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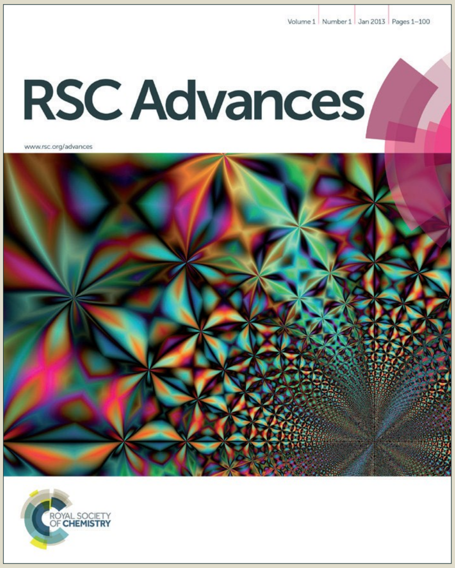

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ARTICLE

A Novel Phthalonitrile Monomer with Low Post Cure Temperature and Short Cure Time

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Liping Sheng[a], Changping Yin[a], Jiayu Xiao[a] *

To depress the post cure temperature and time, 3-(2-aminophenoxy)-phthalonitrile (3-APN) was designed and synthesized via the nucleophilic displacement reaction of 3-nitrophthalonitrile and o-aminophenol. The structure of the desirdedproduct (3-APN) was confirmed by H nuclear magnetic resonance (NMR) and Fourier transform infrade spectroscopy (FTIR). The polymers from the monomer were also characterized by FTIR. Cure behavior of the monomer was investigated by differential scanning calorimetry (DSC). Cure characteristic temperatures were obtained through extrapolation method. Complex viscosity of the melt was measured by rheometric analysis. The results show that there are no residual and shift absorption of nitrile (C≡N) in the infrared spectrogrum of the polymers from 3-APN. Viscosity measurement shows that the monomer exhibits a low complex melt viscosity (0.01-0.1 Pa S) in a wide temperature range (145-250 ℃). The DSC results show that the polymerization enthalpy of the monomer is 414 J g-1, which is 3 times higher than that of the reported auto-catalytic monomers. Thermo-gravimetric (TG) results of the derived polymers under different cure procedures indicate that when this novel monomer is cured at 250-280 ℃ for 0.5-1.0 hours, the thermal stability of the derived polymer is equal to or better than most of the reported PN resins which are cured at 370-420 ℃ for more than 14 hours. And when the curing temperature is gradually increased to 360 ℃ and total cure time is only 2 hours, the cured polymer has even more excellent thermal stability with the T5% up to 518 ℃ and char yield at 800 ℃ up to 77%.

1 Introduction

Phthalonitrile-based (PN) polymers constitute a class of high-temperature thermosetting resins possessing a series of exceptional properties, such as high glass transition temperatures, excellent mechanical properties, outstanding thermal and thermo-oxidative stability, good moisture resistance and superior fire resistance[1-8]. All these attractive properties make these polymers the leading candidates for acting as the matrices of high performance composite materials in various applications[9-12].

However, these resins have one distinct shortage that they are extremely sluggish[3, 5]. They require heat treatment for several days at elevated temperature (350℃) before the gelation occurs. To depress cure temperature and shorten cure time, numerous kinds of catalyst have been mixed in phthalonitrile monomers, including organic amine and organic acids[5], organic acid and amine salt[13], metal salts[14], etc. Among these, a class of organic diamines[15, 16], e.g. m-APB, p-APB, m-BAPS and p-BAPS[17] are becoming more and more popular for their high efficient catalytic performance. They can shorten the cure time from several days to 20-40 hours with a molar ratio of only 5% comparing to the monomers. However, the post cure temperature is still high up to 375 ℃. These small molecular catalysts also have poor processability and a slowing of the curing process has been observed for their volatility[17]. Therefore, another kind of phthalonitrile derivatives which possess auto-catalytic ability and have better processing performances than the organic diamines is developed[6, 18-25]. These derivatives can not only accelerate the polymerization of nitrile, but also participate in the crosslinking reactions, shortening the cure time to 14-30 hours. Whereas, the post cure temperatures are still up to 370-420 ℃[2, 18-23, 25], or perhaps a sacrificing performance at lower temperature and shorter time[26].

That the reported catalysts can't reduce the post cure temperature and time is due mainly to the fact that little nitrile participates in the polymerization. Therefore, the heat treatment temperature and time have to be elevated and extended to obtain a higher conversion of nitrile and an improved performance of resins. If the cure reactivity of PN resins could be improved, the post cure temperature and time might be depressed. With this purpose, some basic research has been carried out by our group. Comparing the auto-catalytic behaviors of the phthalonitrile derivatives detailedly, we found that the amine-containing phthalonitrile derivatives have a better catalytic performance than the hydroxyl-containing ones. This may be due to the fact that active hydrogen in amine is twice of that in hydroxyl. In addition, the relative positions of active hydrogen and nitrile will affect the

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[a] *College of Aerospace Science and Engineering, National University of Defense Technology, Changsha, China 410073*

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x polymerization significantly[20, 27]. Based on these, we tried to change the relative positions of amine and nitrile and design a new monomer, 3-(2-aminophenoxy)-phthalonitrile (3-APN), expecting it will be helpful to solve this problem which has baffled researchers for many years. We also synthesized this monomer and carried out a series of measurements on it. Some interesting and useful results have been found and are presented in this study.

