

# The curing behavior and properties of phthalonitrile resins using ionic liquids as a new class of curing agents

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**Abstract.** Binary blends composed of 1,3-bis (3,4-dicyanophenoxy) benzene (3BOCN) and ionic liquids (ILs) with different molecular structures were prepared. The curing behavior of these 3BOCN/ILs blends were studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and rheological analysis. The study suggested that the blends possessed a wide processing window and the structures of ILs (anion, cation and alkyl chain length at cation) had an effect on curing behavior. The 3BOCN/[EPy]BF<sub>4</sub> resins were prepared at elevated temperature. IR spectra of the resins showed that there were triazine and isoindoline formed in curing process. The TGA and dynamic mechanical analysis (DMA) revealed that the resins have excellent thermal stability together with high storage modulus and high glass transition temperature ( $T_g$ ). Dielectric properties, long term oxidative aging and water uptake measurements of the resins suggested the IL brought some unique properties to the resins.

**Keywords:** *thermosetting resins, thermal properties, phthalonitrile, ionic liquids, curing behavior*

## 1. Introduction

As a class of high-temperature/performance polymer, phthalonitrile (PN) resins have many excellent properties such as high thermal and oxidative stability, flame retardance, the absence of a  $T_g$  before the thermal decomposition temperature, water and chemical resistance [1, 2]. These excellent high-temperature properties make the PN resins attractive for many military and civilian advanced technological applications, such as composite matrices [3, 4], adhesives [5], electrical conductors [6], and carbon precursors [7].

However, the polymerization of neat PN compound is extremely sluggish, the high curing-temperature of PN resins limited their further applications [1]. In order to address this problem, considerable research efforts have been expended on the development for the curing agent. To date, lots of Lewis acids/bases

curing agent, such as metallic salts, strong organic acids, strong organic acids/amine salts and active hydrogen-containing heterocyclic structures have been developed and used [8–17]. In addition to the traditional Lewis acids/bases, our laboratory also reported the cooperative curing effect between phthalonitrile and methyl tetrahydrophthalic anhydride end-capped imide compound (MODA) [18, 19].

To find more kinds of efficient curing agents, we have done a lot of work. Recently we found that a variety of ionic liquids (ILs) could promote the curing process of PN. ILs are organic salts that melt at very low temperature (empirically below 100 °C) [20, 21], which are composed of bulky and nonsymmetrical organic cations (such as pyridinium, pyrrolidinium, imidazolium, tetraalkyl ammonium and tetraalkyl phosphonium) and numerous different organic or inorganic anions (such as tetrafluoroborate, hexafluorophosphate,

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chloride). Different from molecular liquids, ILs have many outstanding properties, for instance, high thermal/chemical stability in the liquid state, vanishingly low vapor pressure, wide electrochemical window and the ability to dissolve easily for a wide range of inorganic/organic materials. ILs are also called ‘designer solvents’ because a long list of ILs with different properties can be obtained by varying the combinations of cations and anions. It was reported that the number of possible combinations of ILs can be up to  $10^{18}$  due to the ability to interchange their corresponding cationic/anionic moieties [22]. Besides, there has also been research work published on the use of ILs for polymerization reactions. In carbon nanotubes modified epoxy compositions, ILs could act as both catalytic epoxy resin crosslinkers and carbon nanofiller dispersing agent [23, 24]. With so many unique advantages, ILs may provide extremely large number of potential efficient and functional curing agents for PN.

The curing of phthalonitrile resins has been a challenging problem in this area, and related research on curing behavior of PN is an important step in solving this problem. The structures of ILs are diverse by varying the combination of cations and anions, consequently, they are suitable model system for researching the correlation between the structure of curing agent and PN curing behavior. In this study, we chose six kinds of common ILs as curing agents for the first time. They are *N*-ethylpyridinium tetrafluoroborate ([EPy]BF<sub>4</sub>), *N*-ethylpyridinium hexafluorophosphate ([EPy]PF<sub>6</sub>), 1-ethyl-3-methylimidazolium Tetrafluoroborate ([C<sub>2</sub>mim]BF<sub>4</sub>), 1-ethyl-3-methylimidazolium hexafluorophosphate ([C<sub>2</sub>mim]PF<sub>6</sub>), 1-butyl-3-methylimidazolium Tetrafluoroborate ([C<sub>4</sub>mim]BF<sub>4</sub>), 1-Octadecyl-3-methylimidazolium Tetrafluoroborate ([C<sub>18</sub>mim]BF<sub>4</sub>), each of them has the different cation or anion from another. The curing behaviors of 3BOCN/IL blends were investigated by TGA, DSC and rheological analysis. The thermal and dielectric properties of 3BOCN/[EPy]BF<sub>4</sub>

system were studied, the results showed that the cured resins possessed high glass transition temperatures, excellent thermal and thermal oxidation stabilities, unique dielectric properties. And the long term oxidative aging and water uptake properties were also studied. These works may open up a new research direction of the PN modification.

## 2. Experiment

### 2.1. Materials

Resorcinol (99.5%), dimethylsulfoxide (DMSO, AR), and Potassium carbonate (K<sub>2</sub>CO<sub>3</sub> 99.0%) were supplied by Chengdu Kelong Chemical Reagent Co., Ltd, Chengdu, China. 4-Nitrophthalonitrile (99%) was purchased from Hong Kong’s Ming Tai Prosperity Chemical Co., Ltd, Hong Kong, China. [EPy]BF<sub>4</sub>, [EPy]PF<sub>6</sub>, [C<sub>2</sub>mim]BF<sub>4</sub>, [C<sub>2</sub>mim]PF<sub>6</sub>, [C<sub>4</sub>mim]BF<sub>4</sub> and [C<sub>18</sub>mim]BF<sub>4</sub> were purchased from Chengjie Chemical Co., Ltd, Shanghai, China. All starting materials were of reagent grade and used without further purification.

### 2.2. Synthesis of 1, 3-bis

#### (3, 4-dicyanophenoxy) benzene 3BOCN

The phthalonitrile monomer 3BOCN was synthesized depending on a reported literature [13]. (Figure 1) <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 8.11–8.14 (d, 2H, Ar-H), 7.91–7.92 (d, 2H, Ar-H), 7.60–7.63 (dd, 1H, Ar-H), 7.53–7.59 (dd, 2H, Ar-H), 7.13–7.14 (s, 2H, Ar-H), 7.12 (s, 1H, Ar-H).

