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Original article

Multiple-SO_3H functioned ionic liquid as efficient curing agent for phthalonitrile-terminated poly(phthalazinone ether nitrile)

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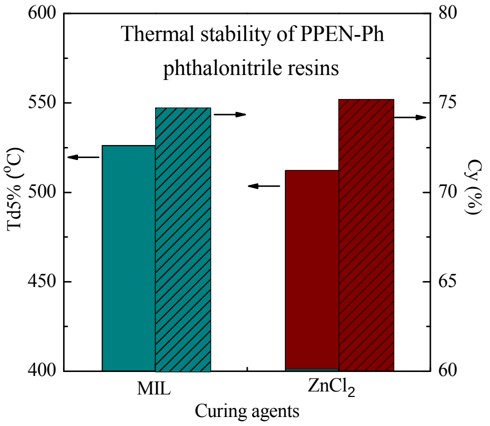
Graphical Abstract



A multiple-SO_3H functioned ionic liquid (MIL) was employed as curing agent of phthalonitrile-terminated poly(phthalazinone ether nitrile) (PPEN-Ph), both the initial curing temperature T_{p0}' and apparent activation energy Ea' were reduced significantly over MIL than the common $ZnCl_2$, moreover, the thermal stability of resulting resin was better on former.

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ABSTRACT

Combined with the advantages of low melting point, high thermal stability and strong acidity, a multiple-SO_3H functioned ionic liquid (MIL) was developed successfully as a curing agent to promote the curing reaction of phthalonitrile-terminated poly(phthalazinone ether nitrile) (PPEN-Ph). The curing kinetics over differential scanning calorimetry (DSC) showed that both the initial curing temperature T_{p0}' and apparent activation energy Ea' (based on Kissinger equation) were reduced significantly over MIL (207.9 °C and 101.5 kJ/mol) compared to the common curing agent $ZnCl_2$ (268.5 °C and 201.5 kJ/mol). Moreover, under identical curing conditions, the resulting thermosetting resin over former ($T_{d5\%}$=526.1 °C) showed better thermal stability than that over latter ($T_{d5\%}$=512.1 °C). These results indicated that MIL should be a good candidate as a curing agent for phthalonitrile resins.

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1. Introduction

Phthalonitrile resins have superior thermal stability, excellent mechanical properties, unique optical and electrical properties, and have been widely employed in advanced technologies, such as aerospace and marine [1-4]. These thermosetting resins are synthesized *via* the thermal curing reaction of phthalonitrile-terminated oligomers in the presence of curing agent. However, relatively high curing temperature and long curing time are the major problems concerning the current state of research and application [5-7]. One of the powerful approaches is to design high-performance curing agent, it is also benefit to enhance the properties of phthalonitrile resins and extend their application, however, there are a few papers on this area to date [8-11].

Most of the curing agents reported for phthalonitrile resins are solid, and this may induce two problems. Usually the dispersion of solid curing agent in precursors should be improved, especially in the case with high curing agent loading [11]. Another one is that the high melting point of curing agent results in high curing temperature [12-14]. As ‘solvent or catalyst’, ionic liquids (ILs) are known as versatile chemicals in diverse fields of the synthetic chemistry [15]. They have unique properties such as low vapor pressure, good thermal stability, high ion conductivity and simple functionality [16], and have been employed in a number of chemical processes, such as separations [17], homogeneous two-phase catalysis [18] and polymerization [19]. Here, we employed multiple-SO_3H functioned ionic liquid (MIL) as curing agent for phthalonitrile resins. The MIL shows low melting point (below 100 ^oC), high decomposition temperature (326 ^oC), and strong acidity (Brønsted acid) [20], which is active for curing phthalonitrile resins. Combined with these advantages, the new curing agent MIL may overcome the shortcoming of the traditional solid curing agent.

Our laboratory has synthesized a series of phthalonitrile-terminated poly(phthalazinone ether nitrile) (PPEN-Ph) [21-23], as organosoluble PPENs show high mechanical strengths and good thermal properties, and they have been applied in many fields [24,25]. In order to improve the curing process of PPEN-Ph, as well as the properties of resulting PPEN-Ph resins, here MIL is employed as curing agent for PPEN-Ph for the first time. In fact, the performance of our MIL for curing PPEN-Ph is better than the common curing agent $ZnCl_2$.

