Self-promoted phthalimide-containing phthalonitrile resins with sluggish curing process and excellent thermal stability

Jianghuai Hu,^a Yancui Liu,^a Yan Jiao,^b Suchun Ji,^a Rui Sun,^a Ping Yuan,^a Ke Zeng*^a, Xuemei Pu^b and Gang Yang*^a

^aState Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, P. R. China

^bCollege of Chemistry, Sichuan University, Chengdu, 610064, P. R. China.

*Corresponding author: (1) e-mail: zk_ican@sina.com (Ke Zeng); (2) e-mail: yanggang65420@163.com (Gang Yang), Tel: +86-28-85462736, Fax +86-28-85462736

Supporting Information

Materials

Dicyclohexylcarbodiimide (DCC), potassium carbonate and tetrahydrofuran (THF) were purchased from Tianjin BoDi Co. Ltd. O-phenylenediamine, Ethanol was purchased from Shanghai Fine Chemical Reagent Co., Ltd. palladium on carbon, 4-nitrobenzoic acid, hydrazine hydrate and other chemicals were purchased from Chengdu Kelong Chemical Reagent Co. Ltd. and were all used as received.

Synthesis of some monomers

Synthesis of phthalonitrile terminated ODPA monomer (CNODPA)

The CNODPA was synthesised according to the literature: T.M. Keller, Imidecontaining phthalonitrile resin, Polymer 34 (1993) 952-955.

CNODPA: IR (KBr, cm-1): 2234(C=N stretching), 1778 (C=O stretching), 1721 (C=O stretching), 1372 (C-N stretching). 1H NMR (400 MHz, DMSO-*d*6): δ 8.17-8.14 (d, 2H, Ar-H), 8.09-8.07 (d, 2H, Ar-H), 7.90 (d, 2H, Ar-H), 7.68-7.62 (t, 6H, Ar-H), 7.51-7.47(dd, 2H, Ar-H), 7.43-7.40 (d, 2H, Ar-H), 7.33-7.31 (d, 2H, Ar-H), 7.28(s, 2H, Ar-H).



Figure S1 The structure of CNODPA

Synthesis of 5,5'-oxybis-Phthalimide (phthalimide terminated ODPA, HIODPA)

To a 100ml, three-necked flask was added 4,4'-Oxydiphthalic anhydride (ODPA) (10g, 32.2mmol), urea (2.32g, 38.6mmol) and 49ml DMF. The mixture was stirred under nitrogen. The temperature of the reaction mixture was increased to 140°C and held at this temperature for 3h. After the mixture was cooled to room temperature, the white solidified product was collected by filtration, washed with water and dried at 70°C under reduced pressure for 12h. Yield: 4.20g, 42.3%. IR (KBr, cm⁻¹): 3190(N-H stretching), 1769(C=O stretching), 1712(C=O stretching), 1360(C-N stretching). ¹H NMR (300 MHz, DMSO-d6, δ): 11.41 (s, H; NH), 7.90-7.87 (d, H; Ar H), 7.53-7.50 (d, H; Ar H), 7.46 (s, H, Ar H).



Scheme S1 synthesis of HIODPA.

Synthesis of Benzimidazole-containing phthalonitrile (BIPN)

Synthesis of 4-benzimidazole aniline

Synthesis of compound 3

To a 250 mL, three-necked flask was added O-phenylenediamine (5.41g, 0.05mol), nitrobenzoic acid (8.02g, 0.048mol) and tetrahydrofuran (THF) (100mL). While stirring, Dicyclohexylcarbodiimide (DCC) (10.3g, 0.05mol) was added into the flask under an inert atmosphere. The mixture was stirred in ice water bath for 24h. The reaction mixture was filtered and the filtrate was collected. The product compound 3 was obtained by bubbling with dry hydrogen chloride into the reaction system, collecting the white precipitate by filtration, subsequently neutralizing the mixture of the white precipitate/THF with NaHCO₃, and evaporation of THF after filtration under reduced pressure. The yield was 75% and the product was used in the next synthetic step without further purification.

Synthesis of compound 4

A solution of compound 3 (9.00 g, 0.035 mol) in acetic acid (90 mL) was refluxed at 120–130°C under nitrogen atmosphere for 12 h. Then the reaction solution

was washed with water after the reaction solution cooled to room temperature. The resulting precipitate (compound 4) was collected by filtration and dried at 70 °C under reduced pressure for 24 h. The yield was 80%.

Synthesis of 4-benzimidazole aniline

A solution of compound 4 (4.78g, 0.02mol) and palladium on carbon (0.24) in Ethanol (50mL) was refluxed under nitrogen atmosphere, and then the solution of hydrazine hydrate (10.01g, 0.2mol) was added dropwise (3-5 seconds per drop, as slowly as possible). The reaction mixture was refluxed for 2h after the solution of hydrazine hydrate was completely added. After cooling, the reaction mixture was filtered and the filtrate was collected. The solution was maintained in a refrigerator overnight for crystallization. The resulting precipitate (4-benzimidazole aniline) was collected by filtration and dried at 70°C under reduced pressure for 24 h. The yield was 63%.