2 Experimental

2.1 Materials

3-Nitrophthalonitrile (AR, 99%) was purchased from Xiya Chemical Industry Co. Ltd (Shangdong, China) and used as received. O-aminophenol (AR, 99%) was commercially available from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and used as received. Chromatographic purity N, N-Dimethylformamide (DMF, HPLC, 99.8%), from Tianjin Kemiou Chemical Reagent Co., Ltd, dehydrated for 3 days by 4 nm molecular sieves beforehand. Anhydrous potassium carbonate (AR, 99%) and sodium hydroxide (AR, 99%) were used as received from Beijing Beihua Fine Chemicals Co., China.

2.2 Synthesis of 3-APN

Scheme 1 illustrates the synthesis of 3-(2-aminophenoxy)-phthalonitrile(3-APN). A three-necked flask equipped with a condenser, a magnetic stirrer, a thermometer, and a nitrogen inlet was charged with 3-nitrophthalonitrile (3.46 g, 0.02 mol), o-aminophenol (2.73 g, 0.025 mol), and 30 ml DMF. Anhydrous potassium carbonate (5.18 g, 0.0375 mol) was added when the mixture above became clear. The mixture was heated to 85 °C and stirred for 5 h under nitrogen. After cooling to room temperature, the resulting dark brown mixture was poured into NaOH solution (0.1 mol L^{-1}), filtered, and washed with distilled water until neutral. Chromatography on silica of the crude product with petroleum ether/ethyl acetate (R_f: 0.3, SiO_2, 1:0.4) as eluent afforded pure product as yellow powder. Yield: 80%. mp: 136.50 °C (determined by DSC). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): δ 7.80 – 7.66 (m, 2H), 7.02 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 7.9 Hz, 1H), 6.91 (d, J = 6.9 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.57 (t, J = 7.6 Hz, 1H), 5.20 (s, 2H).

2.3. Preparation the cured polymers

The cured polymers for IR spectral analysis were obtained using a thermo-gravimetric analysis (TGA) chamber by heating 3-APN at 250 ℃ for 30 min, and at 300 ℃ for another 30min, in nitrogen with a flow rate of 75 ml min-1. Then, the derived polymers were ground into powder for the measurement. The polymers for thermal stability analysis were obtained by the same method following the cure procedure in table 3.

2.4 Characterization

Solution proton nuclear magnetic resonance (^{1}H NMR) spectra was recorded on an Agilent DD2 400-MR spectrometer using DMSO-d_6 as solvents and tetramethylsilane as internal standard.

The Fourier transform infrared (FTIR) spectra wererecorded with a PerkinElmer Spectrum TWO spectrometer. The spectra of 3-APN and its polymers were recorded through the infrared reflectance mode.

DSC diagrams were recorded with a Mettler-Toledo DSC1 STAR System (Zurich, Switzerland) at different heating rates of 2, 5, 10, 15, 20 K min^{-1} under nitrogen atmosphere with a flow rate of 40 ml min^{-1}, from 25 to 400 °C. The sample (about 5 mg) is put in DSC pans(Al) with a small hole in the cap.

Thermal stability was evaluated by TGA on a Mettler-Toledo TGA/DSC1 STAR System (Zurich, Switzerland) at a heating rate of 20 K min^{-1} in nitrogen with a flow rate of 100 ml min^{-1}, from 25 to 800 °C. The sample (about 10 mg) is put in TGA pans(Alumina) with a small hole in the cap.

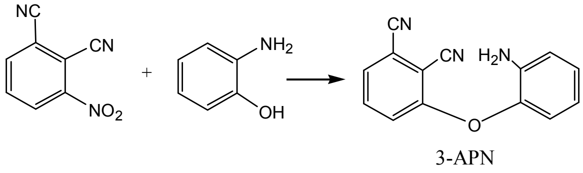
Viscosity study of the monomer was conducted using a HAKKE Rheometer instrument MARS III (Germany) with a heating rate of 2 K min^{-1}, at a frequency of 1 Hz. The samples (0.5-1.0g) were melted between 25 mm diameter parallel plates with an environmental testing chamber of the rheometer.

TGA-IR test was conducted using a PerkinElmer Thermogravimetric Analyzer Pyris 1 TGA and a PerkinElmer FT-IR/FIR Frontier. The heating rate is 20 K min^{-1} under helium atmosphere with a flow rate of 30 ml min^{-1}, from 50 to 400 °C. The sample cell temperature is 300 °C.