### 2.3. Preparation of the 3BOCN/IL blends

All kinds of 3BOCN/ILs blends (molar ratio 1.255:1, 2.152:1, 4.842:1) were prepared by transferring the compounds to a mortar and ground into a smooth paste under the infrared lamps.

### 2.4. Preparation of phthalonitrile polymer networks and samples

Resin-1 and Resin-2 were fabricated by degassing 3BOCN/[EPy]BF<sub>4</sub> blends (molar ratio 4.842:1 and

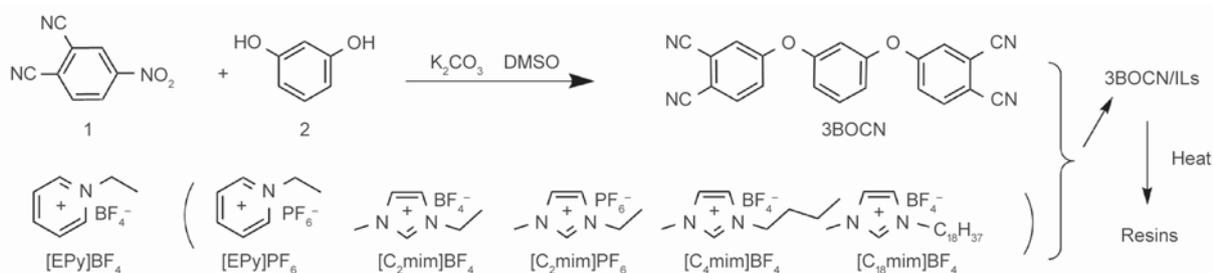


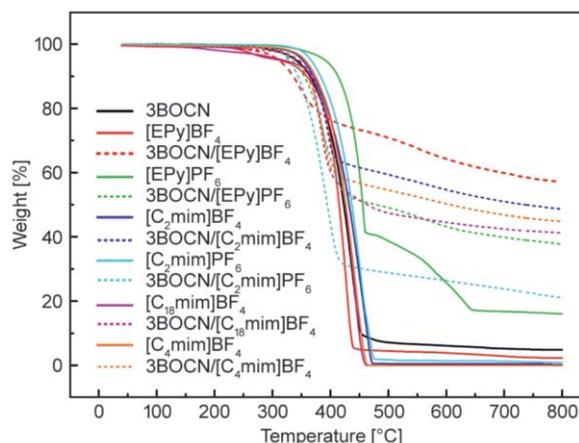
Figure 1. Synthesis of monomer and curing of 3BOCN/ILs blends

2.152:1) in a flask (−0.04 MPa) at 180 °C for 10 min with stirring, and then the melted 3BOCN/[EPy]BF<sub>4</sub> mixtures were poured into the preheated mold, placed in an oven, and heated under N<sub>2</sub> at 220 °C for 8 h, 245 °C for 8 h. After cooling, the samples were removed from mold, free-standing samples were cured under an inert atmosphere of argon at elevated temperatures of 270 °C for 8 h, 295 °C for 8 h, 320 °C for 8 h, 350 °C for 8 h, 380 °C for 8 h.

Polymer samples for DMA were sanded to 30.0×12.5×3.0 mm<sup>3</sup>. Samples for dielectric measurements were 20.0×20.0×1.8 mm<sup>3</sup>. Samples for water uptake measurements were approximately 50×13×2 mm<sup>3</sup>, and samples for oxidative aging studies were approximately 1.5×1.5×1.5 mm<sup>3</sup>.

## 2.5. Characterizations

<sup>1</sup>H nuclear magnetic resonance (NMR, 300 MHz) was obtained with a Bruker Avance-300 NMR spectrometer (Bruker, USA) with DMSO-*d*<sub>6</sub> as the solvent and tetramethylsilane (TMS) as the internal standard. Fourier transform infrared spectroscopy (FT-IR) were obtained from a Nicolet-460 FT-IR spectrometer (Thermo Fisher Scientific, USA) in KBr pellets in the range of 400–4000 cm<sup>−1</sup>. Thermo-gravimetric analysis (TGA) was performed from 40 to 800 °C at a heat rate of 10 °C·min<sup>−1</sup> in nitrogen or air at the flow rate of 60 mL·min<sup>−1</sup> by a TA Instruments Q500 thermo-gravimetric analyzer (TA, USA). Differential scanning calorimetry (DSC) was performed on a TA Instrument Q200 differential scanning calorimeter (TA, USA) under nitrogen atmosphere (50 mL·min<sup>−1</sup>) at a heating rate of 10 °C·min<sup>−1</sup>. Dynamic viscosity measurements were done by using a TA Instruments AR 2000 rheometer (TA, USA) in conjunction with environmental testing chamber for temperature control. The rheological characterization of 3BOCN-IL blends was investigated after the powders melted between the 24 mm diameter parallel plates at a strain of 2.5·10<sup>−4</sup> and a frequency of 1 Hz. The mixtures were tested from 40 to 380 °C in air at a heating rate of 5 °C·min<sup>−1</sup>. And the mixtures melt viscosity was also detected at 200, 220, 240, 260 °C in air as a function of time respectively. Dynamic mechanical analysis (DMA) was performed using a TA Instruments Q800 dynamic mechanical analyzer (TA, USA) under three-point bending mode, and the measurement was performed in nitrogen atmosphere from 40 to 450 °C with a heating rate of 5 °C·min<sup>−1</sup> and at a frequency of 1 Hz and a strain



**Figure 2.** TGA curves of 3BOCN, ILs and 3BOCN/ILs blends (molar ratio 1.255:1) at a heating rate of 10 °C/min

of 2.5·10<sup>−2</sup>%. Dielectric measurements were carried out at different frequencies ranging from 10<sup>−2</sup>–10<sup>7</sup> Hz at room temperature using Novocontrol Concept 50 Broadband Dielectric Spectrometer (Novocontrol Technologies, Germany).

