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Low-melting phthalonitrile monomers containing maleimide group: Synthesis, dual-curing behavior, thermal and mechanical properties



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higher than 450°C in air.

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ARTICLEINFO	A B S T R A C T
Keywords: Phthalonitrile Maleimide Thermosets Processability Thermal properties Curing behavior	Novel dual-functional phthalonitrile monomers containing a maleimide group were synthesized and character- ized. <i>Ortho, meta,</i> and <i>para</i> isomers were obtained and only the <i>meta</i> -isomer can be considered as a low melting phthalonitrile monomer with a melting point of 107.4°C. Analysis of the dual-curing behavior of monomers showed radical homopolymerization of maleimides followed by phthalonitrile polymerization with the formation of isoindoline, triazine, and phthalocyanine ring structures. Two alternative copolymerization processes of maleimide groups via ene reaction and ring-opening amidation were investigated. The approach of dual-curing maleimide and phthalonitrile fragments in a single molecule allowed combining the excellent inherent me- chanical properties of bismaleimide resins and the outstanding thermo-oxidative stability of phthalonitriles. After curing of both functional groups impact strength was as high as 11.81 kJ m ⁻² , flexural strength was 108 MPa. Young's modulus was 4.38 GPa. On the contrary. T _g of this polymeric system was above 370°C and T ₅₅₀ was

1. Introduction

Thermosetting polymers with high thermal stability and superior mechanical properties are widely used in aerospace fields. Heat-resistant thermosets include benzoxazines [1-3] propargylated and allylated phenolics [4-9], cvanate esters [10-12], bismaleimides [13-16], and phthalonitriles [17-21]. Bismaleimides (BMI) are a well-known industrially produced class of high-performance thermosetting resins. They possess a range of attractive properties for aerospace applications such as high glass transition temperatures (230-380 °C), good hot-wet performance, and superior mechanical properties [13,22]. In particular, bismaleimide blends with 2,2'-diallylbisphenol A (DABA) can be viewed as a benchmark against which other commercially available thermosets for structural composite applications [23,24] are compared. BMI were also of interest in the fields of self-healing polymers [25], clickchemistry and UV-induced polymerization [26], and 3D-printing [27]. However, the thermostability of polymer systems composed of maleimide monomers cannot be compared with that of phthalonitriles some of the most heat resistant polymers. The phthalonitrile resins attract attention due to their outstanding thermal and thermo-oxidative stability, excellent mechanical properties, and good moisture resistance.

Phthalonitrile polymerization is usually induced by aromatic diamines or phenols [28-32] leading to the formation of a cross-linked and voidfree polymeric network consisting of aromatic heterocycles [33-36]. These structures provide high thermal stability and low flammability of the resulting polymers (T $_g$ > 400 $^\circ C,~T_{5\%}$ > 500 $^\circ C,~LOI$ > 60%) [18,37–39]. Nevertheless, the high melting temperature of the common phthalonitrile monomers (usually >180 $^{\circ}$ C) [17,40] which is close to their polymerization onset temperature results in a narrow processing window and limits their application.

Many approaches to improve processability of phthalonitriles have been developed. One of them is the introduction of flexible linkages to the molecular structure of phthalonitrile monomers. Aryl [15] or alkyl [41] ether units are often used as such linkages. Wu et al. suggested to combine fluorinated fragments and flexible ether linkages to construct high-performance functional PN with good processability [42]. Recently, we synthesized phosphorus- [43-46] and silicon-containing [47-50] linkers with phthalonitrile fragments to achieve glass transition temperatures of monomers as low as 0 °C. This allowed to obtain CFRP via cost-effective injection techniques [51,52] and dry pre-preg fabrication [20,53] for the first time.

Another approach was the development of dual-function

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phthalonitrile molecules. Introduction of additional flexible and functional moieties can promote curing of phthalonitriles and at the same time usually decreases the softening temperature of monomers. Autocatalytic phthalonitrile monomers with amino groups demonstrate this approach [54] and are also used as synthesis precursors and as curing agents in the present work. A molecule containing both propargyl ether and phthalonitrile fragments was recently developed and described by our research group [38,55]. T_m of the obtained monomers was 117 °C and their superior processability was demonstrated for vacuum infusion resin molding process (VIM) [38]. Recently, Yue Han et al. synthesized low-melting (T_m = 68 $^{\circ}$ C) phthalonitrile monomers with allyl moieties and showed increased toughness of the cured resin (impact strength was 13.63 kJ m⁻²) compared to bi-functional phthalonitriles (8.74 kJ m⁻²) [56,57]. In general, the presence of several functional groups capable of participating in different polymerization mechanisms allows to control the polymerization pathways, which, in turn, alters the properties of the resulting polymer [3].

Prior to this study, several blends containing maleimides and phthalonitriles were prepared to improve thermal stability of the bismaleimide thermosets [3,58,59]. However, only Kaliavaradhan et al. examined the effect of the presence of both maleimide and phthalonitrile in the same molecular structures obtained by Michael addition of 4-(4-aminophenoxy)phthalonitrile to different bismaleimides [59]. Unfortunately, these monomers were characterized by high melting temperatures (>170 °C). Additionally, the introduction of phthalonitrile fragments was carried out through the Michael addition to maleimide double bond, and as a result, the functionality of maleimide group was absent in the resulting monomers.

The general drawback of both phthalonitriles and maleimides is the high brittleness of the cured polymeric material, which is an obstacle for using them as matrices in high-performance composites [13,44]. Fortunately, it is possible to adjust the mechanical properties of maleimide polymers by introducing different comonomers which change the mechanism of polymerization. Due to the presence of the electron-deficient double bond, the maleimide group could be easily involved in such polymerization processes as: anionic or radical homopolymerization, copolymerization by ene reaction, Michael addition with nucleophiles (amines or thiols [60]), as dienophiles in Diels-Alder reactions [61]. Such methods to reduce the brittleness of maleimide polymers were studied in many published studies, but usually the improvement of toughness occurred at the cost of decreased T_g and thermooxidative stability [62–64].