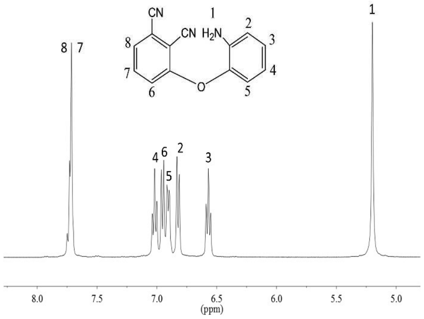
3 Results and discussion

3.1 Synthesis and characteration of the monomer

3-(2-aminophenoxy)-phthalonitrile was synthesized by the nucleophilic displacement of the nitrosubstituent as depicted in Scheme 1. FTIR and ^{1}H NMR techniques were used to identify the structure. As mentioned in the experimental section, all the NMR peaks assigned are in well agreement with the proposed molecular structures. In ^{1}H NMR spectra, the signal of amino protons was detected at 5.20 ppm. The peaks between 6-8 ppm are corresponding to the shifts of Ar-H. The FTIR spectrum shows the characteristic absorption bands at 2234 cm^{-1}, corresponding to cyano group stretching vibration, 3355 cm^{-1} and 3445 cm^{-1} corresponding to primary amino groups stretching vibration, 1628-1452 cm^{-1} corresponding to C=C stretching vibration of benzene ring, 1307-1283 cm^{-1} corresponding to Ar-N stretching vibration, 1264-1191 cm^{-1} corresponding to Ar-O stretching vibration, and 797-727 cm^{-1} corresponding to Ar-H flexural vibration.



Scheme 1. Synthesis route of 3-APN



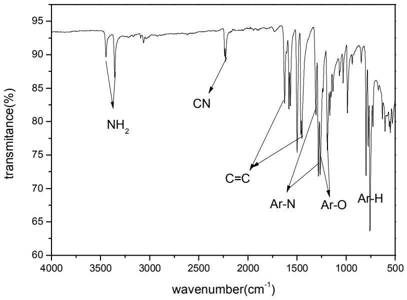
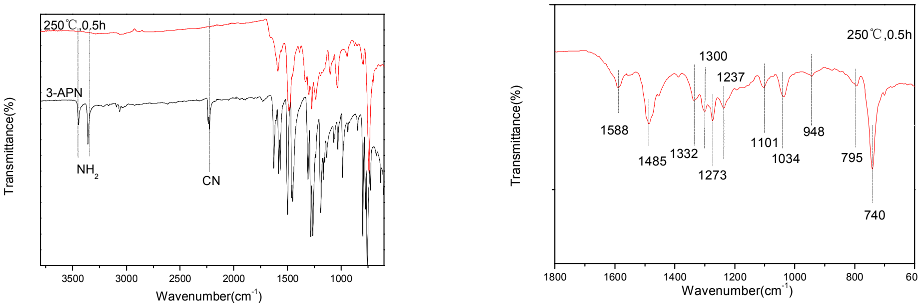


Figure 1. 1H NMR Spectra of 3-APN

Figure 2. FTIR spectra of 3-APN

3.2 Cured polymer



(a) (b)

Figure 3. FTIR spectra of 3-APN and cured 3-APN.

The cured polymer from 3-APN at 250 °C for 30 min was monitored by FTIR as shown in figure 3(a). In figure 3(a), the most obvious change between the monomer and the cured polymer is that the absorption bands at 2234 cm^{-1} and 3355-3455 cm^{-1} disappear completely, no shift and no residual. This is different from the reported PN resins, for example, aromatic ethers/diamine[28, 29], 4-APN[23], and other auto-catalytic PN resins[20, 22, 30-32], which just have a decrease of the nitrile absorption and shift to around 2220 cm^{-1}. This phenomenon indicates that most of the nitrile groups have taken part in the polymerization reaction, or only just a small residual part gives a very weak absorption which can't be detected by IR instrument for the difficulty in grinding the sample into particles with sizes small enough. However, it still express that there is a higher conversion of nitrile in 3-APN than the reported PN resins. The absorption disappearance of amine indicates that the amine group also participates in the crosslinking reactions.

The absorption peaks mainly appear at 600-1700 cm^{-1} as shown in Figure 3(b) and they are identified as following. The characteristic absorption bands at 1588 cm^{-1} and 1485 cm^{-1} can be attributed to stretching vibration of benzene ring, the band at 1332-1237 cm^{-1} corresponds to Ar-N stretching vibration, 1101-1034 cm^{-1} corresponds to Ar-O stretching vibration, 795-740 cm^{-1} corresponds to Ar-H flexural vibration.

