

# Synthesis and Properties of New Polymerized Monomer Reactants Matrix Resins of Pyrrolone–Benzimidazole Copolymers Containing Pyridine Unit

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Received 18 March 2003; accepted 15 September 2003

**ABSTRACT:** A series of new polymerized monomer reactants (PMR) matrix resins of poly(pyrrolone-benzimidazole)s containing a pyridine unit (PPBP) were synthesized by polycondensation of monoethyl ester of *cis*-5-norbornene-endo-2,3-dicarboxylic acid, 2,6-diphenyl ester pyridinedicarboxylic acid or 3,5-diphenyl ester pyridinedicarboxylic acid, and diethyl ester of 4,4'-oxydiphthalic acid with 3,3'-diaminobenzidine in a mixing solution of anhydrous ethyl alcohol and *N*-methylpyrrolidone under given temperature and pressure conditions. The resulting resin solutions showed good solubility in polar organic solvents and stability at room temperature. The corresponding PPBP matrix resin, molded powder, and molded plate were prepared by undergoing amidation, imidization, cyclization, and crosslinking reactions when the reaction temperature

was increased from 80 to 350°C, successively; the crosslinking structure was formed by the reverse Diels–Alder reaction at 270–290°C under 50 MPa pressure (2.5–3.5 MPa displayed by the pressure meter). The chemical reactions and properties of the resulting PPBP were studied by means of FTIR, TGA, and DMA methods, and the results indicated that the kinds of PPBP materials retain excellent thermal stability and processability; when the initial decomposition temperature was above 620°C the  $T_g$  was at 413.5°C for 3,5-PPBP-20 molded plate. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3981–3990, 2004

**Key words:** heteroaromatic copolymers; high-performance polymer; PMR matrix resin; polycondensation; processing

## INTRODUCTION

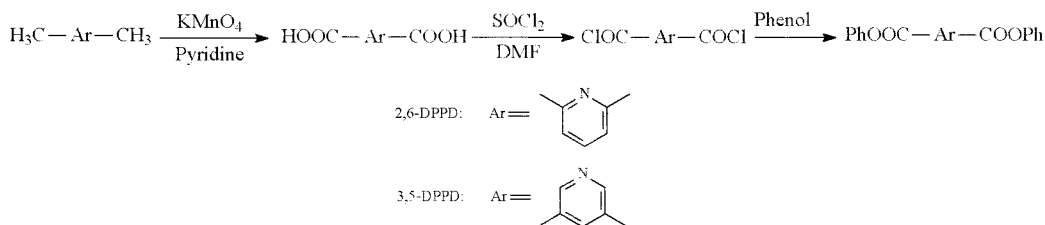
Polybenzimidazoles, that is, polymers with heteroaromatic structures, show a series of outstanding properties: excellent thermal stability, dielectric property, and hydrothermal resistance at high temperature, and both good solubility and good processability.<sup>1</sup> Therefore all kinds of polybenzimidazoles have been synthesized and their properties have been the focus of a number of studies.<sup>2–7</sup> Meanwhile, polyimidazopyrrolone (i.e., another heteroaromatic polymer abbreviated as polypyrrolone or pyrrolone) also has excellent mechanical strength, thermal and thermo-oxidative stabilities, dielectric and corrosion-resisting properties, and an irradiation-proof property at elevated temperatures<sup>8–10</sup>; however, the rigidity of polypyrrolone resulting from its ladder heteroaromatic backbone restricts its solubility in organic solvents, thus

retaining its poor processability, which has been the major limitation for the versatile application of this ladder polymer. Formation of semiladder structures<sup>9</sup> and introduction of a flexible segment in polypyrrolone backbones<sup>9–11</sup> have been found to be effective approaches for improving the solubility and processability of polypyrrolones. A number of studies have attested that the PMR method (*in situ* polymerization of monomer reactants) is an important method of obtaining heteroaromatic polymers with good solubility and processability.<sup>12–15</sup> In particular, PMR-type matrix resins of poly(benzimidazopyrrolone-imide)<sup>16,17</sup> and pyrrolone–benzimidazole copolymer<sup>18</sup> were successfully synthesized, both of which have shown superior processability and excellent thermal stability.

Considering the stability of the pyridine ring and its contribution to the thermal stability and retention of mechanical property of the resulting polymer at elevated temperature,<sup>19</sup> as well as the improvement of inner rotation of the ether bond for flexibility of the resulting heteroaromatic polymers, diphenyl ester-2,6-pyridinedicarboxylic acid (2,6-DPPD) and diphenyl ester-3,5-pyridinedicarboxylic acid (3,5-DPPD) were synthesized in this work (as shown in **Scheme 1**).

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Contract grant sponsor: Research Foundation of the State Key Laboratory of Engineering Plastics; contract grant number: SKLEP0061.



**Scheme 1** Synthesis of 2,6-DPPD and 3,5-DPPD.

Furthermore, the end-capped oligomers of poly(pyrrolone-benzimidazole) copolymers containing pyridine units (PPBP), that is, PMR-type of PPBP resin solutions, were prepared by copolycondensation of 2,6-DPPD or 3,5-DPPD, diethyl ester of 4,4'-oxydiphthalic acid (ODPE), and monoethyl ester of *cis*-5-norbornene-endo-2,3-dicarboxylic acid (NE) with 3,3'-diaminobenzidine (DAB) in a mixture of absolute alcohol/*N*-methylpyrrolidone (NMP) at room temperature. Then the corresponding PPBP matrix resin, molded powder, and molded plate were prepared by undergoing amidation, imidization, cyclization, and crosslinking reaction when reaction temperature was increased from 80 to 350°C; the crosslinking structure was formed by the reverse Diels–Alder reaction at 270–290°C under 50 MPa pressure (2.5–3.5 MPa displayed by the pressure meter). The chemical reactions in the copolycondensation of the monomeric reactant mixture and thermal process of the resulting polymers were studied by means of FTIR, TGA, and DMA methods.