## 3. Results and discussion

### 3.1. Polymerization behaviors of 3BOCN/IL blends

Figure 2 shows the TGA curves of 3BOCN, ILs and the 3BOCN/ILs blends (molar ratio 1.255:1) in nitrogen at the heating rate of 10 °C/min. The *T*<sub>5%</sub> of every kind of ILs we used are over 310 °C (Table 1), suggesting the high thermal stability of ILs, which is of great importance for phthalonitrile curing-agents. The weight decrease of 3BOCN/ILs blends slowed down at around 400 °C and the residual weight retention at 800 °C was higher than 3BOCN and corresponding ILs, indicating that the polymerization of 3BOCN was promoted by ILs during the heating run.

**Table 1.** The TGA data of 3BOCN, ILs and 3BOCN/ILs blends in N<sub>2</sub> at a heating rate of 10 °C/min

	<i>T</i> <sub>5%</sub> [°C]	Char yield at 800 °C [%]	
		Pure <sup>a</sup>	Blend <sup>b</sup>
3BOCN	341.00	4.83	–
[EPy]BF <sub>4</sub>	312.55	2.27	57.22
[EPy]PF <sub>6</sub>	391.30	16.06	37.82
[C <sub>2</sub> mim]BF <sub>4</sub>	352.30	0.10	48.73
[C <sub>2</sub> mim]PF <sub>6</sub>	366.20	0.31	21.17
[C <sub>4</sub> mim]BF <sub>4</sub>	356.28	0.00	44.88
[C <sub>18</sub> mim]BF <sub>4</sub>	318.44	0.00	41.33

<sup>a</sup>Pure 3BOCN or ILs

<sup>b</sup>The blend of 3BOCN and every kind of IL at 1.255:1 molar ratio

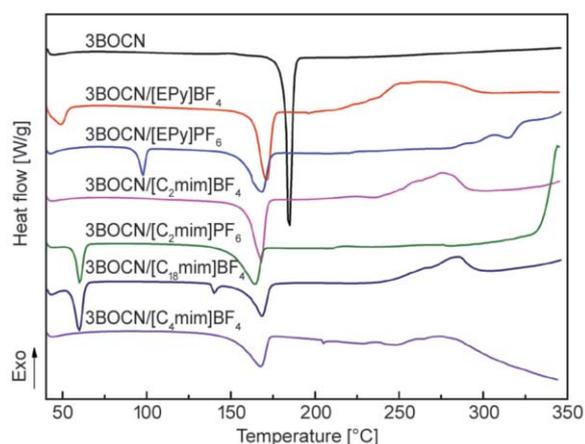
**Table 2.** The DSC data of 3BOCN and 3BOCN/ILs blends in N<sub>2</sub> at a heating rate of 10 °C/min

	$T_{m1}^a$ [°C]	$T_{m2}^a$ [°C]	$T_o^b$ [°C]	$T_p^c$ [°C]
3BOCN	–	184.38	–	–
3BOCN/[NPy]BF <sub>4</sub>	48.60	171.44	215.75	271.20
3BOCN/[NPy]PF <sub>6</sub>	97.33	168.20	276.50	306.97
3BOCN/[C <sub>2</sub> mim]BF <sub>4</sub>	<40	167.54	235.43	275.51
3BOCN/[C <sub>2</sub> mim]PF <sub>6</sub>	59.91	164.56	327.83	>350
3BOCN/[C <sub>4</sub> mim]BF <sub>4</sub>	<40	166.22	258.28	275.17
3BOCN/[C <sub>18</sub> mim]BF <sub>4</sub>	59.58	168.53	234.77	284.78

<sup>a</sup>Melting points<sup>b</sup>The curing onset temperature<sup>c</sup>The peak temperature of the exothermic area

The more 3BOCN was cured into thermoset network, the higher residual weight of blend at 800 °C. The char yield order of 3BOCN/ILs blend at 800 °C showed that the mass fraction of 3BOCN cured by IL decreased in ILs order: [EPy]BF<sub>4</sub> > [C<sub>2</sub>mim]BF<sub>4</sub> > [C<sub>4</sub>mim]BF<sub>4</sub> > [C<sub>18</sub>mim]BF<sub>4</sub> > [EPy]PF<sub>6</sub> > [C<sub>2</sub>mim]PF<sub>6</sub>. This order reflected the catalytic activity of ILs in some way.