3.3 Auto-catalytic behavior of the monomer

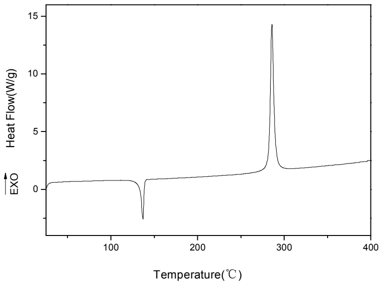


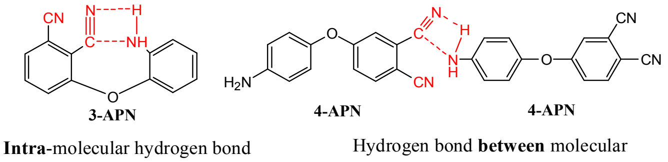
Table 1. Characteristic values of 3-APN and 4-APN from DSC curves.

monomer	T_{mp}/℃	T_p/℃	ΔH/J·g^{-1}	reference
3-APN	136	289	414	This paper
4-APN*	134	293	126	33

4-APN: 4-(4-aminophenoxy)-phthalonitrile

Figure. 4. DSC curves at 10 ℃ min^{-1} heating rate for monomer.

The non-isothermal DSC curves of the monomer are given in Figure 4. As shown, the peaks at 136℃(endothermic) and 289℃ (exothermic) are attributed to the melting point and the polymerization, respectively. This indicates that this monomer possesses a wide processing window (the difference between melting point and polymerization). This is favourable for the resin transfer moulding (RTM) processing. At present, the 4-APN (as shown in table 1), which has a very similar structure with 3-APN, is used as a catalyst in PN resins for its high catalytic performance. Their characteristic values from DSC are compared in Table 1. It is found that their melting points are very close, however, their curing temperatures and reaction enthalpies are different. The reaction enthalpy of 3-APN is 3.3 times as much as that of 4-APN[33]. Combining with the FTIR results that the nitrile absorption of the polymer from 3-APN disappears and there is still a shift absorption of the polymer from 4-APN and other phthalonitrile resins, it is concluded that 3-APN has a higher cure reactivity than 4-APN as well as the other phthalonitrile resins. This result should have some relations with their chemical structures. Comparing these reported monomers' structures carefully[20, 22, 30-32], we found that the distance between the active hydrogen and nitrile in 3-APN can be closer than the others'. Because they can be close to each other via the intermolecular hydrogen bond. Such close a distance is helpful to the cure reaction and endows 3-APN higher polymerization reactivity than the others'. Taking 4-APN as an example[33], the nitrile of 4-APN can be excited by active hydrogen through hydrogen bond between molecules which has lower probability and need higher energy than that of 3-APN through the intra-molecular hydrogen bond (Schem 2). This may be one of the reasons why 3-APN show different behavior comparing to their isomers as reported by Tong Zhao19. The high reaction enthalpy represents a high reaction activity of the monomer, however, it also bring some troubles when curing larger and thick composite parts. But this can be solved by addition some other components which are no or low exothermic, such as fibre, flexibilizer, filler, and so on.



Scheme 2. Different hydrogen bonds in 3-APN and 4-APN.

3.4 Meltability and processability

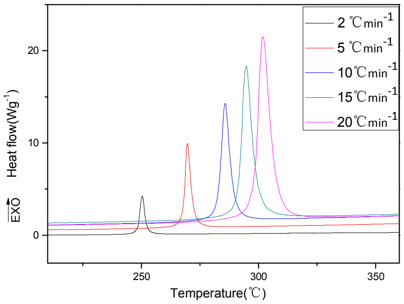
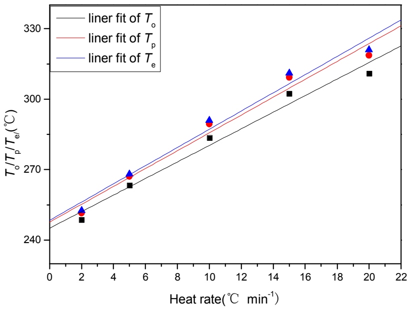


Figure 5. DSC curves at 2, 5, 10,15, 20 ℃ min^{-1} heating rate for 3-APN.

Table 2. Characteristics values of DSC for 3-APN at different heating rates.

Rate/ ℃ min^{-1}	T_o/℃	T_p/℃	T_e/℃	ΔH/J·g^{-1}
2	249	252	253	385
5	268	272	273	408
10	284	289	291	414
15	292	299	301	429
20	300	310	310	434

With heating rate increasing, the peaks of DSC curve move to higher temperatures. To eliminate the influence of heating rate, extrapolation method should be employed to obtain the characteristic temperatures when heating rate is zero which is the used rate in practice. The DSC curves under different heating rates are obtained (Figure 5) and the characteristic temperatures from them are shown in Table 2. Through extrapolation method, the curing temperatures are obtained when heating rate is zero (Figure 6), which are 245, 248, 248 ℃ (onset, peak, and endset temperatures), respectively. Therefore, the revised processing window of the monomer is 111℃(the difference between melting point and onset temperature). And the complex melt viscosity of monomer was measured as a function of temperature from 140 to 270 ℃ (Figure 7). As shown in Figure 7, when above the melting point temperature, the viscosity of the monomer decreases quickly and maintains a low level (0.01-0.1 Pa S) from 145 to 250℃. All these result above show that the monomer not only has high curing reactivity, but also has a proper processing window and viscosity, making it a good candidate for the employment in the more cost-effective processing of polymer composites, such as the RTM, resin infusion moulding and filament winding. This monomer is may be a candidate matrix for high performance composites. But this need more studies to support.