## EXPERIMENTAL

### Reagents and solvents

3,3'-Diaminobenzidine (DAB, Acros Organics, 99%) was dried at 60°C under vacuum; *cis*-5-norbornene-endo-2,3-dicarboxylic anhydride (NA, 99%) was purchased from Nanxiang Chemical Co. (Shanghai) and

was sublimed before use; 4,4'-oxydiphthalic anhydride (ODPA) was dried at 150°C for 2 h under vacuum; *N*-methyl pyrrolidone (NMP) and anhydrous ethyl alcohol (EtOH) were purchased from Chemical Reagent Corp. (Beijing, China) and were distilled before use; 2,6-diphenyl ester pyridinedicarboxylic acid (2,6-DPPD) and 3,5-diphenyl ester pyridinedicarboxylic acid (3,5-DPPD), synthesized in our laboratory, were dried at 120°C for 2 h under vacuum.

### Instruments and characterization

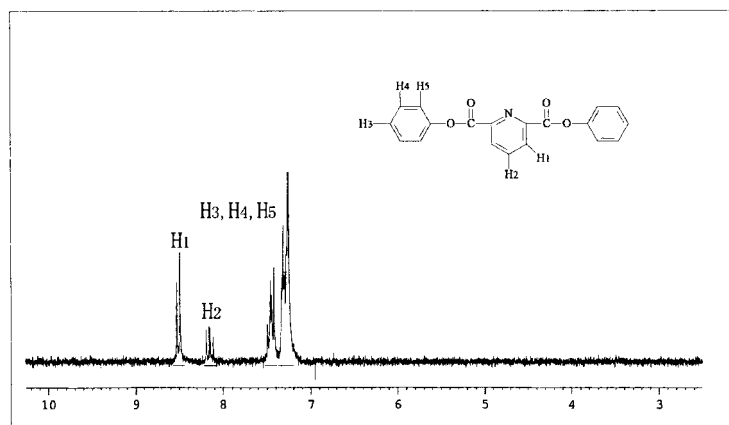
FTIR spectra were recorded on a Perkin–Elmer FTIR-2000 spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT). Thermogravimetric analysis (TGA) curves were carried out using a Perkin–Elmer 7 series thermal analysis system with a heating rate ( $\beta$ ) of 20°C/min under nitrogen, and dynamic mechanical analysis (DMA) was performed in nitrogen using a Perkin–Elmer 7 series thermal analysis system with a  $\beta$  of 5.0°C/min.

### Preparation of starting materials

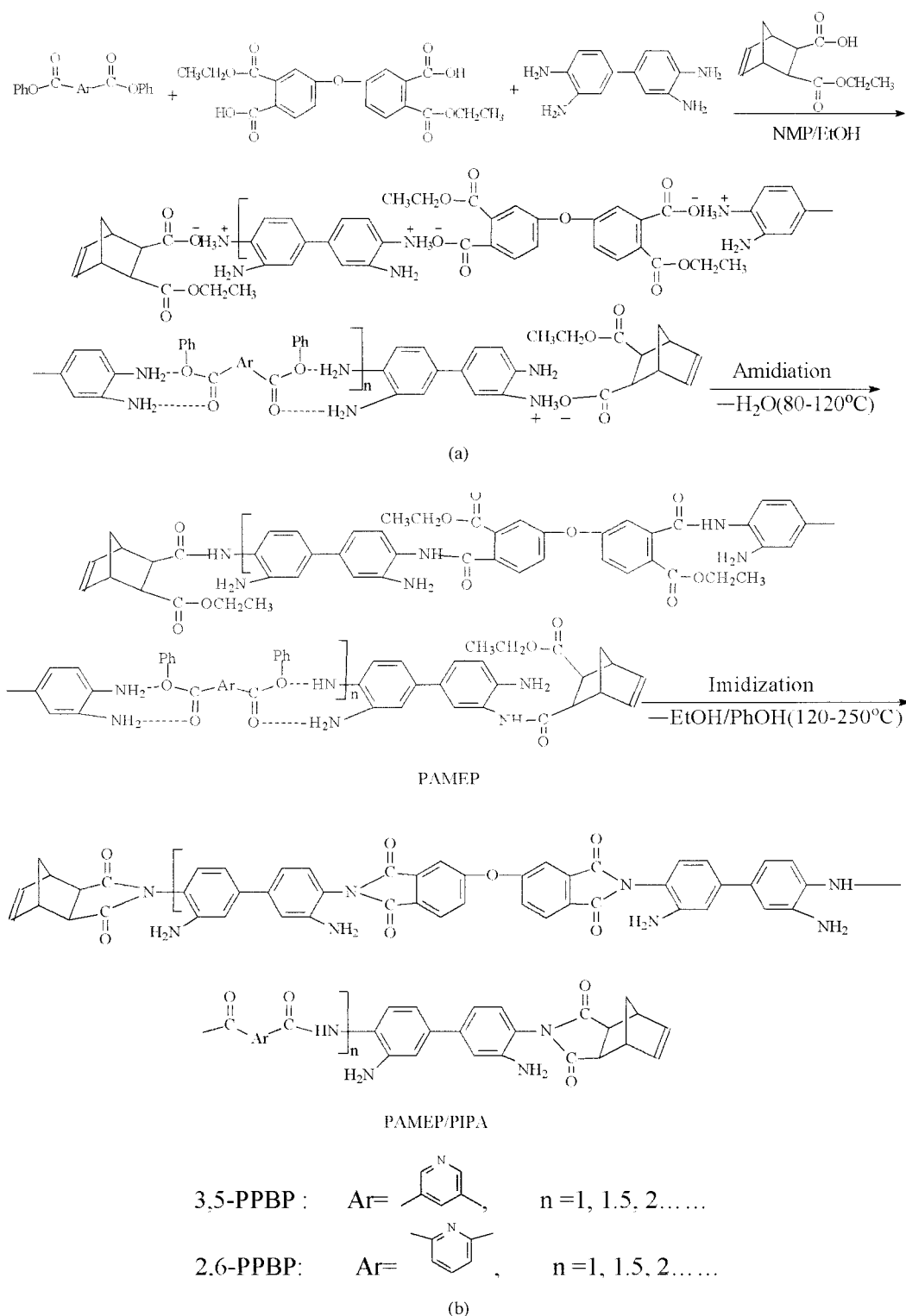
2,6-DPPD and 3,5-DPPD were synthesized according to **Scheme 1**.