2. Results and discussion

The MIL was synthesized *via* three steps as shown in Scheme 1. The ^1H NMR and FT-IR spectra of resulting MIL were shown in Fig. 1, and the assignment of the corresponding spectra were listed in experimental part. The results confirmed that multiple-SO_3H functioned ionic liquid has been prepared successfully [20]. To check the feasibility of employing MIL as curing agent for phthalonitrile-terminated oligomers, herein, trimerization of phthalonitrile was chosen as the model reaction to compare the activity of formation of 1,3,5-triazine (TCPT) over various catalysts (Scheme 2). Under the identical reaction conditions, the total yield of TCPT over MIL was 75.9%, whereas this value just was 43.8% over the common curing agent $ZnCl_2$ (Fig. 2a). Moreover, the FT-IR spectra (Fig. 2b) indicated that the main products over these two catalysts both were TCPT, the peaks around 1525 cm^{-1} and 1363 cm^{-1} were assigned to the vibration of C=N and C-N in TCPT, respectively. And the intensities of peaks around 2222 cm^{-1} attribute to C≡N were declined compared with that in the pristine phthalonitrile (the spectrum was not shown here). Based on these results, it can be concluded that the pre-prepared MIL was an efficient catalyst for trimerization of phthalonitrile.

Trifluoromethanesulfonic acid and chlorosulfonic acid both are strong acid, liquid and can be soluble in polar solvents, and they have been employed as efficient curing agents for trimerization of aromatic nitriles to afford aromatic *s*-triazine polymers [26, 27]. However, these two acids show strong erosion and low thermal stability, which limit their application as curing agent for phthalonitrile resins. Here, the ionic liquid functionalized with $-SO_3H$ group is introduced to catalyze the trimerization of phthalonitrile for the first time, and the catalytic performance is better than that of $ZnCl_2$ as its strong acidity. To further study the performance of curing PPEN-Ph (the structure was shown in Scheme 3) over MIL, curing kinetics was determined by DSC. PPEN-Ph was blended with different curing agents with a mass ratio of 20:1, then the mixtures were successively scanned at different heating rates (5, 10, 15 and 20 ^oC/min) from 25 ^oC to 400 ^oC on DSC. From the DSC curves shown in Figs. S1 and S2 (Supplementary information), it is clear that two distinct curing peaks appear over the curing agents, which indicated that higher post-cure temperature was necessary to complete the curing reaction in these systems. However, in order to discuss conveniently, we just took the first curing peak (T_p’) as an example to calculate the curing parameters (Supplementary Information), and the details about the calculation also can be seen in our previous report [28]. Based on the DSC curves, the curing temperature under isothermal conditions T'_{p0} over MIL and $ZnCl_2$ were 207.9 ^oC and 268.5 ^oC (Fig. 3), respectively, it seems that the curing temperature for PPEN-Ph can be reduced effectively with MIL as curing agent. Furthermore, the apparent activation energy Ea’ was calculated *via* the Kissinger equation, and the value for MIL (101.5 kJ/mol) was nearly half of that over $ZnCl_2$ (201.5 kJ/mol). Thus, the curing reaction with MIL as curing agents can be much more easily proceeded under mild reaction conditions compared with $ZnCl_2$. And this phenomenon maybe was caused by the lower melting point and stronger acidity on MIL.

Thermal stability of the resulting thermosetting resin was also tested to evaluate the performance of curing agents, and the TGA curves of the cured PPEN-Ph were shown in Fig.4, the main data including the temperature at weight loss 5% ($T_{d5\%}$), 10% ($T_{d10\%}$) and the char yields at 800 ^oC (C_{y800}) were summarized in Table 1. After curing over various curing agents, the thermal stability of PPEN-Ph can be improved significantly. Moreover, it is noted that the values of $T_{d5\%}$ and $T_{d10\%}$ over MIL are both higher around 14 ^oC than those over $ZnCl_2$. With these results in hands, we can conclude that as a curing agent for phthalonitrile resin, the performance of MIL is better than $ZnCl_2$.