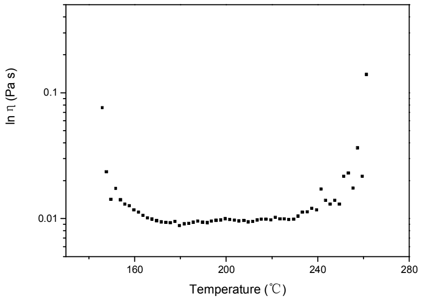


Figure 6. Extrapolation curves of cure temperatures of 3-APN. Figure 7. Complex viscosity of 3-APN as function of temperature.

3.5 Thermal stability

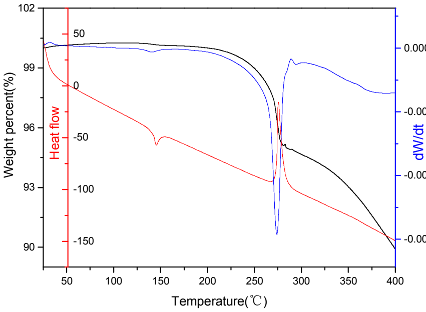


Figure 8. TG, DSC, DTG curves of 3-APN at 5 ℃ min-1 heat rate in nitrogen.

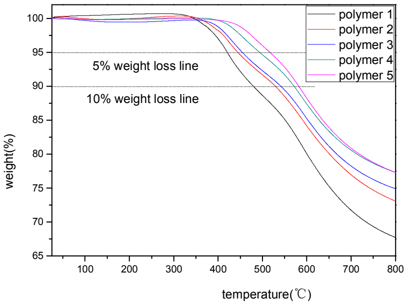


Figure 9. TG curves of polymers derived from monomer under different cure procedures.

TGA was used to evaluate the thermal stability of the monomer and the polymers under different curing procedures. In Figure 8, it shows the DSC, TGA and DTG curves of the monomer from 25℃ to 400 ℃. The total weight loss from 25 to 400℃ is 10%, and it is about 5% weight loss around 272 ℃, at which temperature the peaks of DTG and DSC curves are overlapped. This phenomenon indicates that the weight loss and curing reaction almost occur at the same time. However, there is a common cognition that the reaction between nitriles is an addition-type polymerization and there are no small molecules releasing. Therefore, it could be deduced that there are small molecules releasing in the reaction between amine and nitrile, or that the huge enthalpy (414 J g^{-1}) releasing during the curing reaction accelerates the volatilization of the monomer, which results in the weight loss. However, more evidences are needed to validate this hypothesis.

The TGA curves of the polymers under different curing procedures are compared in Figure 9. As expected, the 5% weight loss temperature and char yield at 800 ℃ of these polymers are elevated with the post cure temperature raising and time extending. When the cure temperature is 360℃ and the total cure time extends to be 2 hours , the $T_{5\%}$ is over 500 ℃, up to 517 ℃, and char yield is high to 77.3%, which indicates that the polymer derived from 3-APN has excellent thermal stability.

However, there are distinct differences between 3-APN and the reported monomers. When the cure temperature is only 250 ℃ and cure time is only 30 min, the char yield at 800 ℃ of the derived polymer is up to 68%, which is equal to the aromatic ether/diamine resin systems whose cure temperature is elevated step by step from 250 to 375 ℃ and cure time extended to 14 hours[15, 34]. This means that the thermal stability of this monomer is comparable with the aromatic ether/diamine resin systems', even without post cure at a high temperature for a long time. Then, the polymer cured at 280℃ for another 30 min has a more higher char yield of 73% at 800℃, which is equal to or even higher than most of the reported phthalonitrile resin systems which are heat treated at over 370 ℃ for more than 20 hours[2, 20, 30, 35-39, 40]. All these results clearly show that this monomer has higher cure reactivity than the other PN resins. It can complete the cure reaction at a far lower cure temperature for far shorter time and does not need post cure at higher temperature for a long time. This can not only reduce the cost and energy consumption, but also shorten the time to improve efficiency, which is very desirable when processing composites.

Table 3. Thermal stability of polymers under different cure procedures.