The present article deals with the synthesis and characterization of novel *para, meta,* and *ortho* isomers of phthalonitrile monomers containing maleimide moieties N-[4-(4-phthalonitrile)phenoxy]maleimide (**PNB-P**), N-[3-(4-phthalonitrile)phenoxy]maleimide (**PNB-M**), and N-[2-(4-phthalonitrile)phenoxy]maleimide (**PNB-O**). Blends of **PNB-M** with **DABA**, 1,3-bis(4-aminophenoxy)benzene (**APB**), or 4-(4-aminophenoxy)phthalonitrile (**3P**) were prepared and studied in order to counter brittleness and improve processability, curing, thermal and mechanical properties. Processes of maleimide and phthalonitrile polymerization were studied by liquid-state NMR, FT-IR, and DSC.

2. Experimental

2.1. Materials

All manipulations with the oxidation and moisture sensitive compounds were carried out under Ar atmosphere. Acetone, *N*,*N*-dimethylacetamide, potassium carbonate, sodium bicarbonate were purchased from Chimmed (Russia), anhydrous sodium acetate was purchased from PanReac AppliChem (Spain), propionic anhydride, 2-aminophenol, 3aminophenol, 4-aminophenol, maleic anhydride, tret-butyl peroxybenzoate were purchased from Acros Organics (USA), 4-nitrophthalonitrile and 1,3-bis(4-aminophenoxy)benzene were purchased from Central Drug House (India), 4,4'-diphenylmethanebismaleimide and 2,2'-diallylbisphenol A were purchased from HOS-technik (Austria) under trade names Homide 121 and Homide 127A respectively and used as received.

2.2. Methods

NMR spectra were recorded on a Bruker Avance II 600 at 600 MHz for ¹H and 151 MHz for ¹³C. Chemical shifts (ppm) are given relative to solvent: references for DMSO were 2.50 ppm (¹H NMR) and 39.50 ppm (¹³C NMR). Fourier Transform Infrared (FT-IR) spectra were recorded on a Bruker Tensor-27 spectrophotometer in the range of 4000–400 cm⁻¹ using KBr pellets. HPLC and GPC analysis was performed on an Agilent 1260 chromatography system equipped with reversed-phase column ZORBAX Eclipse Plus C18 (T column = 30° C; eluent – 50% aqueous acetonitrile (ν/v); flow rate = 1.0 ml/min) for HPLC and two PL1113–6300 ResiPore (300 \times 7.5 mm) columns (T column = 30°C; eluent – tetrahydrofuran; flow rate = 1.0 ml/min) for GPC. Differential scanning calorimetry (DSC) was performed on Netzsch DSC214 Polyma at heating rates of 5 °C/min, 10 °C/min, and 15 °C/min. Rheological behavior was measured with MCR 302 rheometer using cone 7 at 200 rpm in the temperature range from 50 to 400 °C at a heating rate of 2 °C/ min. Thermal stability was evaluated via thermogravimetric analysis (TGA) on Netzsch TG 209 P3 Tarsus, at a heating rate of 10 $^{\circ}$ C/ min in range of 40-980 °C in Ar or air purge rate of 50 ml/min. Elemental analysis was performed at the Laboratory of Microanalysis of INEOS RAS, Moscow.

2.3. Synthesis

1,3-Bis(3,4-dicyanophenoxy)benzene was synthesized according to a well-known procedure with quantitative yield (98%) [65]. Synthetic procedure and NMR spectra for **30**, **3M**, **3P**, **40**, **4M**, **4P** are presented in the supplementary materials.

2.3.1. 4-[3-(2,5 dione-1H-pyrrole-1-yl)phenoxy]benzene-1,2-dicarbonitrile (**PNB-M**)

4-((3-(3,4-Dicyanophenoxy)phenyl)amino)-4-oxobut-2-enoic acid **4M** (20.0 g, 0.069 mol) was dissolved in 25 ml of propionic anhydride (0.2 mol) in a 250 ml round-bottom flask equipped with a reflux condenser and magnetic stirrer. Sodium acetate (4.00 g, 0.049 mol) was added as a catalyst to promote the dehydration reaction. The reaction mixture was stirred at room temperature and monitored by thin layer chromatography (TLC). After 7 h, the solution was slowly poured into 400 ml of aqueous solution of sodium bicarbonate. The precipitated product was filtered and dissolved in acetone. The acetone solution was poured into distilled water. This procedure was repeated several times until neutral pH of the product aqueous solution was achieved. The product was filtered and dried under vacuum at 70 °C. Yield: 18.1 g (96%) of white powder.

¹H NMR (DMSO-*d*₆, 600 MHz) δ: 8.14 (d, 1H⁷, J_{6,7} = 8.70 Hz), 7.87 (d, 1H⁸, J_{6,8} = 2.51 Hz), 7.60 (dd, 1H⁴, J_{3,4} = 8.37, J_{3,5} = 7.70 Hz), 7.45 (dd, 1H⁶, J_{6,7} = 8.70 Hz, J_{6,8} = 2.51 Hz), 7.32 (d, 1H³, J_{3,4} = 8.37 Hz), 7.24 (d, 1H⁵, J_{3,5} = 7.70 Hz); 7.23 (s, 1H²), 7.19 (s, 2H¹) (for ¹H-spectrum with peak assignment see Fig. S15). ¹³C NMR (DMSO-*d*₆, 151 MHz) δ: 169.58, 160.43, 153.93, 136.42, 134.79, 133.36, 130.79, 123.65, 123.15, 122.44, 119.19, 118.24, 116.80, 115.86, 115.37, 108.71 (16/16) (Fig. S16). Anal. Calc. for C₁₈H₉N₃O₃ (M_r = 315.28): C, 68.57; H, 2.88; N, 13.33%. Found C, 68.42; H, 2.91; N, 13.41%.

4-[4-(2,5 dione-1H-pyrrole-1-yl)phenoxy]benzene-1,2-dicarbonitrile **PNB-P** and 4-[2-(2,5 dione-1H-pyrrole-1-yl)phenoxy]benzene-1,2dicarbonitrile **PNB-O** were synthesized by the same procedure from **4P** and **4O** respectively, with minor modifications described in the results section.