### 2,6- or 3,5-Pyridinedicarboxylic acid

A mixture consisting of 84 mL of 2,6-dimethylpyridine (or 3,5-dimethylpyridine) and 84 mL of H<sub>2</sub>O (H<sub>2</sub>O/



**Figure 1** <sup>1</sup>H-NMR spectrum of 2,6-DPPD.



Scheme 2 Chemistry of PMR-type PPBP matrix resins.

pyridine, 2.2 L, v/v = 1:1) was charged to a 2-L three-neck round-bottom flask equipped with a reflux condenser, thermometer, and mechanical stirrer, then heated to 90°C; potassium permanganate (884 g) was then added in several portions, after which the mix-

ture was refluxed for 19 h. After cooling and filtering, the filtrate was distilled and neutralized with hydrochloric acid; the resulting white precipitate was recrystallized from acetic acid and vacuum dried to obtain 2,6-pyridine-dicarboxylic acid (mp > 300°C; yield:

95%) or 3,5-pyridinedicarboxylic acid (mp > 300°C; yield: 95%).

#### 2,6- or 3,5-Pyridinedicarboxylic acid chloride

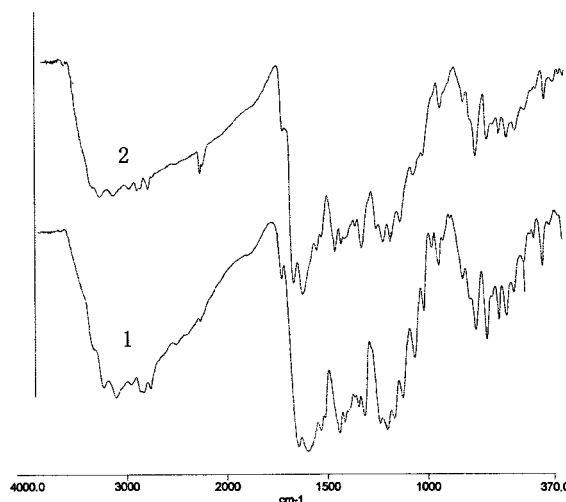
2,6-Pyridinedicarboxylic acid (45 g) (or 3,5-pyridinedicarboxylic acid), 300 mL of thionyl chloride, and 1 mL of DMF were mixed and refluxed for 2 h. The obtained solution was concentrated under vacuum, and the residue was mixed with ether, filtered off, washed with ether, and dried to yield 2,6-pyridinedicarboxylic acid chloride, recrystallized from chloroform (mp: 56.5°C, yield: 65.5%), or 3,5-pyridinedicarboxylic acid chloride, recrystallized from chloroform (yield: 85.5%).

#### 2,6- or 3,5-Diphenyl ester pyridinedicarboxylic acid

2,6-Pyridinedicarboxylic acid chloride (50 g) (or 3,5-pyridinedicarboxylic acid chloride), 80 g of phenol, and 10 mL of pyridine were refluxed under N<sub>2</sub> until free of HCl gas. The obtained reaction solution was distilled under vacuum to remove excess phenol, and yielded 2,6-diphenyl ester pyridinedicarboxylic acid or 3,5-diphenyl ester pyridinedicarboxylic acid, recrystallized from xylene. For 2,6-diphenyl ester pyridinedicarboxylic acid (mp > 300°C; yield: 92%), <sup>1</sup>H-NMR (220 MHz, CDCl<sub>3</sub>, δ) illustrates the presence of biphenyl protons (7.3–7.5 ppm, s, 10H) and protons in ring-substituted pyridine (8.1–8.2 ppm, t, 1H; 8.5 ppm, d, 2H), as shown in Figure 1, and mass spectrometry (MS) also indicates the molecular ionic peak of 2,6-pyridinedicarboxylic acid chloride (319 *m/e*). For 3,5-diphenyl ester pyridinedicarboxylic acid (mp = 182–184°C; yield: 75%), meanwhile, MS also indicates its molecular ionic peak at 319 *m/e*.

#### Preparation of PMR-type of poly(pyrrolone-benzimidazole)s containing pyridine units (PPBP)

ODPA (2.8227 g, 8.75 mmol) and ethyl alcohol (8.56 mL) were charged to a 25-mL flask fitted with magnetic stirrer and reflux condenser. The mixture was refluxed for 3.5 h with stirring to yield diethyl ester of ODPE solution; meanwhile, a monoethyl ester of NE solution was prepared by refluxing a mixture of NA (1.9153 g, 11.67 mmol) and ethyl alcohol (6.07 mL) for 3.5 h. A solution of DAB (5.0000 g, 23.34 mmol) and 2,6-DPPD (2.7911 g, 8.75 mmol) dissolved in 22.3 mL of NMP/EtOH (v/v = 1 : 1) was charged to a 100-mL three-neck flask fitted with a stirrer, N<sub>2</sub> inlet, and gas outlet, after which the above ODPE and NE solutions were successively added. The mixture was stirred for 5–6 h at room temperature to yield a homogeneous matrix resin solution with solid content of 40%. The NE : DPPD : ODPE : DAB mole ratio used was 2.00 :



**Figure 2** FTIR spectra of 2,6-PPBP-20 molding powders: (1) cured at 70°C for 8 h; (2) cured at 150°C for 2 h.

$m : m : (2m + 1)$ , where  $m$  is the theoretical degree of polymerization to form an oligomer.