3. Conclusion

Based on above results, we can conclude that employing ionic liquid to promote the curing rate and reduce the curing temperature of phthalonitrile resin was feasible. Introduction of multiple-SO_3H functioned ionic liquid (MIL) as curing agent into phthalonitrile-terminated poly(phthalazinone ether nitrile) (PPEN-Ph) oligomers, resulted in considerable reduction of curing temperature and apparent activation energy without compromise in their thermal stability, compared with present common curing agent $ZnCl_2$. Although the curing pathway of PPEN-Ph over MIL and other properties of resulting thermosetting resins are studied currently under way, this work still can supply some valuable information for the researchers in this filed to explore high-performance curing agent for phthalonitrile resins.

4. Experimental

4.1 Materials and equipments

DHPZ was purchased from Dalian Polymer New Material Co., Ltd. and recrystallized with DMAc. Anhydrous K_2CO_3 was ground and dried in vacuum at 110 ºC for 24 h prior to use. All solvents and other reagents were purchased from commercial sources and used as received.

Infrared spectra were recorded on a Thermo Nicolet Nexus 470 Fourier transform infrared spectrometer, using potassium bromide pellets of solids. High performance liquid chromatogram (HPLC) was performed on an HP1100 liquid chromatography. Electrospray ionization-mass spectrometry (ESI-MS) was performed on a HP1100LC/MSD mass spectrometer equipped with an Agilent Extend® C18 column in a liquid chromatography mode. Samples were determined by selected ion monitoring with ESI negative ionization mode (CID=50 V). ^{1}H NMR (400 MHz) spectra were obtained on a Bruker Avance II 400M nuclear magnetic resonance spectrometer operating at 25 °C using D_2O as solvent and listed in parts per million downfield. Thermogravimetric analysis (TGA) curves were measured on a Mettler TGA1 thermal gravimetric analysis instrument in flowing nitrogen (50 mL/min) at a heating rate of 20 °C/min from 30 to 800 °C. Glass transition temperature (T_g) and curing temperature of maximum peaks (T_m) were determined with a Mettler DSC1 differential scanning calorimeter (DSC) under nitrogen flow at different heating rate from 25 to 400 °C. The T_g value was taken at the inflection point, and T_m was recorded at the exothermal peak of DSC curves.

4.2 Synthesis of multiple-SO_3H functioned ionic liquid (MIL)

1,4-Bis(imidazole-1-yl)butane **1** [29]: Imidazole (4.1 g, 60 mmol), NaOH (2.4 g, 60 mmol) and DMSO (20 mL) were placed into a flask. The mixture was heated at 60 ºC for 2 h, and then 1,4-dibromobutane (6.0 g, 28 mmol) was added. After stirring at 60 ºC for another 2 h, the reaction mixture was cooled down to room temperature and then poured into 200 mL of water. Finally, the mixture was filtered and water was removed under reduced pressure. The crude products were purified by washing with diethyl ether and dried under a vacuum for 24 h at 50 ºC.

The resulting white solid **1** (3.8 g, 20 mmol) was mixed with 1,4-butane sulfonate (10.88 g, 80 mmol) under stirring at room temperature for 72 h. And then the solid product **2** was washed with ethyl ether for three times and dried under vacuum over night.

Stoichiometric amount of sulfuric acid was added to the pre-prepared white solid **2**, and the mixture was stirred at 60 ºC for 12 h to form the multiple-SO_3H functioned ionic liquid. The MIL phase was washed repeatedly with toluene and diethyl ether to remove non-ionic residues, and dried under vacuum over night. ^{1}H NMR (D_2O): δ 8.67 (s, 2H, -NC*H*=N(10)), 7.37-7.34 (d, 4H, -NC*H*=C*H*N(8,9)), 4.64 (s, 2H, -HSO_4(7)), 4.09 (t, 8H, -CH_2N(5,6)), 2.76 (t, 4H, -CH_2CH_2N(4)), 1.86 (m, 4H, -NCH_2CH_2(3)), 1.74 (m, 4H, -$CH_2CH_2SO_3H$(2)), 1.55 (m, 4H, -CH_2SO_3H(1)). FT-IR (KBr, cm^{-1}): ν 3143, 3080 ($\nu_{C\text{-}H}$ in imidazole ring), 2964 ($\nu_{C\text{-}H}$ in –CH_2), 1699, 1580 ($\nu_{C=C}$ in imidazole ring), 1460 ($\delta_{asC\text{-}H}$ in -CH_2), 1034 ($\nu_{sS=O}$ in -SO_3H).