2.3.1.1. PNB-P. Yield 92%. $^{1}\mathrm{H}$ NMR (DMSO- $d_{6},$ 600 MHz) $\delta:$ 8.13 (d,

 $\begin{array}{l} 1\mathrm{H}^5,\,J_{4,5}=8.70~\mathrm{Hz}),\,7.89~(d,\,1\mathrm{H}^6,\,J_{4,6}=2.51~\mathrm{Hz}),\,7.47~(d,\,2\mathrm{H}^3,\,J_{2,3}=9.01),\,7.45~(dd,\,1\mathrm{H}^4,\,J_{4,5}=8.70~\mathrm{Hz},\,J_{4,6}=2.51~\mathrm{Hz}),\,7.33~(d,\,2\mathrm{H}^2,\,J_{2,3}=9.01~\mathrm{Hz}),\,7.21~(s,\,2\mathrm{H}^1)~(\mathrm{Fig.~S13}).\ ^{13}\mathrm{C}~\mathrm{NMR}~(\mathrm{DMSO-}d_6,\,151~\mathrm{MHz})~\delta;\\ 169.84,\,160.62,\,153.04,\,136.40,\,134.74,\,128.9,\,128.79,\,123.21,\,122.41,\,120.53,\,116.78,\,115.88,\,115.37,\,108.606~(14/14),~(\mathrm{Fig.~S14}).~\mathrm{Anal.}\\ \mathrm{Calc.~for}~\mathrm{C}_{18}\mathrm{H_9N_3O_3}~(M_r=315.28);~\mathrm{C},\,68.57;~\mathrm{H},\,2.88;~\mathrm{N},\,13.33\%.~\mathrm{Found}~\mathrm{C},\,68.36;~\mathrm{H},\,2.97;~\mathrm{N},\,13.43\%. \end{array}$

2.3.1.2. *PNB-O.* Yield 86%. ¹H NMR (DMSO- d_6 , 600 MHz) δ : 8.09 (d, 1H⁷, J_{6,7} = 8.70 Hz), 7.69 (d, 1H⁸, J_{6,8} = 2.18 Hz), 7.60 (dd, 1H⁴, J_{3,4} = 8.37, J_{4,5} = 7.70 Hz), 7.52 (d, 1H⁵, J_{4,5} = 7.70 Hz), 7.46 (dd, 1H³, J_{3,4} = 8.37 Hz, J_{2,3} = 7.03 Hz), 7.36 (d, 1H², J_{2,3} = 7.03 Hz), 7.23 (s, 2H¹) (Fig. S17). ¹³C NMR (DMSO- d_6 , 151 MHz) δ : 169.28, 160.14, 150.17, 136.21, 135.07, 131.27, 131,16,126.45, 123.37, 122.63, 122.09, 121.58, 116.55, 115.76, 115.24, 108.8 (16/16) (Fig. S18). Anal. Calc. for C₁₈H₉N₃O₃ (M_r = 315.28): C, 68.57; H, 2.88; N, 13.33%. Found C, 68.32; H, 2.95; N, 13.51%.

2.4. Monomer mixing and curing

Blends were prepared by mixing **PNB-M** with comonomers in a 100 ml round-bottom flask with a magnetic stirrer at 120 °C under vacuum (1 mmHg) until a clear homogeneous mixture was obtained. After stirring 15 g of the blend (**PNBM-DABA** or **PNBM-3P**) was poured into a steel mold ($100 \times 100 \times 2$ mm or $100 \times 100 \times 4$ mm) to obtain molded specimens for analytical studies or mechanical tests. The mold was placed into an oven and cured at 180 °C for 8 h. The molded plate of polymer was released and post-cured in an oven by heating to 240 °C, 280 °C, 330 °C or 375 °C (10 °C/h) and held at the final temperature for 8 h. A similar procedure was used to prepare the samples of control blends (**PN-3P, BMI-DABA, BMI-PN, BMI-PN-DABA**).

2.5. Kinetics studies

Dynamic DSC studies of curing kinetics were carried out using NETZSCH Thermokinetics 3.1 Software. Reaction parameters such as activation energy and pre-exponential factor were obtained by the Ozawa-Flynn-Wall method. Then the obtained parameters were assumed as initial values for the non-linear regression analysis of DSC curves. Experimental and predicted curves of the dual-stage curing reactions of monomers and their blends were shown in Figs. S12–15.The proposed kinetic models were in good agreement with the experimental DSC curves.

2.6. Mechanical testing

Dynamic mechanical analysis (DMA) was performed on DMA Q800 by scanning the specimens (55 mm \times 5 mm \times 2 mm) over a temperature range of 50–500 °C with frequency of 1 Hz and under inert atmosphere. The dependences of storage modulus (E'), loss modulus (E''), and loss factor (tan δ) of the polymer specimens on temperature were obtained. Mechanical tests were performed using Hounsfield H100KS, Tinius Olsen H5KS, and Instron 5985 testing machines.

The impact strength was determined using Charpy impact tester equipped with a 2.5 J impact energy pendulum according to ISO 179-2 standard. Fracture toughness in terms of critical-stress-intensity factor (K_{Ic}) and critical strain energy release rate (G_{Ic}) were determined according to ASTM D5045 on single-edge-notch bending specimens. K_{Ic} and G_{Ic} parameters were not monitored for specimens cured at a series of different temperatures because of the complex procedure for testing. At least five samples were utilized to obtain the results of each mechanical test. Average values and their standard deviations were calculated.

3. Results and discussion

3.1. Synthesis of dual-function monomers

Dual functional monomers **PNB-P**, **PNB-M**, **PNB-O** were successfully synthesized in three steps from the corresponding aminophenols (Fig. 1). In the first step phthalonitrile functionalized anilines **2P**, **2M**, **2O** were prepared via nucleophilic aromatic substitution reaction of aminophenols and 4-nitrophthalonitrile according to the literature procedure [54].