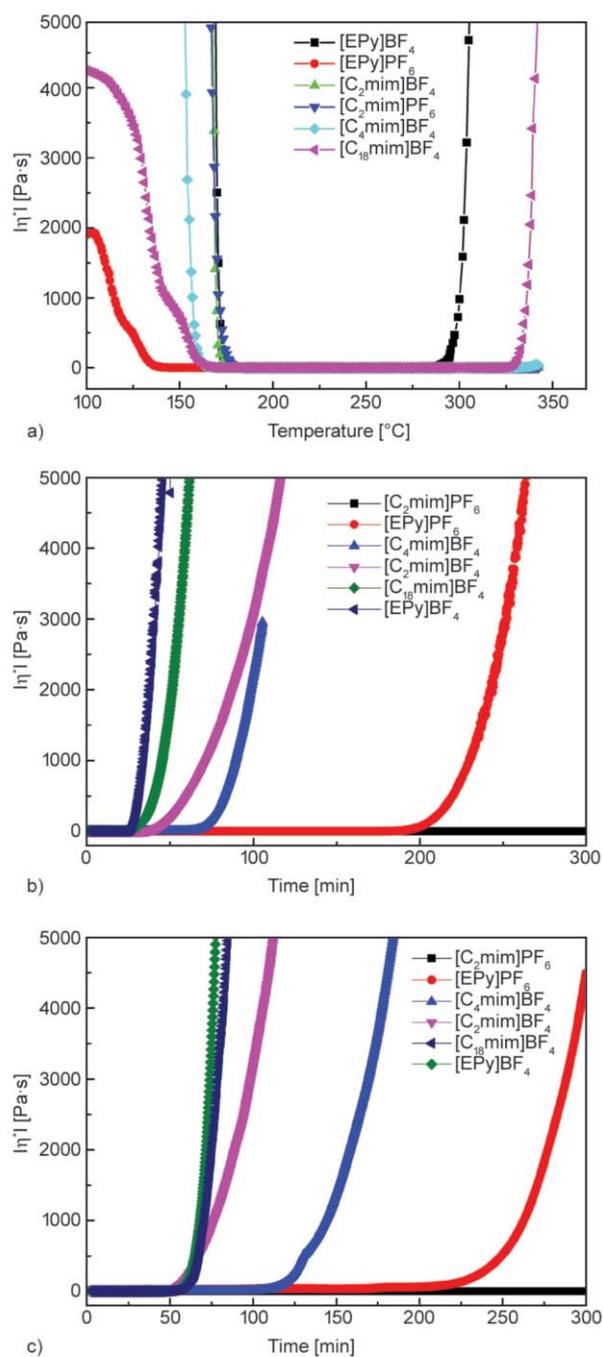
The thermal behavior of 3BOCN/ILs blends (molar ratio 1.255:1) were also studied by DSC at the heating rate of 10 °C/min in nitrogen (Figure 3, Table 2). There were two endothermic peaks in 3BOCN/[EPy]BF<sub>4</sub>, 3BOCN/[EPy]PF<sub>6</sub> and 3BOCN/[C<sub>2</sub>mim]PF<sub>6</sub> blends corresponding to the melting transition of IL and 3BOCN. 3BOCN/[C<sub>2</sub>mim]BF<sub>4</sub> and 3BOCN/[C<sub>2</sub>mim]BF<sub>4</sub> exhibited only one melting point between 40 and 350 °C, because the melting point of [C<sub>2</sub>mim]BF<sub>4</sub> and [C<sub>2</sub>mim]BF<sub>4</sub> is below 40 °C. Unexpectedly, we found another small endothermic peak at 140.5 °C in 3BOCN/[C<sub>18</sub>mim]BF<sub>4</sub> curve between the melting point of [C<sub>18</sub>mim]BF<sub>4</sub> and 3BOCN, this phenomenon might attribute to that a portion of 3BOCN dissolved in [C<sub>18</sub>mim]BF<sub>4</sub> precipitated a new crystal form after 3BOCN/[C<sub>18</sub>mim]BF<sub>4</sub> blend cool down. Curve of pure 3BOCN showed no exothermic transition at elevated temperature indicating 3BOCN was hard to polymerize by itself. While the polymerization of 3BOCN could be promoted by ILs. The curing onset temperature of blends increased in ILs order: [EPy]BF<sub>4</sub> < [C<sub>18</sub>mim]BF<sub>4</sub> < [C<sub>2</sub>mim]BF<sub>4</sub> < [C<sub>4</sub>mim]BF<sub>4</sub> < [EPy]PF<sub>6</sub> < [C<sub>2</sub>mim]PF<sub>6</sub>, which had some correlation to char yield order of 3BOCN/ILs blends at 800 °C: [EPy]BF<sub>4</sub> > [C<sub>2</sub>mim]BF<sub>4</sub> > [C<sub>4</sub>mim]BF<sub>4</sub> > [C<sub>18</sub>mim]BF<sub>4</sub> > [EPy]PF<sub>6</sub> > [C<sub>2</sub>mim]PF<sub>6</sub>. These rankings are the reflection of ILs catalytic activity in different aspects. Particularly, the difference in rank of [C<sub>18</sub>mim]BF<sub>4</sub> may due to that

**Figure 3.** DSC curves of 3BOCN and 3BOCN/ILs blends (molar ratio 1.255:1) at a heating rate of 10 °C/min

the molecular weight of [C<sub>18</sub>mim]BF<sub>4</sub> is much higher than other kinds of ILs. When 3BOCN was blended with different ILs in fixed molar ratio, the mass ratio of 3BOCN in 3BOCN/[C<sub>18</sub>mim]BF<sub>4</sub> was much lower than others leading to a rank down in char yield. From the TGA and DSC data, it can be found that the catalytic activity of ILs changes with the structures of cation and decreases in anion order: [Bf<sub>4</sub>] > [Pf<sub>6</sub>].

To learn more about the polymerization behavior of 3BOCN/ILs blends as well as the relationship between ILs structure and curing behavior, dynamic viscosity measurements were employed. In Figure 4a, the melt viscosities of 3BOCN/ILs blends were determined as function of temperature at the heating rate of 5 °C/min. In every curve of the blends, we could observe a rapid decrease in viscosity around the melting point of 3BOCN and the melt viscosities were very low (3~4 Pa·s) which was evidence of their good processability. With the increase of temperature, the viscosities of 3BOCN/[EPy]BF<sub>4</sub> and 3BOCN/[C<sub>18</sub>mim]BF<sub>4</sub> moved up sharply at 306.0 and 319.7 °C respectively, while the rest of blends didn't have obvious viscosity transition, indicating that [EPy]BF<sub>4</sub> and [C<sub>18</sub>mim]BF<sub>4</sub> have higher catalytic activity to promote the curing of 3BOCN than other ILs. The Figure 4a also revealed that the process windows of all 3BOCN/ILs blends were very large (>130 °C), which is good for the fabrication of large size composite sections.

In Figure 4b and 4c the melt viscosities of 3BOCN/ILs blends were determined as function of time at 260 (Figure 4b) and 240 °C (Figure 4c). The time when the blends began to polymerize quickly varied with ILs. 3BOCN/[EPy]BF<sub>4</sub> blend was the fastest to



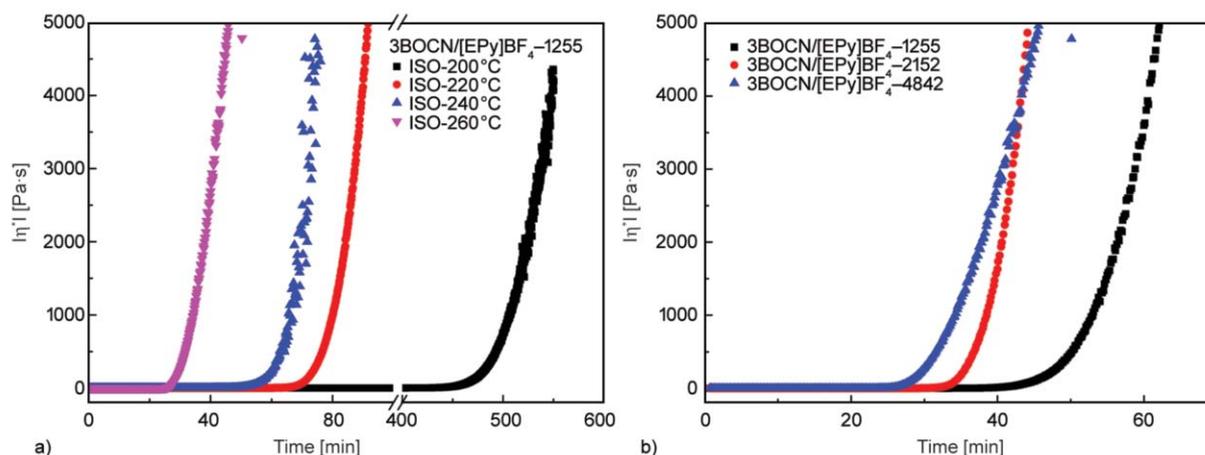
**Figure 4.** Melt viscosity curves for 3BOCN/ILs (molar ratio 1.255:1). (a): Melt viscosity vs. temperature at heating rate of 5 °C/min; (b) and (c): Melt viscosity vs. time at 260 and 240 °C

