.5	20	19.0
PUF-6#	30	—	70	130	1	2.5	20	19.5