The most challenging step was the preparation of the maleimide ring. Despite the fact that it is possible to obtain maleimide from amine by a one-pot reaction in acetone [66], N-maleamic acids 3P, 3M and 3O were isolated separately to decrease side-product formation. It has been previously reported in [14] that high temperature (around 80 °C) and an excess of anhydride are necessary to avoid the formation of isomaleimide instead of the desired maleimide (Fig. S19). The reaction condition optimization was carried out using amide 3M. The reaction was first carried out in propionic anhydride without any other solvent using sodium acetate as the base. A significant amount (around 10%) of the product of Michael addition to the maleimide carbon-carbon double bond was observed in the NMR spectra of the product mixture (Fig. S20). The strong electron-withdrawing effect of the phthalonitrile group results in high susceptibility of the maleimide double bond to Michael addition. Therefore, trimethylamine was used to promote condensation between the amide and the carboxylic acid under milder conditions. However, the reaction proceeded slowly, and undesirable Michael addition side-product was also formed (Fig. S21). Finally, sodium acetate was used as the Brønsted base without the addition of trimethylamine. The reaction was carried out at room temperature and no evidence of the isomaleimide formation was found by NMRspectroscopy. The other two isomers PNB-O and PNB-P were also obtained under these optimized conditions. The reactivity and yield of the cyclization reaction increased in the following order: $3O < 3M \approx 3P$. The lower reactivity of 30 might be primarily explained by steric hindrances.

It is worth noting that the purification of **PNBs** monomers from residual propionic acid and anhydride following synthesis is critical for an accurate polymerization study. Even minor impurities of acids could significantly inhibit both the radical homopolymerization of maleimides and the Michael addition reaction due to protonation of the imide carbonyl oxygens, enhancing the electrophilicity of the maleimide cycle (see Fig. S22) [67]. Therefore, all monomers were precipitated by pouring their acetone solutions into distilled water. This procedure was repeated several times until all acidic impurities were removed.

High purities of all monomers were confirmed by HPLC, elemental analysis, ¹H and ¹³C NMR spectra. The NMR spectra of all synthesized compounds with peak assignments can be found in the supplementary materials in Figs. S1–18. HPLC data can be found in Fig. S23.

3.2. Melting and curing behavior of dual-curing monomers and their blends

Non-isothermal DSC curves of the **PNB**-monomers are presented in Fig. 2. Parameters calculated from DSC measurements of the investigated monomers and blends are shown in Table S1. All three monomers showed an endothermic transition due to melting followed by two exothermic peaks corresponding to the polymerization reactions of maleimide and phthalonitrile moieties. 4,4'-diphenylmethanebismaleimide (**BMI**) and 1,3-bis(3,4-dicyanophenoxy)benzene (**PN**) were shown in Fig. 2 for comparison to demonstrate the absence of phthalonitrile polymerization without catalysts (**PN**) and the presence of an exothermic peak of maleimide homopolymerization (**BMI**). The melting point of **PNB-M** was the lowest (107.4°C) compared to **PNB-P** (210.4°C) and **PNB-O** (200. 8°C). Subsequent cooling revealed that crystallization of **PNB-M** from the melt-state is significantly hindered and the DSC



Fig. 1. (A) Synthetic routes towards PNB-P, PNB-M, PNB-O (PNB-s).



Fig. 2. DSC curves of dual-function **PNB**-monomers compared to 4,4'-diphenylmethanebismaleimide (**BMI**) and 1,3-bis(3,4-dicyanophenoxy)benzene (**PN**).

curve collected during the second heating showed only an amorphous solid-state with glass transition around 33.7°C (see Fig. S24). Polymerization of **PNB-P** and **PNB-O** started immediately after melting, which does not allow performing the heating-cooling-heating cycle DSC experiments with them and leads to short processing windows for these monomers.

Polymerization of the maleimide double bond proceeds through radical homopolymerization with peak maxima at 287.9°C (PNB-P), 231.3°C (PNB-M), 278.9°C (PNB-O) [13]. We assumed that the peak maximum of PNB-M was at the lowest temperature because the withdrawing effect of the phthalonitrile fragment on the maleimide double bond increased from meta position in PNB-M to para and ortho positions in PNB-P and PNB-O. It has been reported that the presence of a withdrawing group in the backbone of maleimide increased the homopolymerization temperature and reduced the reactivity of the double bond [68]. ¹H NMR spectrum of **PNB-M** bulk-polymerized at 180°C for 24 h showed a linear homopolymer pPNB-M soluble in methylene chloride or acetone (Fig. S25) [69]. DSC curve of this polymerized product established three glass transitions that could result from the wide and complex molecular weight distribution (MWD) of pPNB-M (Fig. S26). Indeed, the GPC experiment showed a linear polymer with a wide MWD (Fig. S27) and a low degree of polymerization (polystyrene

standards). The maximum conversion of maleimide polymerization at 180°C was about 55% when determined by integration of the NMR peaks. A further increase in temperature above 180°C leads to the polymerization of phthalonitrile fragments and therefore, to the formation of insoluble cross-linked polymer.

The radical mechanism of maleimide polymerization was observed on the DSC curve of blend PNB-M with 1% wt. tret-butyl peroxybenzoate as free-radical initiator (Fig. S28). After addition of the initiator the maleimide polymerization DSC peak shifted to a lower temperature, the original maleimide homopolymerization peak of PNB-M remained but significantly decreased. The double bonds are likely sterically hindered at the high degree of crosslinking and cannot be fully polymerized below the decomposition temperature of the initiator. The addition of hydroquinone, on the contrary, shifts the polymerization peak to a higher temperature due to the inhibition of free-radical polymerization. There was no evidence that the phthalonitrile fragments underwent free-radical polymerization as was suggested by Z Liu et al. [70]. The peak maximum of phthalonitrile polymerization on the DSC curve of the PNB-M blend with tret-butyl peroxybenzoate decreased only by 10°C probably due to the earlier maleimide polymerization the product of which in turn promoted phthalonitrile polymerization. It was reported that succinimide structures obtained from the homopolymerization of maleimides can insignificantly degrade into amines at 300°C [71,72]. It is well known that even minor amounts of amine could initiate phthalonitrile polymerization. Therefore, we proposed that the mechanism of self-catalyzed polymerization of the phthalonitrile fragments may be related to the minor decomposition of the succinimide structures into amines at 300°C, which in turn can catalyze the polymerization of phthalonitrile fragments. The equimolar blend of BMI and PN was also studied by DSC, and its curve showed an exothermic peak of phthalonitrile polymerization (Fig. S29) similar to those observed for the PNB monomers, which serves as additional proof of the catalytic effect of the polymerized maleimide moieties on the curing of phthalonitrile fragments.