polymerize. While 3BOCN/[C<sub>2</sub>mim]PF<sub>6</sub> blend was the most sluggish, its viscosity kept low during the test process (600 minutes). The gelation points were showed in Table 3, gelation time increased in ILs order at both 260 and 240 °C: [EPy]BF<sub>4</sub> < [C<sub>18</sub>mim]BF<sub>4</sub> < [C<sub>2</sub>mim]BF<sub>4</sub> < [C<sub>4</sub>mim]BF<sub>4</sub> < [EPy]PF<sub>6</sub> < [C<sub>2</sub>mim]PF<sub>6</sub>, which is in agreement with the order of onset temperature in DSC result.

The curing behavior of different 3BOCN/ILs blends discussed above were investigated by TGA, DSC and rheological analysis. And these data all revealed that PN curing behavior changed with the structures of ILs. According to the experimental result, we can sum up a ranking of ILs catalytic activity: [EPy]BF<sub>4</sub> > [C<sub>18</sub>mim]BF<sub>4</sub> > [C<sub>2</sub>mim]BF<sub>4</sub> > [C<sub>4</sub>mim]BF<sub>4</sub> > [EPy]PF<sub>6</sub> > [C<sub>2</sub>mim]PF<sub>6</sub>. The physic and chemical properties of ILs vary with some structural factors (anion, cation, alkyl chain length at cation) [25–31]. These factor also play decisive roles on the catalytic activity of ILs to PN curing. Firstly, it is obvious that ILs with [BF<sub>4</sub>] have much better curing efficiency than [PF<sub>6</sub>], suggesting the dominating influence of the anion on catalytic activity. Besides the anion, the cation has a strong influence too. ILs with [EPy] cations are more efficient than those with [C<sub>2</sub>mim] cation: [EPy]BF<sub>4</sub> > [C<sub>2</sub>mim]BF<sub>4</sub>, [EPy]PF<sub>6</sub> > [C<sub>2</sub>mim]PF<sub>6</sub>. Moreover, the catalytic activity is relative to alkyl chain length at cation: [C<sub>18</sub>mim]BF<sub>4</sub> > [C<sub>2</sub>mim]BF<sub>4</sub> > [C<sub>4</sub>mim]BF<sub>4</sub>, which is similar to the relationship between melting point and alkyl chain length at cation: when the alkyl chains at cation become larger, the electrostatic forces between cation and anion decreases, resulting in lower melting point, but when the alkyl chains are greater than a certain length, the Van der Waals forces play an important part, resulting in the increase in melting point. ([C<sub>18</sub>mim]BF<sub>4</sub>: 60.5 °C, [C<sub>2</sub>mim]BF<sub>4</sub>: 15 °C, [C<sub>4</sub>mim]BF<sub>4</sub>: -71 °C) [31]. In a word, the structures of ILs have an effect on curing behavior, the effect may be related to interaction

**Table 3.** The data of 3BOCN/ILs (molar ratio 1.255:1) gelation point in dynamic viscosity measurements

	Gelation temperature at heating rate of 5 °C/min [°C]	Gelation time at 260 °C [min]	Gelation time at 240 °C [min]
3BOCN/[EPy]BF <sub>4</sub>	306.0	25.6	40.0
3BOCN/[EPy]PF <sub>6</sub>	>350	174.4	207.1
3BOCN/[C <sub>2</sub> mim]BF <sub>4</sub>	>350	37.3	45.6
3BOCN/[C <sub>2</sub> mim]PF <sub>6</sub>	>350	>500	>500
3BOCN/[C <sub>4</sub> mim]BF <sub>4</sub>	>350	65.0	100.0
3BOCN/[C <sub>18</sub> mim]BF <sub>4</sub>	319.7	30.5	42.5



**Figure 5.** Melt viscosity vs. time cure for 3BOCN/[EPy]BF<sub>4</sub> blend (a) at various temperature in 1.255:1 mass ratio, (b) in 1.255:1, 2.152:2, 4.842:1 molar ratios at 260°C

between anion and cation and charge distribution in them.