4.3 Synthesis of TCPT

TCPT can be prepared from phthalonitrile over MIL or $ZnCl_2$. A procedure with MIL was given as a typical example. Phthalonitrile (10 mmol, 1.28 g) along with 0.165 g of MIL (0.25 mol, 2.5 mol%) was added into a 50-mL three-necked round-bottom flask equipped with mechanical stirrer. After N-methyl pyrrolidone (NMP) (5 mL) was added as solvent, the reaction mixture was stirred at 200 °C for 8 h under air atmosphere. And then the reaction solution was diluted with NMP and analyzed by HPLC and HPLC-MS. To collect the product of TCPT, the reaction solution was poured into large amount of deionized water, filtered to collect the solid, and washed with deionized water for several times. Finally, the black solid was obtained after Soxhlet-extraction with acetic acid and methanol for 24 h, respectively.

4.4 General procedure for thermal curing of PPEN-Ph

Phthalonitrile-terminated PPEN (PPEN-Ph) has been synthesized successfully in our lab [27], based on the previous results, higher density of terminal cyano groups will be benefit for thermal curing, in this work, the molecular weight of PPEN-Ph was fixed around 800 (Tg = 165 ºC). Thermosetting resins were prepared by the direct thermal curing of PPEN-Ph in the presence of curing agents, a typical experiment was carried out as following. A mixture of PPEN-Ph and curing agent with a mass ratio of 20:1 was blended, ground, and pressed into a sheet. This sheet was then cured successively at 250 °C for 2 h, 280 °C for 2 h, 300 °C for 4 h, and 350 °C for 4 h under air atmosphere, to afford a black solid.

Acknowledgment

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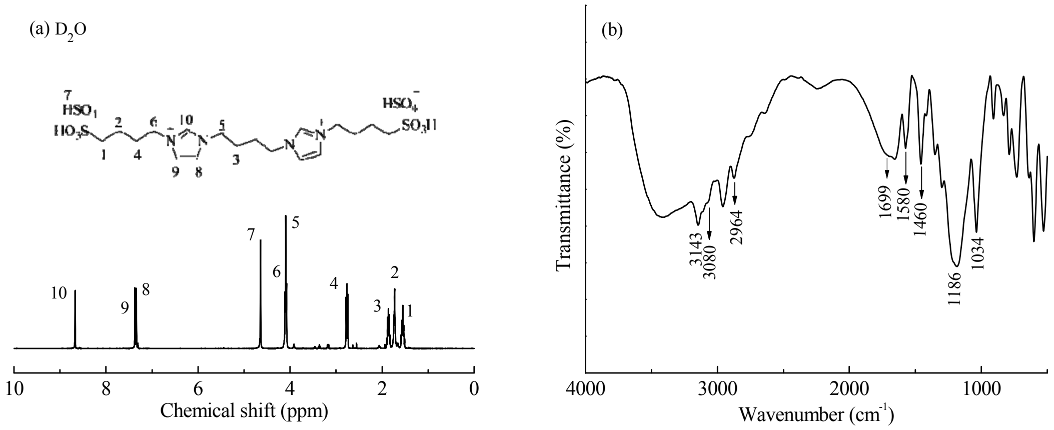


Fig.1 Characterization of MIL. (a) ^1H NMR spectrum; (b) FT-IR spectrum.

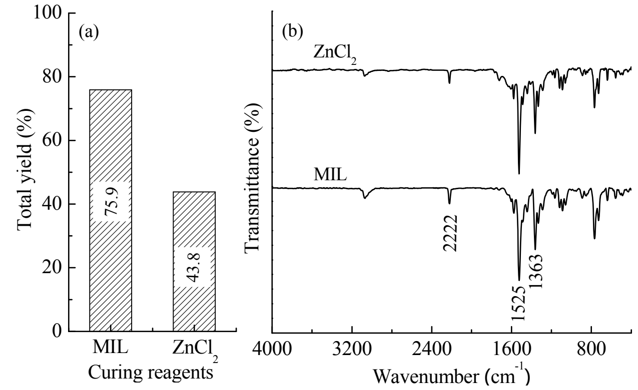


Fig.2 Trimerization of phthalonitrile over MIL and $ZnCl_2$. (a) Total yield of 1,3,5-triazine; (b) FT-IR spectra of products.