To investigate the dual-curing behavior of **PNB**-monomers, different blends with comonomers (**DABA**, **APB**, **3P**) were obtained (**Table 1**). DSC curves for these blends are shown in Fig. 3, and relevant parameters are listed in Table S1. The reaction mechanisms were examined by NMR of the adducts obtained from **PNB-M** heated with **DABA** or **3P** (Figs. S30–31). Proposed mechanisms for the polymerization of PNB-M, PNBM-DABA and PNBM-3P were summarized in Fig. 4.

Since **DABA** is the most common comonomer used for improving the mechanical properties of bismaleimides, an investigation of the **PNB-M** blend with **DABA** was a task of the highest priority. There were two exothermic peaks on the DSC curves of blends containing **PNB-M** and **DABA** (Fig. 3). The first peak was an assigned to the copolymerization of **DABA** with **PNB-M**. The second peak was related to the phthalonitrile curing. The temperature of phthalonitrile curing of all **DABA**-containing

Table 1

Abbreviations of the blends and their components mass ratios.

Blend	Dual- functional monomer PNB-M	Amine comonomer (APB)	comonomer DABA	Phthalonitrile with amino group (3P)
4PNBM- DABA	89.1	-	10.9	-
2PNBM- DABA	80.4	-	19.6	-
PNBM- DABA	67.2	-	32.8	-
PNBM- 3P	57.3	-	-	42.7
PNBM- APB	90.1	9.9	-	_

Control blends	Bisphthalonitrile monomer PN	Bismaleimide BMI	comonomer DABA	Phthalonitrile with amino group (3P)
PN-3P	93.9	-	-	6.1
BMI-	-	90.7	9.3	-
DABA				
BMI-PN	50.2	49.8	-	-
BMI-PN-	35.2	34.8	30	-
DABA				



Fig. 3. DSC curves of the PNB-M blends with comonomers DABA, 3P and APB.

systems was lower than for the pure **PNB-M** monomer due to the fact that **DABA** can additionally facilitate the polymerization of phthalonitrile fragments by OH-groups [3]. Increasing **DABA** content in the blend from **4PNBM-DABA** to **PNBM-DABA** lead to a shift of the peak maximum to a lower temperature from 326.5°C to 299.4°C. The DSC curves of the phthalonitrile-bismaleimide control systems with and without **DABA** (**BMI-PN-DABA** and **BMI-PN**) showed a similar difference in the peak maxima of the phthalonitrile polymerization due to the catalytic effect of the OH-groups on the phthalonitrile fragments curing (Fig. S29).

The reaction of **DABA** and **PNB-M** proceeded by a well-known pathway through an ene reaction that was proven by IR and NMR spectroscopy. Only products of the mono- **6 m** and di-addition **7 m** via ene reactions were observed for the **PNBM-DABA** blend (Fig. S30). No evidence of products of Diels-Alder reactions of **PNB-M** with the ene adducts were observed in NMR spectra. It was earlier reported that in the case of diallyl bisphenol A, Diels-Alder reaction did not occur due to steric hindrance [73,74].

On the DSC curves of the PNB-M blend with the amine-containing compounds 3P and APB, two peaks were observed. The first one might be related to the amidation of maleimide or Michael addition of amine to the maleimide double bond [75] and the second one may be associated with the polymerization of phthalonitrile. However, an NMR study of the reaction between **3P** and **PNB-M** showed only the imide ring opening with the formation of amide (amidation) and no adducts of the reaction between 3P and PNB-M by Michael addition were observed (Fig. S31). Moreover, the homopolymer can be seen in the NMR spectra of the PNBM-3P blend heated at 180°C due to the anionic polymerization of the maleimide groups promoted by amines [14]. Maleic diamide derivative 5 pm (Fig. S31) was isolated by flash column chromatography from the products obtained after heating of blend PNBM-3P. We assumed that the amidation reaction of **PNB-M** might be enabled by the withdrawing effect of the phthalonitrile affecting the maleimide double bond [76,77]. The amidation reaction was additionally confirmed by an IR-study described further.

3.3. IR-study of monomers and blends

FT-IR measurements were performed on **PNB-M**, **PNB-O**, **PNB-P** monomers and **PNBM-DABA**, **PNBM-3P**, **PNBM-APB** blends polymerized at different temperatures to additionally investigate their curing behaviors, and the IR-spectra are presented in Fig. 5 and in Figs. S32–34 for **PNB-O**, **PNB-P**, and **PNBM-APB**.

In the FT-IR spectra of **PNB-M** and **PNBM-DABA**, **PNBM-3P**, **PNBM-APB** blends polymerized above 180°C and **PNB-P** and **PNB-O** polymerized at 280°C the characteristic absorption bands of C=C maleimide linkage around 830 cm⁻¹ and 698 cm⁻¹ disappeared [78]. The signal located at 3105 cm⁻¹ specific to the maleimide double bonds also disappeared. An absorption band corresponding to the C-N-C maleimide (at 1147 cm⁻¹) decreased for all samples while a new absorption band around 1180 cm⁻¹ (C-N-C succinimide) [79] increased. A decrease of the absorption peak at 1627 cm⁻¹ indicated that the allyl group reacted at 180°C in the case of **PNBM-DABA** blend curing.

In the case of **PNBM-3P** and **PNBM-APB**, stretching bands of C=O (amide I mode) at 1641 cm⁻¹ and 1668 cm⁻¹ can be seen after polymerization in addition to the band of the succinimide ring. These bands overlapped with the isoindoline characteristic absorption band at 1652 cm⁻¹ when further curing was carried out at the temperature higher than 280°C. After polymerization of **PNBM-3P** and **PNBM-APB**, the amino bands at 3472 and 3379 cm⁻¹ disappeared (NH₂ asymmetric and symmetric stretching vibrations). Presence of the amide absorption bands on the IR-spectra together with the NMR analysis show the ring-opening amidation of imide in the polymerization processes of **PNBM-3P** at 180°C.