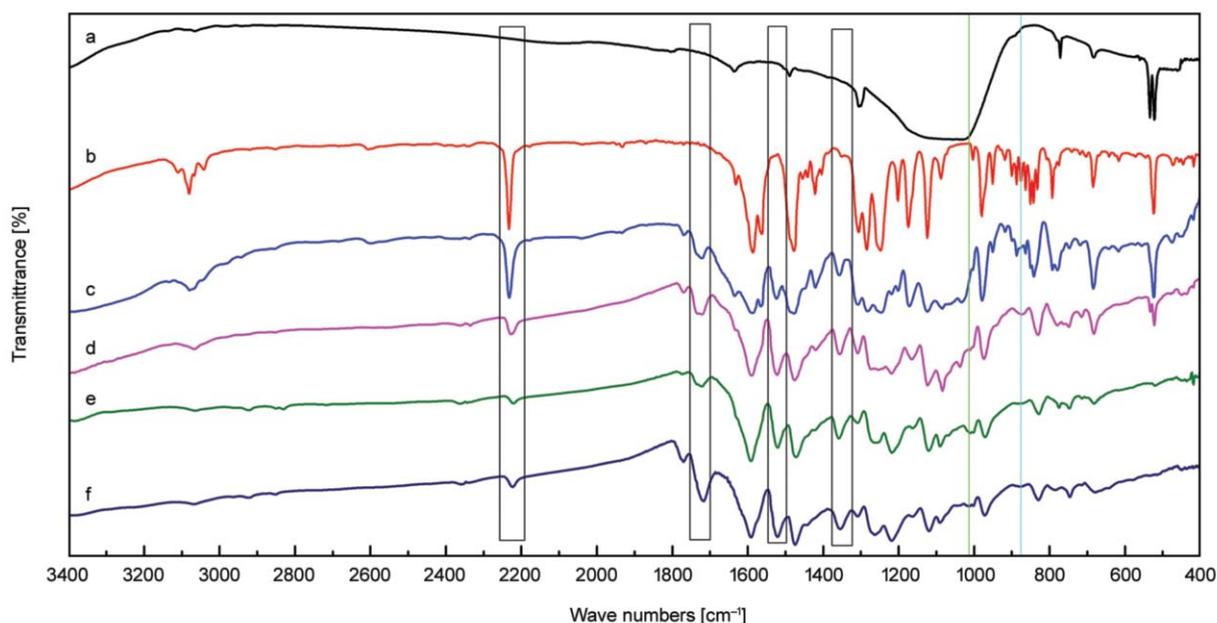
Rheometric studies on 3BOCN/[EPy]BF<sub>4</sub> blend were also conducted to learn about the influence of IL concentration and heating temperature on the curing behavior. Melt viscosity increase as a function of reaction time for polymerization of 3BOCN/[EPy]BF<sub>4</sub> at 200, 220, 240 and 260 °C in 1.255:1 mass ratio are shown in Figure 5a, and 3BOCN/[EPy]BF<sub>4</sub> in 1.255:1, 2.152:1, 4.842:1 molar ratios at 260 °C are shown in Figure 5b. From the curves, it is evident that the blends can keep in low viscosity for a long time. And as expected, the higher the temperature or the higher

the content of IL, the faster the rate of viscosity increased.

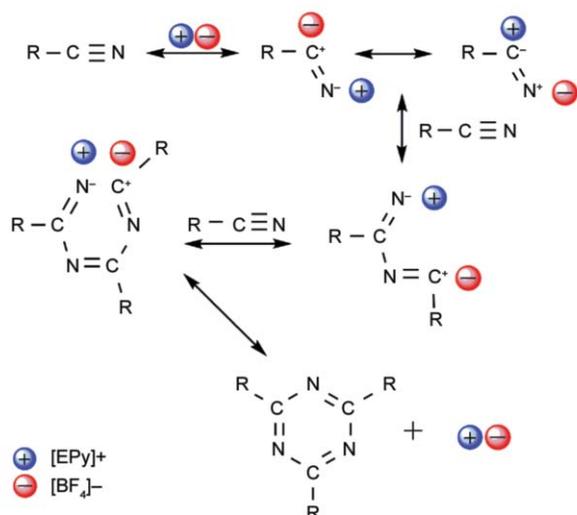
## 3.2. Properties of polymer network

### 3.2.1. FT-IR

To observe the polymerization reaction and polymer structure, IR measurement was conducted on 3BOCN/[EPy]BF<sub>4</sub> cured at elevated temperatures, as shown in Figure 6. Nitrile group absorption peak at around 2230 cm<sup>-1</sup> for 3BOCN was evidently weakened. Meanwhile new strong absorption peak at around 1520 and 1360 cm<sup>-1</sup> assigned to triazine was observed. Moreover, typical isoindoline peak at 1720 cm<sup>-1</sup> was



**Figure 6.** IR spectra of 3BOCN, [EPy]BF<sub>4</sub> and polymers (3BOCN/[EPy]BF<sub>4</sub> molar ratio 2.152:1) cured at elevated temperatures. (a) [EPy]BF<sub>4</sub>; (b) 3BOCN; (c) 240 °C for 8 h; (d) 240 °C for 8 h, 245 °C for 8 h, 270 °C for 8 h; (e) 240 °C for 8 h, 245 °C for 8 h, 270 °C for 8 h, 295 °C for 8 h, 320 °C for 8 h; (f) 220 °C for 8 h, 245 °C for 8 h, 270 °C for 8 h, 295 °C for 8 h, 320 °C for 8 h, 350 °C for 8 h, 380 °C for 8 h.



**Figure 7.** Probable curing mechanism of 3BOCN/[EPy]BF<sub>4</sub> system

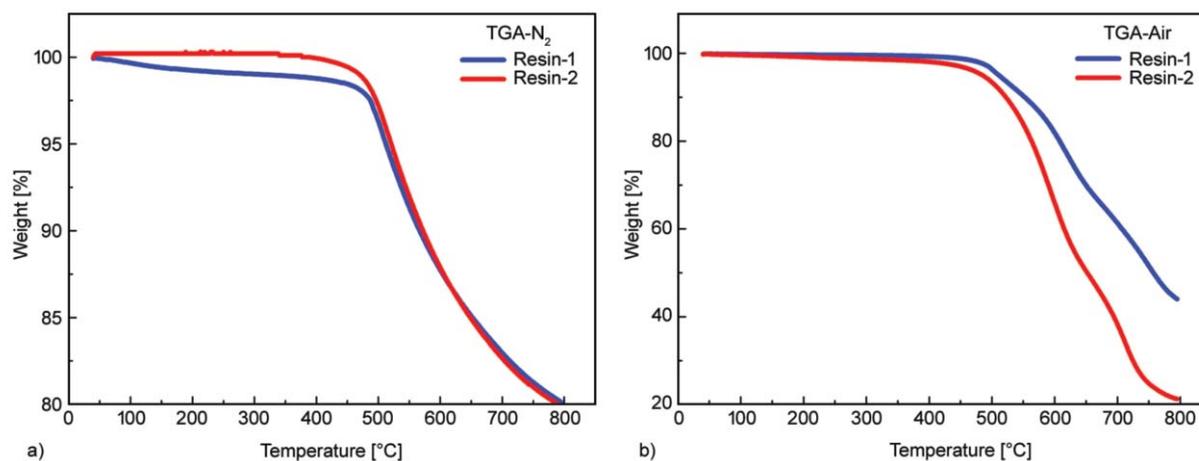
also observed [32]. However, peak assigned to characteristic absorptions representative of phthalocyanine (1010 cm<sup>-1</sup>) [33] formation can be hardly found. Additionally, the peak of nitrile group became weaker gradually with the curing degree, and there was still residual nitrile group even after post-cured of 3BOCN/[EPy]BF<sub>4</sub> system, which may due to the steric hindrance of the unreacted nitrile groups at the ortho-position of triazine ring [34]. Figure 7 showed the probable curing mechanism of 3BOCN/[EPy]BF<sub>4</sub> system.