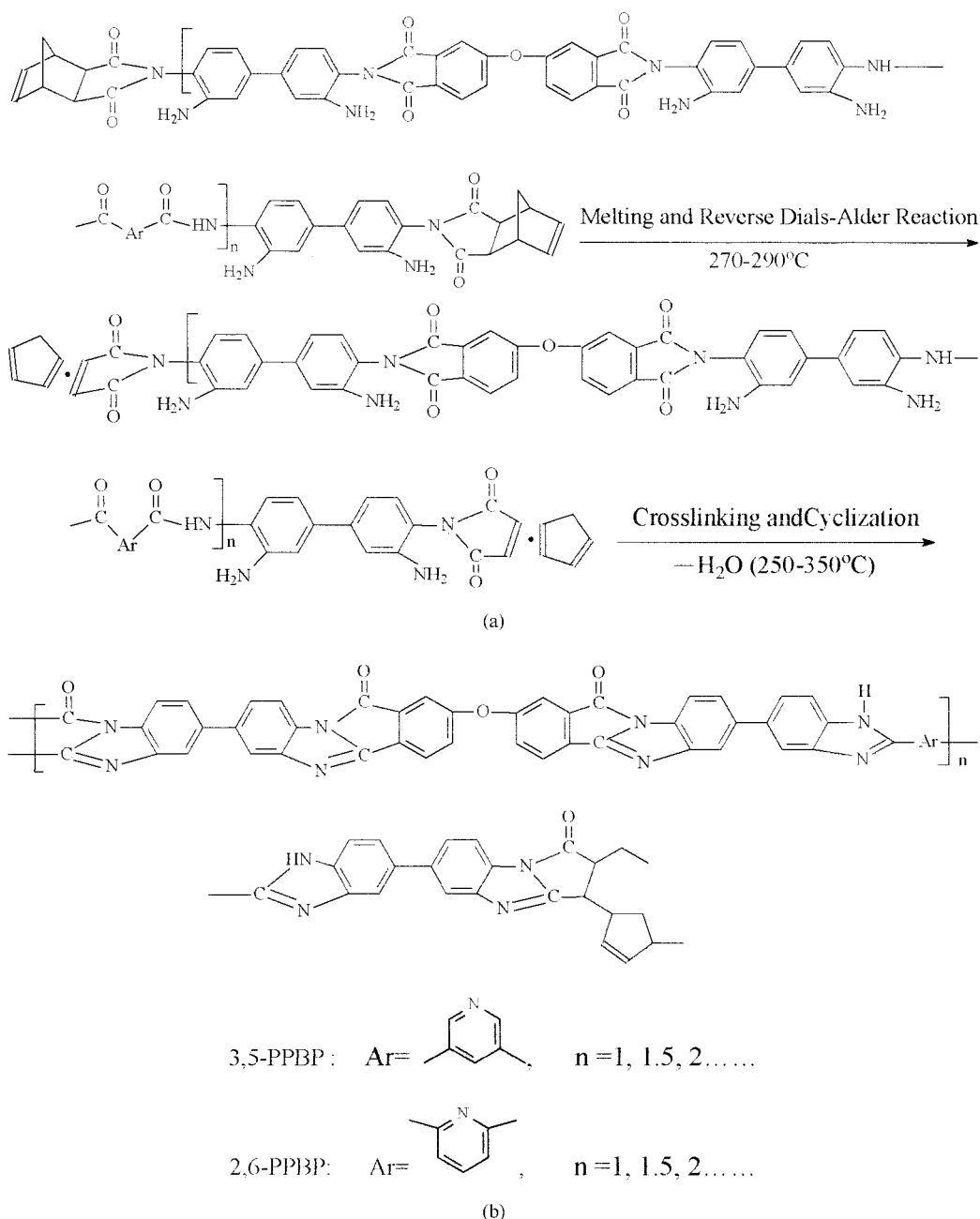
When  $m$  was set at 2, 3, and 4, respectively, the obtained oligomers had corresponding calculated theoretical molecular weights of 1500, 2000, and 2500; the resulting matrix resins containing units of pyrrolone and benzimidazole were designated as 2,6-PPBP-15, 2,6-PPBP-20, and 2,6-PPBP-25 in this work. 3,5-PPBP-15, 3,5-PPBP-20, and 3,5-PPBP-25 were prepared by the same procedure as outlined above using 3,5-diphenyl ester pyridinedicarboxylic acid.

#### Synthesis of PPBP neat molding resin powders

The above PPBI matrix resin solutions were evaporated with a rotary evaporator at 60°C to remove some of the lower boiling point solvents, and the viscous liquids obtained were dried at 70°C for 8 h under vacuum to produce the corresponding solid resins. The neat molding resin powders of PPBP-15, PPBI-20, and PPBP-25 were thermally baked to obtain the corresponding solid resins at 150°C for 2.0 h and 200°C for 0.5 h, respectively.