The increase of curing temperature resulted in the decrease of peak height of the characteristic absorption band of the cyano groups at 2233 cm⁻¹. However, the significant decrease of the cyano groups absorption was not observed for the cured PNB monomers until 280°C due to the higher temperature of the phthalonitrile polymerization without any comonomers. Furthermore, the nitrile absorption band shifted to lower wavenumbers, which could indicate the formation of triazine derivatives [80]. The characteristic absorption bands of triazine rings could also be found at the range from 1520 to 1545 cm⁻¹ but only after curing at 375°C. The characteristic peak of triazine ring at 1325 cm⁻¹ was unidentifiable due to the overlapping of peaks. At the same time, there was obvious formation of phthalocyanine rings observed as absorption bands in the range from 1010 to 1020 cm⁻¹ appeared starting at the low-temperature curing stages (180-240°C) [45]. The characteristic band of isoindoline structures at 1652–1660 cm⁻¹ appeared only after polymerization at the temperatures above 240°C. Such behavior of polymerization might be related to the steric factor hindering the formation of phthalocyanines only at the high degrees of crosslinking. The



maleimide homopolymerization or amidation or ene reaction adducts

Fig. 4. Proposed polymerization pathways of PNB-M, PNBM-DABA and PNBM-3P.



Fig. 5. IR spectra of neat and cured at different temperatures PNB-M (A), PNBM-DABA (B) and PNBM-3P (C).

results of the IR study indicate a high degree of conversion of the phthalonitrile and maleimide moieties during polymerization reactions of all investigated blends and monomers.

3.4. Non-isothermal polymerization kinetic analysis

Kinetic parameters such as activation energy and pre-exponential factor were calculated as described in the experimental section (Table S2). Maleimide polymerization was described as an n-th order reaction (Eq. (1)) and phthalonitrile polymerization was described with the Prout–Tompkins equation, which is a short form of the Šesták–Berggren equation (Eq. (2)).

$$f(\alpha) = (1 - \alpha)^n \tag{1}$$

$$f(\alpha) = (1 - \alpha)^n \alpha^a \tag{2}$$

The DSC curves of all investigated monomers and the **PNMB-DABA** blend were successfully fitted as two-step sequential reactions (Fig. S38). The calculated E_a values for **PNB-P**, **PNB-M**, and **PNB-O** were 91.5 kJ/mol, 106.9 kJ/mol and 134.1 kJ/mol, respectively

(Figs. S35–37). These values are similar to the activation energies of the maleimide homopolymerization reported in the range 120–160 kJ/mol. The highest activation energy of **PNB-O** can be related to steric hindrance of the maleimide double bond. Activation energy of the **PNBM-DABA** blend was 85.9 kJ/mol, which is lower than the activation energy of pure **PNB-M**, while pre-exponential factor of **PNB-M** was similar to **PNBM-DABA**. It can explain the absence of **PNB-M**'s homopolymerization adducts in the cured **PNBM-DABA** blend. The calculated activation energies of phthalonitrile polymerization were similar to those reported earlier [54,81]. Phthalonitrile polymerization was described as autocatalytic first-order reactions probably due to the formation of catalytic moieties during phthalonitrile polymerization. It was reported that isoindoline structures were able to accelerate further phthalonitrile polymerization [81].

3.5. Rheological behavior and processability

The dynamic viscosity changes in the course of curing reactions were monitored via viscosity studies. Viscosity-temperature and isothermal curves for the **PNB-M** monomer, **PNBM-3P**, and **PNBM-DABA** are shown at Fig. 6. The temperature of viscosity decrease to 1000 mPa s ($T_{1000mPas}$), curing onset temperature (T_{onset}), processing window, and gel time at 180 °C are the parameters determining the possibility of resin application in composite manufacturing using such methods as resin transfer molding (RTM) or vacuum infusion (VIM) [52]. These parameters were obtained from the viscosity data and summarized in Table 2. Processing window was calculated as the difference between T_{onset} and $T_{1000mPas}$ [57]. Viscosity-temperature profiles for all **PNB** monomers can be found in Fig. S39. The presence of a peak on the viscosity temperature curves is evidence of the formation of a linear polymer during **PNB** monomer homopolymerization. After the peak viscosity decrease due to polymer melting. Increasing temperature to 280 °C leads to a rapid increase of viscosity due to the phthalonitrile fragment polymerization in all monomers and blends.

The temperature of 180 °C is commonly used as a curing temperature for phthalonitriles. Therefore, the resin gel time at this temperature is an important parameter for estimating the processability character and curing time. At 180 °C the viscosity increase of the system containing DABA occurs more rapidly than for the pure PNB-M monomer likely due to the lower activation energy of the ene reaction compared to the homopolymerization reaction [13]. The viscosity of PNBM-3P increased to 2000 mPa s during the first 30 min of isothermal heating at 180 $^\circ$ C likely due to the amidation reaction between PNB-M and 3P with the formation of maleic diamide, followed by a further rapid increase after 220 min due to phthalonitrile fragments curing. The T_{1000mPas} of PNBM-DABA was 76.2 °C, which is lower than 87 °C observed for the recently reported low-melting phthalonitrile system [57] and could be acceptable for RTM and VIM fabrication. At the same time, this value was lower than 97.5 for the BMI-PN-DABA blend due to the lower melting point of PNB-M compared to PN and BMI.

3.6. Thermal properties of cured polymers

Thermal stability of all obtained polymers was studied using thermal analysis under nitrogen and air atmospheres. TGA curves are shown in Figs. 7 and 8. Parameters characterizing degradation behavior including weight loss temperatures ($T_{5\%}$ and $T_{10\%}$) and char yields at 900 °C (Y_c) are presented in Table 3.

As can be seen from Table 3, thermal stability increases in the following order: **PNB-O** - **PNB-P** - **PNB-M**. The electron-withdrawing phthalonitrile ring in the *para-* and *ortho-* positions of the phenyl ring in monomers **PNB-O** and **PNB-P** could reduce the electron density at the imide nitrogen compared with the *meta-* position of **PNB-M**. Delocalization of electron density from the imide nitrogen to the carbonyl group would result in an increase of the strength of the C—N bond in the

Table 2

Parameters calculated from rheological study of PNB-monomers and blends.