### 3.2.2. Thermal and dynamic mechanical properties

The thermal and thermal-oxidative stability of post-cured 3BOCN/[EPy]BF<sub>4</sub> resins was investigated by TGA in nitrogen and air atmosphere at a heating rate of 10 °C/min. Figure 8a showed the thermal stability

of cured resin samples in different mass ratio under N<sub>2</sub> atmosphere. The thermal stability of the cured Resin-1 (3BOCN/[EPy]BF<sub>4</sub> molar ratio 4.842:1) and Resin-2 (3BOCN/[EPy]BF<sub>4</sub> molar ratio 2.152:1) were close and both of them exhibited excellent thermal stability up to 450 °C in N<sub>2</sub> and their T<sub>5</sub> and T<sub>10</sub> are higher than 512 and 567 °C respectively. Particularly, the char yield of these resin reached up to 80% (Table 4), suggesting that the phthalonitrile resins cure by ionic liquids have outstanding thermal stability and may be excellent carbon precursors<sup>7</sup>. The cured resins also exhibited good thermal-oxidative stability in air atmosphere as showed in Figure 8b. Both of Resin-1 and Resin-2 show thermal-oxidative stability to about 480 °C. But when the temperature was higher than 500 °C, the Resin-2 decomposed faster than Resin-1 and they finally had char yield of 21.3 and 44.1% respectively, which might due to the higher content of ILs in Resin-2. In a word, the data of TGA shows that the thermal and thermos-oxidative stability of 3BOCN/[EPy]BF<sub>4</sub> system are excellent and rank the highest value compared with other curing system [13, 18, 19].

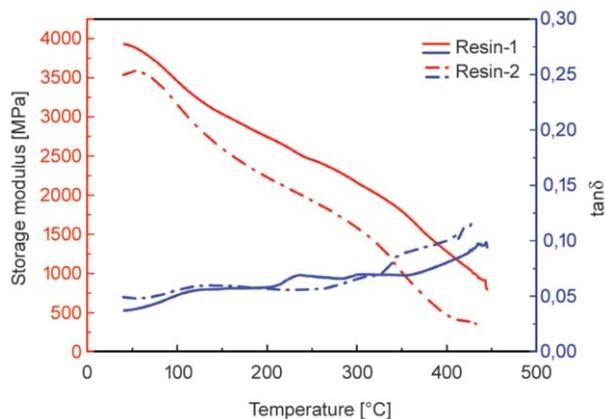
DMA were performed on Resin-1 and Resin-2 in N<sub>2</sub> atmosphere. We observed (Figure 9) that the storage modulus of the two resins gradually decreased from 40 to 450 °C, while this decrease didn't result in complete loss of mechanical properties at elevated temperature, which is evidence for the good high-temperature mechanical properties. Meanwhile, no peak of T<sub>g</sub> was observed in tanδ curves, indicating T<sub>g</sub> of the two resins are higher than 450 °C. During the heating process between 40 and 400 °C, the storage modulus of Resin-1 changed from 3930 to 1280 MPa, while the storage modulus of Resin-2 changed from 3588



**Figure 8.** TGA curves of 3BOCN/[EPy]BF<sub>4</sub> (Resin-1 4.842:1 molar ratio; Resin-2 2.152:1 molar ratio) post-cured resins at the heating rate of 10 °C/min in (a) N<sub>2</sub>, (b) air

**Table 4.** TGA data of 3BOCN/[EPy]BF<sub>4</sub> (Resin-1 4.842:1 molar ratio; Resin-2 2.152:1 molar ratio) post-cured resins at the heating rate of 10 °C/min in N<sub>2</sub> and air.

Resins	TGA in N <sub>2</sub>			TGA in air		
	T <sub>5</sub> [°C]	T <sub>10</sub> [°C]	Char yield at 800 °C [%]	T <sub>5</sub> [°C]	T <sub>10</sub> [°C]	Char yield at 800 °C [%]
Resin-1	512.4	566.9	80.1	505.5	541.6	32.3
Resin-2	520.7	572.2	80.0	485.1	522.2	21.3

**Figure 9.** Dynamic mechanical properties of 3BOCN/[EPy]BF<sub>4</sub> (Resin-1 4.842:1 molar ratio; Resin-2 2.152:1 molar ratio) post-cured resins

to 480 MPa. The relatively lower storage modulus of Resin-2 may due to that the residual IL in Resin-2 was more and acted as plasticizers.