#### Thermal curing of molding resin powders to molded resin plates

PPBP molding powder (5 g) was added at room temperature to a  $\phi$  50-mm die that had been preheated at 200°C, after which the die was heated and 2.5–3.5 MPa of pressure was applied when the die temperature reached 270°C; meanwhile, the pressure was released and reapplied three times at 6-min intervals to remove all traces of volatile material evolved. Under the pressure, the die was heated to 320°C for 15 min and kept at that temperature for 3 h; the temperature was increased to 340°C for 2 h, after which the pressure was



**Scheme 3** Chemical and thermal process in preparation of PMR-type PPBP matrix resin.

released when the die was cooled to 200°C under pressure. The molded resin plate was removed from the die, which was placed in an oven and heated in nitrogen to 340°C at a heating rate of 35°C/h for postcuring treatment.

## RESULTS AND DISCUSSION

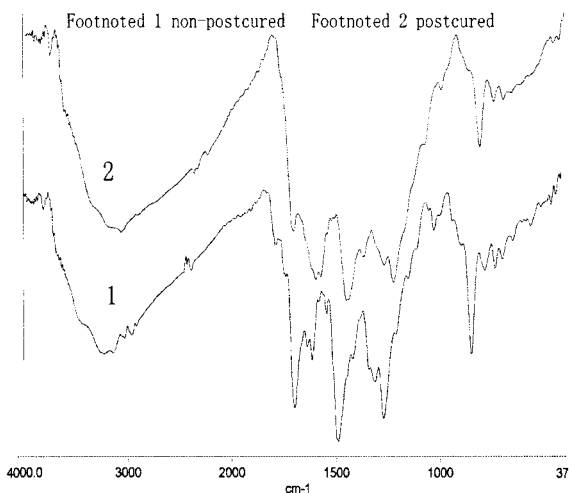
### Chemistry of PPBP matrix resins

PPBP matrix resins were prepared by using the PMR process in this study, as shown in **Scheme 2**. Reactions of the monomer solutions in NMP/EtOH were carried

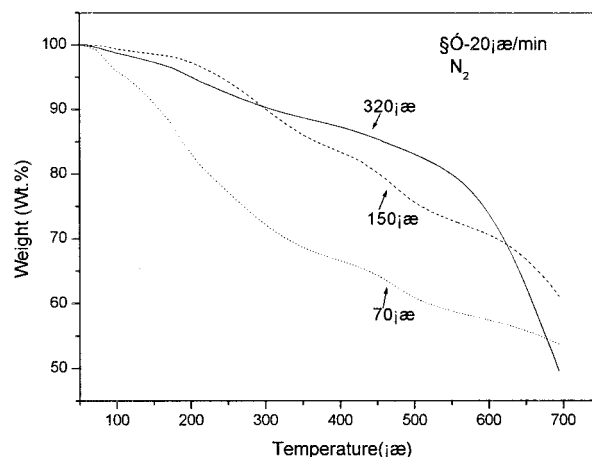
out and yielded a matrix resin solution containing 40% solids at room temperature; meanwhile, a carboxylic acid-amine saltlike oligomer that was end-capped with NE was formed by the copolycondensation of aromatic tetramine with diethyl ester of aromatic dianhydride, diphenyl ester of 2,6-pyridinedicarboxylic acid or diphenyl ester of 3,5-pyridinedicarboxylic acid and NE at room temperature, whereas the carboxylic acid-amine saltlike oligomer retained the designed molecular weight of 1500 ( $n = 2$ , PPBP-15), 2000 ( $n = 3$ , PPBP-20), or 2500 ( $n = 4$ , PPBP-25), respectively. In other words, the molecular weight of the oligomer

is also equal to that of the corresponding molding powder. The resulting matrix resin solution showed a high degree of solubility in polar organic solvents and good stability at room temperature; it was a homogeneous solution with an absolute viscosity of 0.10–0.12 Pa s<sup>-1</sup>, and no precipitation, gelation, or phase separation were observed when it was stored at room temperature. The matrix resin solution was heated to remove some of the lower boiling point solvents, including byproducts at 80–250°C, and a neat molding resin powder (i.e., PPBP matrix resin) was formed at the same time.

According to **Scheme 2**, a series of chemical reactions undergo changes of thermal curing conditions during the process of forming PPBP matrix resin.<sup>1,20</sup> When the curing temperature was at 80–120°C, the amidation occurred initially and the amide bond (–OC–NH–) in the matrix resin was obtained by evolving a mole of H<sub>2</sub>O from the carboxylic acid-amine salt segment. Thus the end-capped polyamide with *o*-substituted ethyl ester and pyridine ring (PAMEP) was obtained, after which PAMEP was passed through a thermal cyclization/imidization reaction at 120–250°C and would be transformed into an end-capped polymer with aromatic imide and pyridine amide units (PIPA). Moreover, it would retain an appropriate fluidity of the melt because its molecular weight was controlled. FTIR spectra of 2,6-PPBP-20 matrix resin obtained under different baking conditions are shown in Figure 2, where FTIR spectra (1) and (2) illustrate the matrix resins cured at 70°C for 8 h and at 150°C for 2 h under vacuum, respectively. The absorptions located at 3452, 3333, and 3207 cm<sup>-1</sup> ( $\nu_{\text{N-H}}$ ) gradually decreased in intensity as the baking temperature increased from 70 to 150°C, indicating that the aromatic amine group was altered into an amide link and the latter was further altered into an