Monomer/ Blend	T _{1000mPas} , °C	T _{onset} , °C	Processing window (°C)	Gel time at 180 °C, min
PNB-P	214.7	241.2	26.5	_
PNB-M	107.4	232.6	125.2	143
PNB-O	202.5	224.0	21.5	-
PNBM-DABA	76.2	258.1	181.9	92
2PNBM-	95.5	253.4	157.9	127
DABA				
PNBM-3P	107.3	248.2	143.9	223
BMI-PN-	97.5	212.1	114.6	-
DABA				

- - parameter was not investigated.



Fig. 7. TGA curves for cured polymers under nitrogen atmosphere.

succinimide moiety and as a consequence – an increase of the thermal stability of the polymer [43]. The trend observed for oxidation resistance was similar to the one for thermal stability.

Polymerized blends **PNBM-DABA** and **PNBM-3P** showed high thermal stability. $T_{5\%}$ was above 450 °C, and char yield in nitrogen was as high as 75.9% for **PNBM-DABA**. As expected, these values exceed the $T_{5\%}$ (less than 400 °C) and char yield (less than 50%) of the polymerized blend of bismaleimide **BMI** with **DABA** [13,83] because phthalonitriles possess better thermal properties. The higher char yields also lead to the high limiting oxygen indeces (LOI) of the cured **PNBM-DABA** and **PNBM-3P** systems according to Van Krevelen equation [84]. However, thermo-oxidative stability of these cured blends was still lower than in the case of the system containing only the phthalonitrile monomer (**PN**-



Fig. 6. Time sweep curves of viscosity collected at 180 °C (A) and viscosity-temperature profiles (B) for monomer PNB-M and its blends.



Fig. 8. TGA curves for cured polymers under air atmosphere.

Table 3

Results obtained from TGA measurements of cured polymers.

monomer/blend	Nitrogen			Air	
	T _{5%} ,°C	T _{10%} ,°C	$\rm Y_{c}$, %, 900 °C	T _{5%} ,°C	T _{10%} ,°C
PNB-P	403	452	65.1	413.8	469.6
PNB-M	414	467	68.0	419.0	475.8
PNB-O	385	423	61.3	392.9	439.8
PNBM-DABA	456	505	75.9	458.8	507.9
PNBM-3P	488	530	77.5	470.9	510.5
BMI-DABA [82]	407	423	37 (at 800 °C)	-	-
PN-3P [57]	503	543	73.2	504	534

3P).

Curves of storage modulus (G') and tan δ were obtained by DMA measurements for the **PNBM-DABA** (Fig. 9) and **PNBM-3P** (Fig. 10) blends cured at different temperatures. Parameters including G' at RT and 300 °C, T_g are all presented in Table 4. Once more, the measurement could not be performed for cured **PNB** monomers due to the brittleness of samples caused by excessive cross-linking.

For the **PNBM-DABA** blend cured at 240 °C two peaks were observed on the tan δ curves. This can be associated with a relatively high content of the more flexible products of copolymerization of **DABA** with maleimides compared to the cured phthalonitrile fragments. The increase of curing temperature results in the decrease of storage modulus at 50 °C possibly due to a greater impact of cured phthalonitrile fragments on the storage modulus. The first glass transition temperature of **PNBM-DABA** was similar to **BMI-DABA** when both were cured at 240 °C, but after the curing temperature was increased to 280 °C, T_g of **PNBM-DABA** increased to 357.6 °C due to phthalonitrile polymerization while the T_g of **BMI-DABA** remained almost the same. It is obvious from the DMA and TGA experiments that thermal performance of the cured **PNBM-DABA** blend significantly exceeded the commonly used **BMI-DABA** system.

Storage modulus for the **PNBM-3P** blend cured at 180 °C was lower than 3 GPa due to the incomplete crosslinking. Two glass transition temperatures were also detected if the samples were cured at temperatures below 240 °C. It is likely that one of them was related to the transition of the homopolymerized double bond of maleimide and another to the phthalocyanine and isoindoline moieties of the polymerized phthalonitrile. The **PNBM-DABA** and **PNBM-3P** blends cured at 375 °C showed a decrease of modulus simultaneously with an increase of glass transition temperature. We assumed that a high degree of crosslinking density might lead to an increase in the internal stress that caused damage to the structure of the polymer. Moreover, minor destruction of the maleimide polymer structure might also have taken place.

3.7. Mechanical properties of cured polymers

Flexural, fracture, and impact tests of the blends (**PNBM-DABA** and **PNBM-3P**) which were cured at different temperatures were performed to evaluate the influence of the maleimide and phthalonitrile polymerization on the mechanical properties of the polymers. Flexural modulus, flexural strength, and impact strength obtained are shown in Fig. 11. Flexural strength and modulus of **PNBM-DABA** cured at 180 °C were 123 MPa and 5.07 GPa, respectively, which was much higher than those observed for the conventional phthalonitrile systems [44] and at the same level as the strength and modulus of the bismaleimide-DABA resin systems [13,85,86]. These mechanical properties of **PNBM-3P** were lower and they can be considered typical for phthalonitrile resins. This can be explained by the absence of flexible molecular structures produced by the ene reaction of the maleimide group with **DABA**.

The flexural modulus, impact, and flexural strength of the **PNBM-DABA** cured blend decreased as the curing temperature increased. Flexural modulus (4.69 MPa) of the **PNBM** monomer cured with DABA at 240 °C was much higher than that (4.02 GPa) of the cured **BMI-DABA** resin. At the same time, flexural strengths of these polymers were almost the same.

The flexural modulus and strength of **PNBM-3P** cured at 180 °C were very low (2.82 GPa and 58 MPa, respectively). According to the IR study, the phthalonitrile polymerization at this temperature was characterized by low conversion and as a result, the polymerization proceeds with the formation of a material with a cross-linking density which is too low.