Label	Cure procedure	$T_{5\%}$/℃	$T_{10\%}$/℃	Char yield at 800℃
Polymer 1	250℃, 30min	421	480	68
Polymer 2	250℃, 30min + 280℃, 30min	445	530	73.
Polymer 3	250℃, 30min + 280℃, 30min + 320℃, 20min	455	542	75
Polymer 4	250℃, 30min + 280℃, 30min + 320℃, 20min +350℃, 20 min	494	572	77
Polymre 5	250℃, 30min + 280℃, 30min + 320℃, 20min +350℃, 20 min + 360℃, 20 min	517	582	77

3.6 Cure mechanism

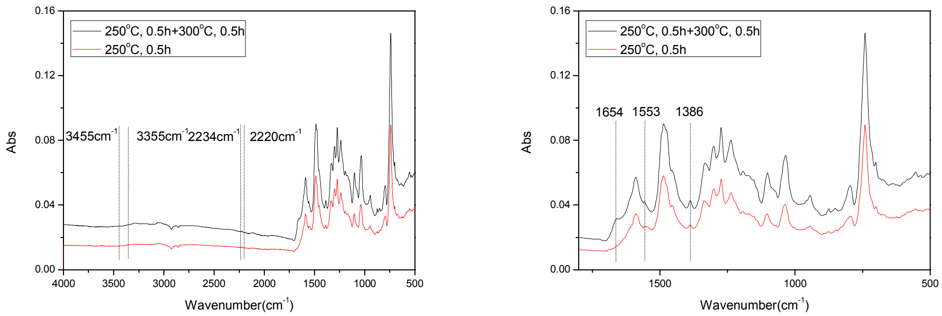
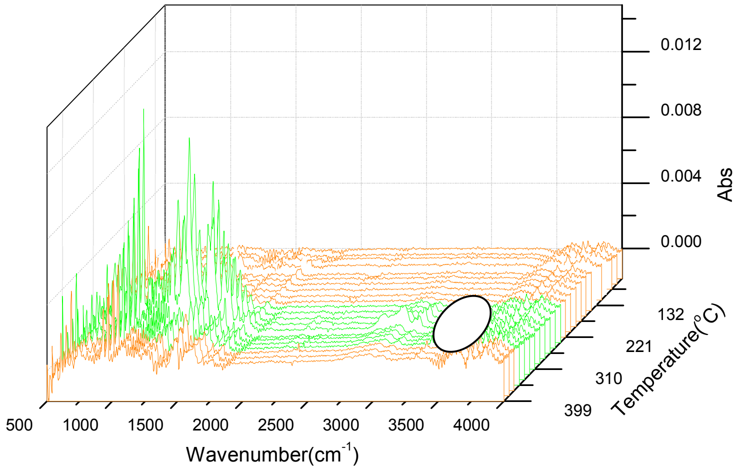


Figure 10. cured polymers from 3-APN under different cure procedures.