Synthesis of BIPN

To a 100mL, three-necked flask was added compound 2 (see body part) (3.44g, 0.0065mol) and dry NMP (25mL), and then 4-benzimidazole aniline (1.50g, 0.0065mol) was added. The reaction solution was heated to 50°C and stirred until solutes dissolved. The reaction was performed at 135–145°C for 6 h in NMP in the presence of an amount of toluene (25mL) to allow azeotropic distillation of the water formed as a by-product in the reaction. Then the reaction solution was washed with water after the reaction solution cooled to room temperature. The resulting precipitate (BIPN) was collected by filtration and washed by methanol. Then the precipitate was purified by activated carbon in a large amount of acetone solvent. The filtrate was collected by filtration and evaporation of acetone under reduced pressure. Yield: 0.66g, 14.1%. IR (KBr, cm⁻¹): 3366(N-H stretching), 2234(C=N stretching), 1778(C=O stretching), 1709(C=O stretching), 1378(C-N stretching). ¹H NMR (300 MHz, DMSO-d6, δ): 12.98 (s, H; NH), 8.31-8.28 (d, 2H; Ar H), 8.16-8.12 (d, H; Ar H), 8.10-8.06 (q, 2H, Ar H), 7.88 (s, H; Ar H), 7.63-7.61 (d, 9H; Ar H), 7.49-7.39 (d, H, Ar H), 7.42-7.39 (m, H; Ar H), 7.32 (s, H, Ar H), 7.29-7.27 (d, H, Ar H), 7.22-



Scheme S2 synthesis of 4-benzimidazole aniline.



Scheme S3 synthesis of BIPN monomer and polymers.



Figure S2 the TGA curve of PIPN monomer in nitrogen atmosphere

NOTE: The loss of weight (about 0.40%) around 156°C should be ascribed to the evaporation of solvents ((DMF, NMP or acetonitrile) or crystalline water. And since the boiling point of NMP is higher than 200°C, NMP cannot be the residual solvent which caused the loss of weight. Simultaneously, the TGA curve of PIPN monomer indicates that the NMP was completely removed. **Table S1** shows the probable calculated elemental analysis results which take the evaporation of solvents or crystalline water into account. As shown in **Table S1**, The calculated elemental analysis result which takes the evaporation of crystalline water into account is closest to the found value. Therefore, the loss of crystalline water is a rational explanation for the loss of weight around 156°C.

The formation of calculated elemental analysis can be described as following: $0.40\% \times E_S + 99.60\% \times E_P = E_c$

Where E_S are the calculated element percentages of the corresponding solvents or water, E_P are the calculated element percentages of the PIPN, and E_c are the calculated element percentages of the solvent-containing PIPN.

Element	Found	PIPN	Water*	DMF*	Acetonitrile*
C (%)	67.93	68.44	68.16	68.36	68.40
N (%)	10.56	10.64	10.60	10.68	10.73
H (%)	2.55	2.68	2.72	2.71	2.70

Table S1 The found and calculated results of elemental analysis.

*The calculated results of elemental analysis when the evaporation of solvents or crystalline water were taken into account.



Figure S3 DSC curves of the PIPN (a) temperature scan (10 °C/min) to 325°C, and isothermal curing at 325 °C, (b) temperature scan (10 °C/min) to 350°C. **NOTE:** The variation of heat flow at initial curing stage in **Figure S3a** is caused by the cease of heating process. This is confirmed by **Figure S3b**.

BIPN	NMP	DMF	THF	H_2SO_4
BIPN monomer	+	+	+	+
BIPN (post-				
cured polymer)				

Table S2 Solubility of PIPN monomer and polymer^a

^a Measured at a solid contents of 10mg/mL. Solubility: += soluble; +- = partly soluble; -- = insoluble.



Figure S4 Complex viscosity as a function of temperature for PIPN.

NOTE: The rapid decrease in viscosity on 130°C and 180°C were corresponding to the loss of free water and crystalline water, respectively.



Figure S5 Complex viscosity vs. time curve at 350°C for CNODPA.



Figure S6 Mulliken analysis on charge density of PIPN.



Figure S7 Mulliken analysis on charge density of BIPN.



Figure S8 Solid-state UV-Vis reflectance spectra of PIPN: (monomer) monomer, (600) cured at 325°C for 600min.



Figure S9 TGA and DTG curves of HIODPA (solid line) in nitrogen atmosphere and (dash dot line) in air.

NOTE: The TGA and DTG curves of HIODPA show that the oxidation of phthalimide group did not occurred before 500 °C, and decomposition peaks of HIODPA monomer might be ascribed to the evaporation or sublimation.



Figure S10 TGA and DTG curves of CNODPA (solid line) in nitrogen atmosphere and (dash dot line) in air.

NOTE: The TGA and DTG curves of CNODPA show that the oxidation of phthalonitrile group did not occurred before 500°C, and decomposition peaks of HIODPA monomer might be ascribed to the evaporation or sublimation.



Figure S11 TGA and DTG curves of BIPN (solid line) in nitrogen atmosphere and (dash dot line) in air.