Despite the fact that amines were considered as comonomers which could improved toughness of polymers obtained via maleimide polymerization through Michael addition reactions [60], as explained earlier, significant amidation of maleimide with observable production



Fig. 9. DMA curves of the PNBM-DABA blend post-cured at different temperatures (4 h). (A) storage modulus; (B) loss factor (tan \delta).



Fig. 10. DMA curves of the PNBM-3P blend post-cured at different temperatures (4 h). (A) storage modulus; (B) loss factor (tan δ).

 Table 4

 Parameters obtained from DMA measurements of the cured polymer blends.

Prepolymer blend	Curing temperature (°C)	T _{g1} (°C) (tan delta)	T _{g2} (°C) (tan delta)	G' RT (MPa)	G' 300 °C (MPa) (retention of G' 50 °C)
PNBM-	180	262.5	366.2	4895	546 (11.1%)
DABA	240	291.2	369.4	4612	672 (14.6%)
	280	_	357.6	4367	2125
					(48.7%)
	330	_	368.4	4243	2521
					(59.4%)
	375	_	436.2	3421	1742
					(50.9%)
PNBM-3P	180	278.6	349.8	2811	1059
					(37.7%)
	240	288.1	352.1	4003	1562
					(39.0%)
	280	_	364.3	4007	2011
					(50.2%)
	330	-	377.1	3965	2563
					(64.6%)
	375	_	446.3	3250	2368
					(72.9%)
BMI-DABA	240	287.3	-	4287	425 (9.9%)
	280	290.1	-	3954	512 (12.9%)
PN-3P	375	-	476.2	4069	3122
					(76.7%)

of maleic diamide was observed for these blends. As the result, such polymers consist of highly crosslinked phthalonitrile fragments, which leads to high brittleness. The rapid decrease of mechanical properties that was observed after curing at 375 °C (a typical post-curing end temperature for phthalonitriles) is likely due to the presence of the more

rigid units of phthalonitrile polymerization products leading to shrinkage and micro-cracking of the polymer samples.

Impact strength is one of the most important toughness parameters which needs to be evaluated for the application of resins in composite manufacturing. The variation caused by curing temperature was similar to the variation in flexural and strength modulus. It is important that the value of impact strength was as high as $11.81 \text{ kJ} \cdot \text{m}^{-2}$ for **PNBM-DABA** cured at 330 °C which is within the range required for resin application in structural composite matrices [13]. This value was higher than the impact strength of the **BMI-DABA** system cured at 240 °C despite the significant difference in glass transition temperatures of these polymer systems. This likely originated from the balance in the flexible and rigid moieties formed after both the phthalonitrile and the maleimide polymerizations. Impact strength of the **PNBM-3P** system cured at 330 °C was only 8.49 kJ \cdot m⁻² and that can be associated with the higher stiffness of the polymer structure compared to **PNBM-DABA**.

The critical stress intensity factor (K_{Ic}) and critical strain energy release rate (G_{Ic}) are indicators of the material's ability to resist fracture. Their values were 1.08 MPa*m^{0.5} and 308 J*m⁻², respectively, for **PNBM-DABA** cured at 330 °C which is on the same level as the **BMI-DABA** systems (K_{Ic} = 0.8–1.4 MPa*m^{0.5}; G_{Ic} = 250–500 J*m⁻²) [13,85,87]. Fracture toughness parameters of the cured **PNBM-3P** at 330 °C were significantly lower (K_{Ic} = 0.67 MPa*m^{0.5} and G_{Ic} = 124 J*m⁻²). As it was expected, K_{Ic} values decreased with the increasing phthalonitrile content from **PNBM-DABA** to **PNBM-3P**, as reflected by the higher glass transition temperatures.

4. Conclusions

Novel self-catalyzed phthalonitrile monomers containing an N-maleimide group in different positions of the benzene ring were synthesized. Chemical structures were confirmed by 1 H and 13 C NMR, FTIR, and



Fig. 11. Flexural strength (A), flexural modulus (B), and impact strength (C) of the PNBM-DABA and PNBM-3P blends cured at a series of temperatures (180 °C, 240 °C, 230 °C, 330 °C, 375 °C) with comparison to the phthalonitrile PN-3P and bismaleimide BMI-DABA systems.

elemental analysis. The investigation of their curing behavior revealed homopolymerization of the maleimide double bond followed by selfcatalyzed formation of the phthalocyanine, isoindoline, and triazine structures from the phthalonitrile moieties. Only the meta- isomer PNB-M exhibited a low melting point of 107.4 °C while T_m of the para- and ortho- isomers were 210 °C and 200 °C. Therefore, PNB-M was chosen to obtain polymer materials and blended with comonomers for maleimide groups such as diallylbisphenol A (DABA) and 4-(4-aminophenoxy) phthalonitrile (3P). The PNBM-DABA blend exhibited polymerization via ene reaction of the allyl and maleimide groups while PNBM-3P showed ring-opening amidation with further phthalonitrile polymerization. The blends showed low viscosity at 100 $^\circ$ C in the melted state and wide processing windows which could be considered for application in RTM and VIM composite manufacturing technologies. The mechanical and thermal properties of the cured **PNBM-3P** blend were similar to the conventional phthalonitrile systems. Mixing of PNB-M with DABA allowed to easily obtain a material with an enhanced thermal performance compared to the bismaleimide-DABA systems. At the same time, flexural modulus, flexural strength, and fracture toughness of the cured **PNB-M** with **DABA** was on the same level as the bismaleimides: K_{Ic} was 1.08 MPa*m^{0.5}, G_{Ic} was 308 J^*m^{-2} , and impact strength was 11.81 kJ*m⁻² We showed that the mechanical properties and brittleness of phthalonitriles could be significantly improved with only a minor loss of thermal performance by introducing maleimide groups into the phthalonitrile monomer structure. Additionally, we hope that the dualfunctional monomers demonstrated will allow others to utilize the photopolymerization and self-healing possibilities of maleimides in the field of new phthalonitrile systems development.

Author statement

All persons who meet authorship criteria are listed as authors, and all authors certiff that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript. Furthefinore, each auth6r certifies that this material or similar material has not been and will not be submitted to or published in any other publication before its appearance in the Hong Kong Journal of Occupational Therapy.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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