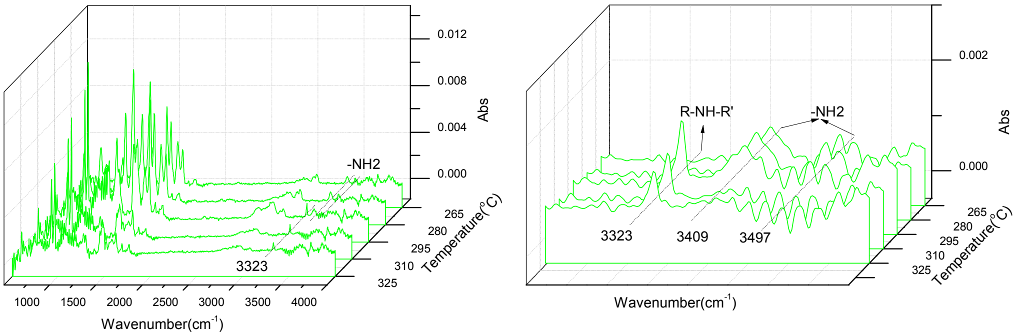
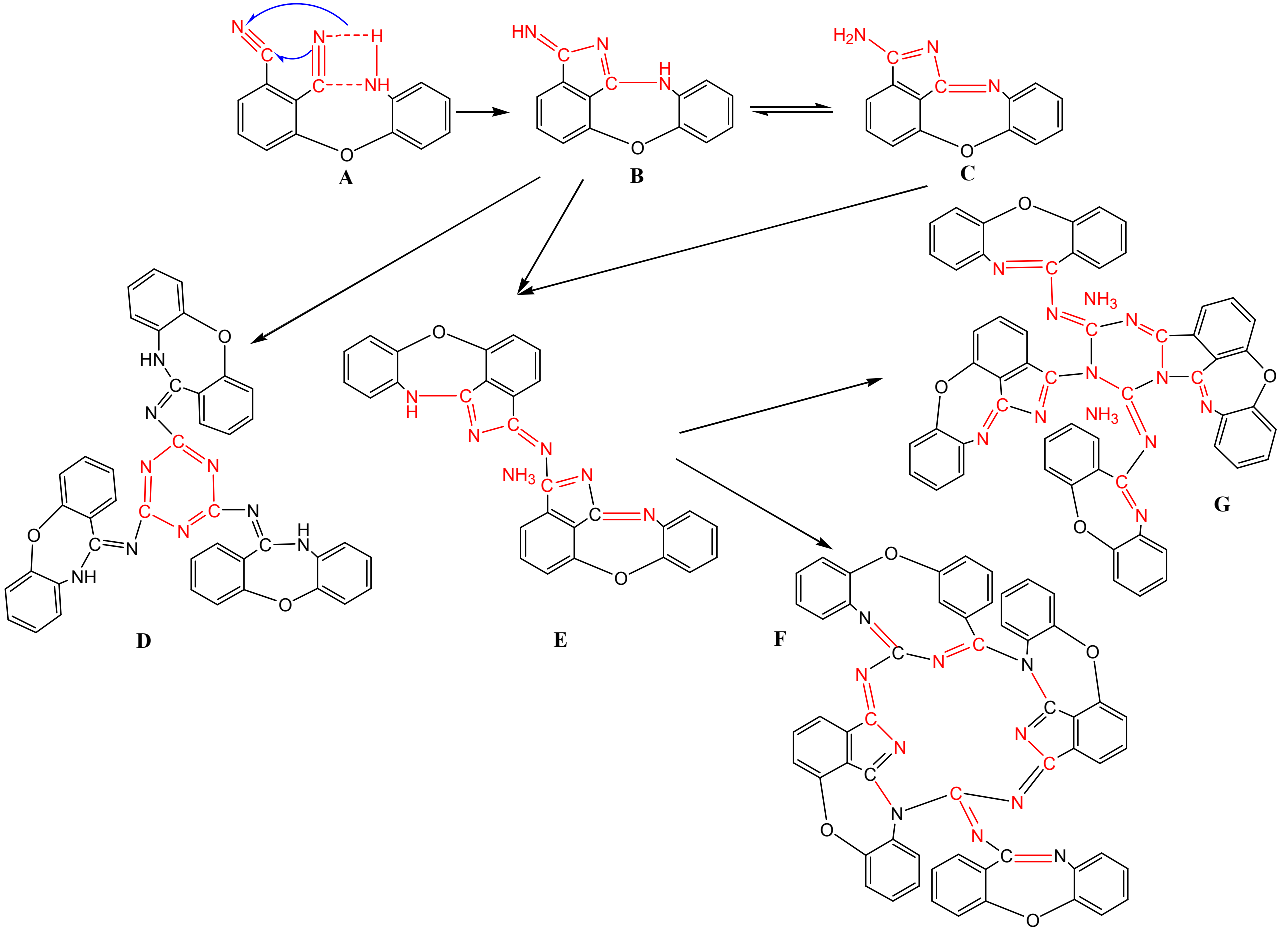


Figure 11. The on-line IR spectra throughout TGA testing.



Scheme 3. Possible polymerization process of 3-APN under heat treatment.

To further explain the phenomenon as presented above, the IR spectra of the polymers derived from different cure procedures are demonstrated in Figure 10. As mentioned previously, the absorptions of nitrile and amine disappear together under different cure procedures. There is a slight increase at 1654, 1553 and 1386 cm^{-1} after raising the cure temperature and extending the cure time. This may be due to the fact that the contents of C=N and triazine increase slightly[7, 29]. By examining Figure 11, it is found that 3-APN emerged gradually and the infrared absorption peaks shift to the high wavenumber with the increase of the temperature. When the temperature is high to 285, the content of 3-APN reaches the highest. After that, it began to reduce and a new peak appearances at 3323 cm^{-1} (R-NH-R'), which also decrease with the further increasing of temperature. This indicates that 3-APN converts to another compound quickly, which is also transformed into another substance at the same time.

Combining the results of IR, DSC, TGA, and TGA-IR, the possible curing process can be deduced as following in Scheme 3. First, it is easy for 3-APN converting to the conformation of A due to the hydrogen bond in this molecule. With the cure temperature raised, the N-H bonds are broken, the active hydrogen transfers to the farther nitrile easily through the five-membered ring in the molecule, and B is formed, whose mole molecule weight is 235 g mol^{-1}(a small molecule) and can move easily. B and C are reversible. The small molecule B or C will react with each other and cross-linked, producing D, E, F and G. Therefore, the cured polymers may be D, E, F, and G or the mixture of them. Although this is a deduced cure process according the limited information, it can still explain some interesting phenomenon and will not change the fact that the properties of monomer and derived polymer are excellent.