**Figure 3** FTIR spectra of 2,6-PPBP-20 molding plate with and without postcuring at 340°C.

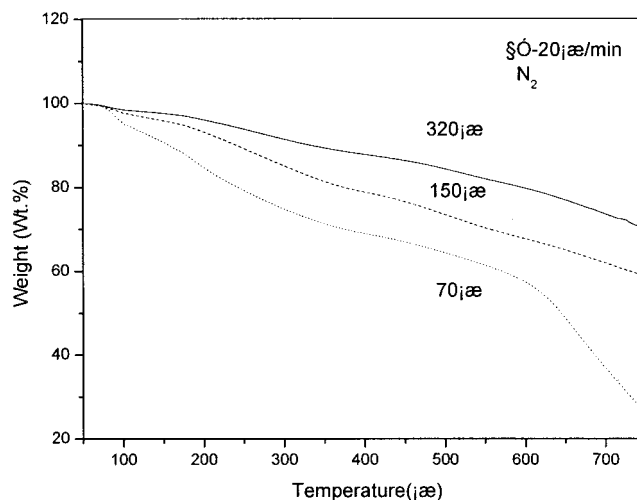


**Figure 4** TGA thermogram of 2,6-PPBP-20 molding powders (70°C for 8 h; 150°C for 2 h) and molding plate (320°C for 3 h).

imide link as the temperature increased. The absorptions located at 1650–1735 cm<sup>-1</sup> ( $\nu_{\text{CO}}$ ), attributed to the amide (–OC–NH–) and ester (–OC–O–) bands in PIAP, decreased slightly in intensity as the baking temperature increased, whereas absorption of the imide band at 1780 cm<sup>-1</sup> gradually increased in intensity as the baking temperature increased. Analysis of the FTIR spectra in Figure 2 is in accord with the reaction mechanism shown in **Scheme 2**.

### Preparation of molded PPBP resins

The molding powder based on PIAP (i.e., PPBP molding powder) was thermally cured under pressure by molding compression technique to yield crosslinked molded materials that consisted of pyrrolone and



**Figure 5** TGA thermogram of 3,5-PPBP-20 molding powders (70°C for 8 h; 150°C for 2 h) and molding plate (320°C for 3 h).

TABLE I  
TGA Parameters of PPBP Molding Powders and Molded Plates<sup>a</sup>

Sample	<i>n</i>	Tempt. cured (°C)	<i>T<sub>d</sub></i> (°C)		<i>T<sub>5</sub></i> (°C)		<i>T<sub>10</sub></i> (°C)	
			Mpo	Mpl	Mpo	Mpl	Mpo	Mpl
2,6-PPBP-15	1.0	70	650	—	138	—	179	—
		150	645	—	283	—	341	—
2,6-PPBP-20	1.5	70	694	—	112	—	157	—
		150	651	—	240	—	301	—
		340	—	590	—	201	—	309
2,6-PPBP-25	2.0	70	694	—	119	—	167	—
		340	—	608	—	281	—	474
3,5-PPBP-15	1.0	70	695	—	128	—	171	—
		150	660	—	286	—	346	—
3,5-PPBP-20	1.5	340	—	744	—	265	—	465
		70	611	—	101	—	156	—
		150	638	—	171	—	241	—
3,5-PPBP-25	2.0	340	—	634	—	225	—	333
		70	694	—	101	—	157	—
		340	—	575	—	225	—	340

<sup>a</sup> Mpo, molded powder; Mpl, molded plate; *T<sub>d</sub>*, initial decomposition temperature; *T<sub>5</sub>*, temperature at 5% of weight loss; *T<sub>10</sub>*, temperature at 10% of weight loss; Tempt. cured, temperature cured of the PPBP resin.

benzimidazole structures formed by complete crosslinking and cyclization reaction under 50 MPa pressure (2.5–3.5 MPa displayed by the pressure meter) at 270–290°C (i.e., PPBP molding plate shown by reaction in **Scheme 3**). For preparation of a PPBP molding plate, an adequate molten flow was required to ensure that the molten fluid would fill out the die. There are two converse processes affecting the flow behavior of the molten fluid in thermal processing<sup>15,16</sup>: (1) melting of the molding powder with low molecular weight to yield a flowing fluid and (2) chemical crosslinking and chain extending caused by the reaction of end caps. The key factors in thermal processing were the die temperature and applied pressure, which were controlled carefully to produce a molded plate with high quality. Generally, the processing temperature started at 250–290°C and completed at 340–350°C; a pressure of 2–4 MPa was used. To prepare a PPBP molding plate under optimal conditions, temperatures < 280°C could not produce molten fluid resin with proper flowing character to fill the whole space in the die, whereas temperatures > 290°C would accelerate the crosslinking of the reactive end caps. The choice of a suitable pressure to apply was difficult to decide, given that inadequate pressure application could cause either a spillover of molten resin from the die or a molded material with poor quality. Consequently, PPBP molded material with high quality was prepared by thermally curing the molding powder at 270–340°C under 2.5–3.5 MPa pressure for 3–4 h; furthermore, the resulting PPBP material was postcured at 350°C in nitrogen for 10 h to achieve both crosslinking and cyclization reactions. Finally, the spectra presented in Figure 3 show the pyrrolone band at 1759 cm<sup>-1</sup> [see spectrum (1)] and its relative inten-

sity was increased after the material was postcured by the above postcuring procedure [see spectrum (2)]. The results of molding compression and corresponding FTIR analysis demonstrate that the resulting PMR-type of PPBP matrix resin were characterized by good processibility.