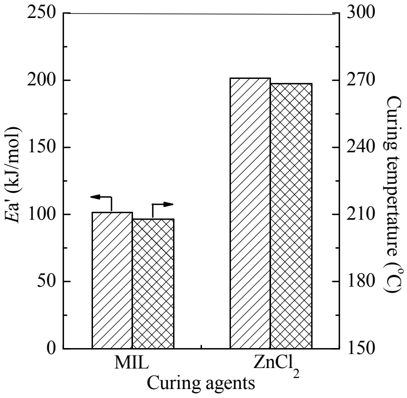


Fig.3 The apparent activation energy *E*a' and the curing temperature under isothermal conditions calculated from curing kinetics.

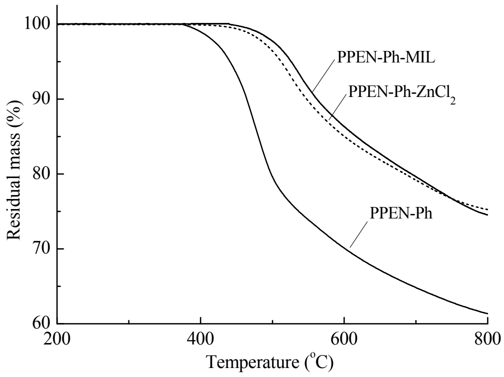
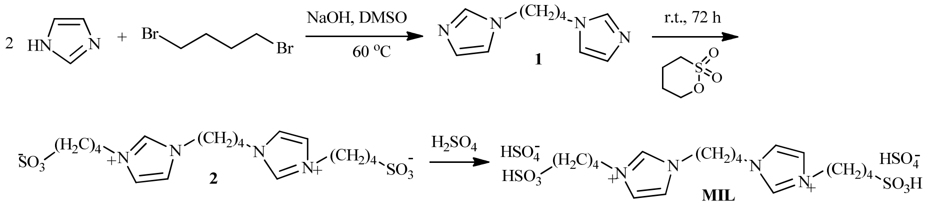
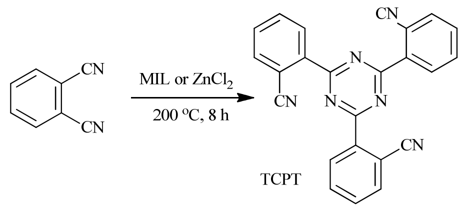


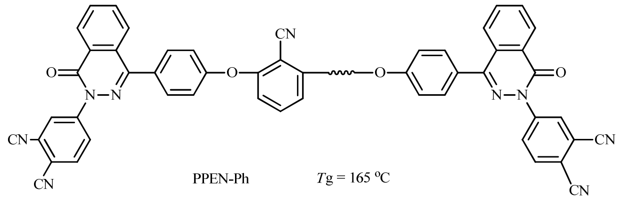
Fig.4 TGA curves (20 °C/min, N_2) of PPEN-Ph and the products after curing over various curing agents.



Scheme 1. Preparation of multiple-SO_3H functioned ionic liquid.



Scheme 2. Synthesis of TCPT from phthalonitrile over catalyst.



Scheme 3. The structure of PPEN-Ph.

Table 1

The main data of TGA curves of resulting PPEN-Ph resins over various curing agents.

Curing agents	$T_{d5\%}$ (°C) [a]	$T_{d10\%}$ (°C) [b]	C_{y800} (%)[c]
--	440.7	464.3	61.3
MIL	526.1	561.8	74.5
$ZnCl_2$	512.1	547.7	75.2

[a] $T_{d5\%}$ represents the temperature at weight loss 5%.

[b] $T_{d10\%}$ represents the temperature at weight loss 10%.

[c] C_{y800} represents the char yields at 800 °C.