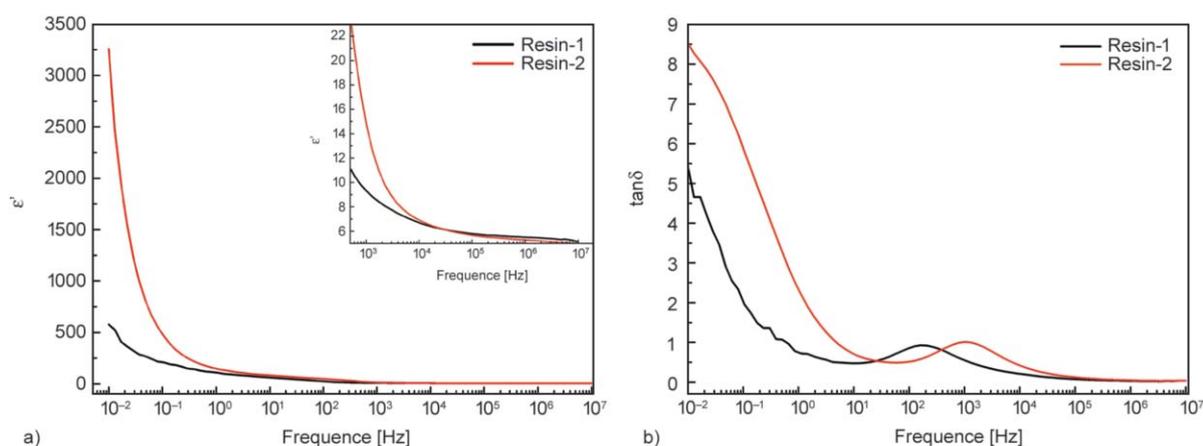
### 3.2.3. Dielectric property

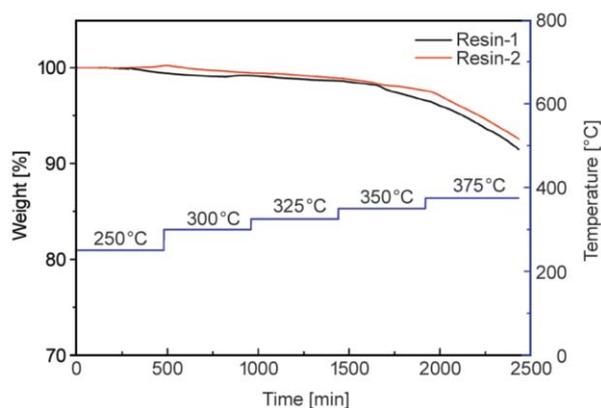
As a kind of salt melt at room temperature, the curing agent [EPy]BF<sub>4</sub> may bring some changes in dielectric property to cured resins. The dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\tan\delta$ ) as a function of frequency for samples in room temperature were illustrated in Figure 10. The result suggested that the

dielectric constant of these resins were very high at low frequency and decreased sharply with the increase of frequency from  $10^{-2}$  to  $10^5$  Hz and kept in range of 6.6~5.1 in frequency from  $10^5$ ~ $10^7$  Hz. The dielectric loss ( $\tan\delta$ ) values of these resins also showed similar decrease trend, but there were peaks at  $1.63 \cdot 10^2$  and  $1 \cdot 10^3$  Hz in curves of Resin-1 and Resin-2 respectively, which might due to that the IL caused heterogeneous phase in resins. Finally, the  $\tan\delta$  of the two resins decreased to about 0.03 in high frequency.

From the data of  $\epsilon'$  and  $\tan\delta$ , it can be concluded that the introduction of ionic liquid had significant effect on the dielectric properties of phthalonitrile resins and this effect changed with content of IL. The high dielectric constant and unique dielectric loss were brought to 3BOCN/IL resins by ILs, and these resins may be potential candidates for electronic industry and military applications [35], such as electrochemical devices, capacitors, active vibration control, aerospace, underwater navigation and surveillance, etc. [36, 37]

Additionally, the effect of IL content on the DMA and Dielectric data corresponded to the above-mentioned probable curing mechanism of 3BOCN/[EPy]BF<sub>4</sub> system.

**Figure 10.** Dielectric constant curves (a) and dielectric loss curves (b) of 3BOCN/[EPy]BF<sub>4</sub> (Resin-1 4.842:1 molar ratio; Resin-2 2.152:1 molar ratio) post-cured resins



**Figure 11.** Long-term aging of 3BOCN/[EPy]BF<sub>4</sub> (Resin-1 4.842:1 molar ratio; Resin-2 2.152:1 molar ratio) post-cured resins

### 3.2.4. Long-term aging and water absorption capability

The effect of long-term aging or heating at high temperatures under air is a very important factor in the practical use of PN resins under real world conditions. We simulated these conditions in TGA by subjecting samples (in  $1.5 \times 1.5 \times 1.5 \text{ mm}^3$ ) to stepwise heating at a series of temperatures between 250 and 375 °C at 8 h temperature intervals in flowing air (60 ml/min). Figure 11 and Table 5 show long-term aging data for Resin-1 and Resin-2. Upon heating from 250 to 350 °C, a cumulative weight loss of 3.42 and 2.40% was observed for Resin-1 and Resin-2, respectively. When the resins were further heated to 375 °C, the oxidative destruction of them became faster, and finally a cumulative weight loss of 8.52 and 7.44% was observed at the end of this experiment. Although the initial decomposition temperature of neat ILs are below 350 °C, the resins cured by ILs could keep stable at 350 °C for a long time. On the other hand, although the content of ILs in Resin-2 (20% mass fraction) was the double of Resin-1 (10% mass fraction), the aging results showed that the long-term oxidative stability of Resin-2 was close to Resin-1 and even better, this phenomenon indicated that PN resins cured by ILs in proper content could bear long-term aging at high temperature under air.

Another important aspect of PN resins is their water absorption capability [34]. Samples of Resin-1 and Resin-2 were dried in a vacuum oven at 120 °C for 24 h before water absorption studies. Then they were heated in distilled water for 48 h at 100 °C, and the

**Table 5.** Long-term aging data of 3BOCN/[EPy]BF<sub>4</sub> (Resin-1 4.842:1 molar ratio; Resin-2 2.152:1 molar ratio) post-cured resins.

Samples	Total weight loss [wt%]				
	250	300	325	350	375
Resin-1	0.00	0.82	1.36	3.42	8.52
Resin-2	0.00	0.53	1.09	2.40	7.44

weight increases were noted. The maximum amount of water absorbed over this time period were approximately 3.24 and 6.89% by weight for Resin-1 and Resin-2, respectively, which were relatively higher than PN cured by aromatic diamine [1]. The result indicated that the content of [EPy]BF<sub>4</sub>, as a kind of ILs easy to absorb water, has an influence on the water absorption of resulting resins. So we may be able to limit the water absorption capabilities of PN resins by changing the mass ratio of ILs or choosing some ILs that have higher hydrophobicity, e.g. [C<sub>18</sub>mim]BF<sub>4</sub>.

## 4. Conclusions

Ionic liquids were used as a new class of curing agent to promote the curing reaction of phthalonitrile monomers. Some kind of ILs with different cation or anion were blended with 3BOCN, and the study on curing behavior of 3BOCN/ILs blends suggested that the structures of ILs (anion, cation and alkyl chain length at cation) had a great impact on the catalytic activity.

The 3BOCN/[EPy]BF<sub>4</sub> resins were prepared at elevated temperature. IR showed that the nitrile group absorption peak was weakened, meanwhile triazine and isoindoline were formed in curing process. The prepared resins exhibited excellent thermal stability and long term oxidative stability together with high storage modulus and high  $T_g$ . And the high dielectric constant and unique dielectric loss make these resins the potential materials in electronic industry and military applications. And the water absorption capabilities of PN resins may be controllable by changing consumption and the kinds of ILs.

This study may open up a new research direction of the PN modification.

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