#### Thermal properties of PPBP molded resins

Thermostability, an outstanding characteristic of heteroaromatic polymers, as mentioned earlier,<sup>1,20</sup> was thus the thermostability of the resulting PPBP was studied by means of TGA method. Thermograms of the molded powder cured at different temperatures

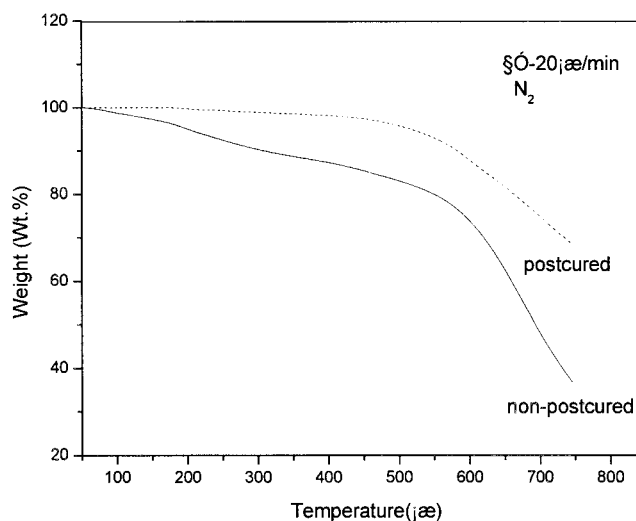
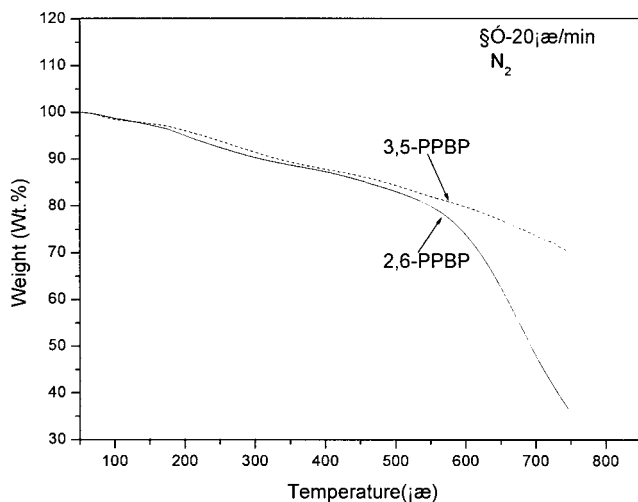


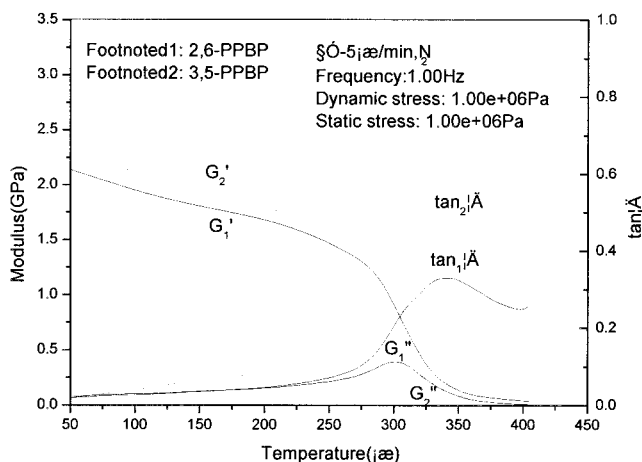
Figure 6 Effect of postcuring on TGA curves of 2,6-PPBP-20 molded plate.

are illustrated by TGA curves presented in Figure 4 and Figure 5. Results from Figure 4 show that the initial decomposition temperature of the resulting 2,6-PPBP-20 increased with the increase of curing temperature; for example, the molding powder cured at 70°C undergoes a 30% weight loss at 300°C, whereas that cured at 150°C had a 5% weight loss at the same temperature, similar to that of its molded plate cured at 300–340°C. However, the thermograms of 3,5-PPBP-20 in Figure 5 illustrate better thermostabilities than those of 2,6-PPBP-20: weight losses at 300°C of the molding powder cured at 70°C, one cured at 150°C, and the molded plate cured at 320°C were 25, 10, and 5%, respectively. The TGA parameters from Figures 4 and 5 are listed in Table I. For the PMR PPBP molding powder, the corresponding  $T_5$  and  $T_{10}$  values generally increased the curing temperature increased; the molecular weight of the designed oligomer and the variety of monomer based on pyridine also affected their  $T_5$ ,  $T_{10}$ , and  $T_d$  values in varying degrees. Although the effect of the molecular weight and variety of monomer on the TGA parameters would be greater than that of the curing temperature, these variables result in the effect of molecular weight and structure of the oligomer on its molten fluid when processing molded plate.

Figure 6 shows TGA thermograms of 2,6-PPBP-20 molded plate with or without postcuring at 350°C/10 h in nitrogen. Compared with a freshly molded plate, the  $T_{10}$  value of a postcured molded plate increased to 600°C. Its  $T_5$  value would also be enhanced to 500°C, that is to say, the postcuring process would cause its  $T_5$  and  $T_{10}$  values to increase to 300°C, respectively, and no weight loss was observed from 100 to 450°C. The weight loss of the non-postcured sample from 100 to 450°C was attributed to the volatile material evolved during thermal treatment. Figure 7 illustrates



**Figure 7** TGA curves of 2,6-PPBP-20 and 3,5-PPBP-20 molded plates postcured.

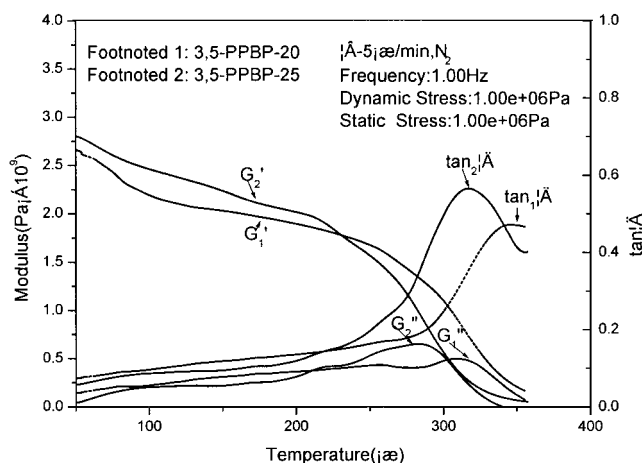


**Figure 8** DMA spectra of PPBP-20 molded plate obtained by using 2,6-DPPD and 3,5-DPPD.

a difference of the thermostability of postcured 2,6-PPBP-20 and 3,5-PPBP-20 molded plates: the postcured 3,5-PPBP-20 molded plate showed 25% weight loss at 750°C, although the weight loss of the postcured 2,6-PPBP-20 molded plate reached 60% at the same temperature. This may be attributable to the structural symmetrization of PMR PPBP material obtained by using 3,5-diphenyl ester pyridinedicarboxylic acid as one of monomers.