4 Conclusions

In this paper, a novel chemical structure of 3-APN is designed and synthesized to depress the post cure temperature and time. A series of measurements are carried out and some interesting results are found and presented. Firstly, IR spectrum of the derived polymer shows that there is no residual and no shift of the absorption band at 2234 cm^{-1}, which means that there must be a high conversion of nitrile. The exothermic enthalpy of this monomer measured by DSC is 3 times higher than the reported auto-catalytic phthalonitrile derivatives, which means that this monomer has much higher cure reactivity. Furthermore, the results of TGA show that the thermal stability of the polymers from 3-APN is better than most of the reported PN resins. Even without post cure at high temperature for a long time, the thermal stability is still outstanding. All the results indicate that the initial purpose may be realized. The monomer has a higher cure reactivity and can react at lower temperature for short time with a high conversion and awards a more excellent thermal stability to the derived polymer.

Acknowledgements

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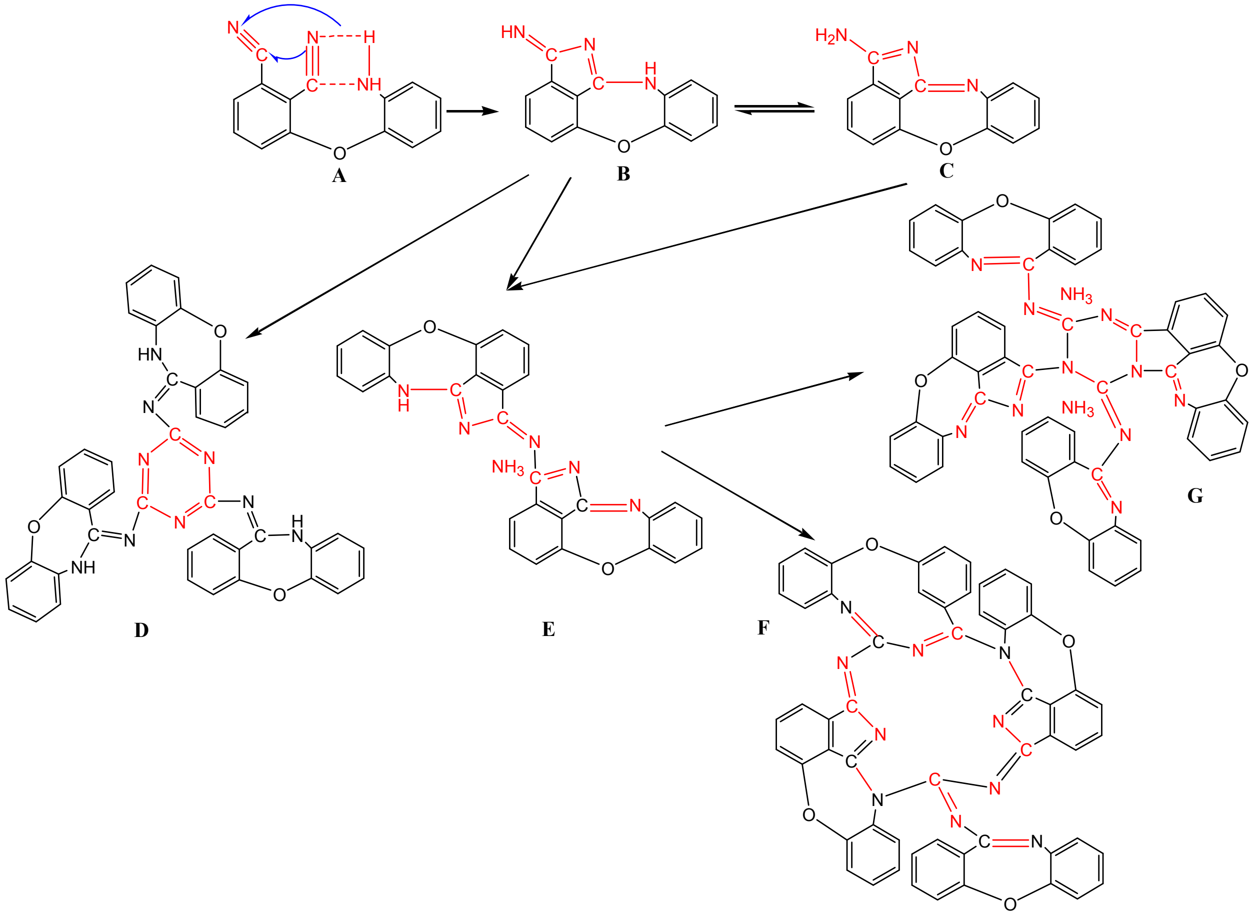
GRAPHICAL ABSTRACT

Title: A Novel Phthalonitrile Monomer with Low Post Cure Temperature and Short Cure Time

Author: Liping Sheng, Changping Yin, Jiayu Xiao

All the measurement results show that the monomer have a higher cure reactivity and can cure at lower temperature in a short time with a high conversion and give an more excellent thermal stability to the derived polymers. To explain the interesting phenomenon, the curing process of this novel monomer was deduced as following by combining the results of IR, DSC, TGA, TGA-IR.



Scheme 3. Possible polymerization process of 3-APN under heat treatment.