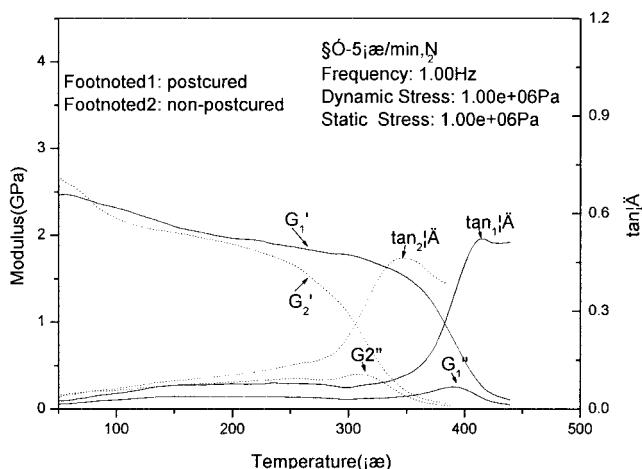
#### Dynamic mechanical properties of the PPBP molded plate

Figure 8 shows the DMA spectra of PPBP-20 molded plate obtained by using 2,6-DPPD and 3,5-DPPD. The results in Figure 8 show that the PPBP molded plate using 2,6-DPPD and 3,5-DPPD as aromatic monomer basically has similar dynamic mechanical curves, although the molded plate obtained by 3,5-DPPD is characterized by better dynamic mechanical proper-



**Figure 9** DMA spectra of 3,5-PPBP molded plate.





**Figure 10** Effect of postcuring process on dynamic mechanical properties of 3,5-PPBP-20 molded plates (postcured at 340°C for 10 h, in N<sub>2</sub>).

ties than those of the plate obtained by 2,6-DPPD. This agrees with the above-mentioned characteristics of their thermal properties. Effects of molecular weight of the designed oligomer, using 3,5-DPPD as one of monomers, on dynamic mechanical properties of corresponding PPBP molded plates are illustrated by DMA curves presented in Figure 9. For the 3,5-PPBP-25 molded plate, its dynamic mechanical properties are inferior to those of 3,5-PPBP-20, which is attributed to the better melting fluid of 3,5-PPBP-20 resin with lower molecular weight during the processing of molded plates. The postcuring process plays an important role in improving the properties of PMR heteroaromatic polymers.<sup>14-18</sup> Its effect on 3,5-PPBP-20 molded plate is shown in Figure 10. According to Figure 10, the onset temperature of the reduction of storage modulus ( $G'$ ) was at 250°C for the molded plate without postcuring, whereas that of the postcured molded plate was increased to 350°C (i.e., the postcured 3,5-PPBP-20 molded plate showed an almost constant storage modulus until the temperature reached 350°C). In particular, its  $\tan \delta$  value was remarkably enhanced and the peak temperature measured in its  $\tan \delta$  curve was at 413.5°C, defined as the

glass-transition temperature ( $T_g$ ) of the materials<sup>16</sup>; meanwhile, the  $T_g$  value of 3,5-PPBP-25 molded plate was at 389.13°C. The DMA results presented in Figures 8, 9, and 10 demonstrate that the monomer molar ratio based on the PPBP-20 molded plate would be suitable for the preparation of PMR-type matrix resins consisting of pyrrolone, benzimidazole, and pyridine structures. The postcuring process still promotes an obvious improvement in the thermal and mechanical properties of the resulting PMR matrix resin containing pyrrolone structure,<sup>16-18</sup> as well as the PPBP matrix resin using 3,5-DPPD. This is explained by the fact that the pyridine monomer has better thermostability and dynamic mechanical property than those of monomers that use 2,6-DPPD. The measured DMA parameters of the molded plate of 3,5-PPBP in Figure 10, listed in Table II, also indicate this kind of significant effect.

**CONCLUSIONS**

This work has shown that a new series of PMR-type of poly(pyrrolone-benzimidazole) copolymers containing a pyridine moiety (i.e., PPBP matrix resins) were synthesized by polycondensation of 2,6-DPPD or 3,5-DPPD and ODPE with DAB in a mixing solution of anhydrous ethyl alcohol and *N*-methylpyrrolidone under given temperature and pressure conditions, using NE as an end-capped reagent. The experimental results indicate that the monomer molar ratio, the kind of monomer, temperature and pressure conditions, as well as polymerization conditions affect the properties of the obtained PPBP matrix resins. Solutions of the resulting PPBP matrix resins showed good solubility in polar organic solvents and stability at room temperature, whereas the related molding powder exhibited ease of processability, and the resulting PPBP molded plates were characterized by excellent thermal stability and dynamic mechanical property. Furthermore, the monomer molar ratio based on the PPBP-20 molded plate would be suitable for the preparation of PMR-type matrix resins consisting of pyrrolone, benzimidazole, and pyridine structures. The postcuring process still promotes an obvious improve-

**TABLE II**  
DMA Data of 3,5-PPBP Molded Plate

Sample	Retention of $G'$ (%) <sup>a</sup>				Loss modulus, $T_p$ (°C) <sup>b</sup>		Loss tangent, $T_p$ (°C) <sup>b</sup>	
	300°C		350°C		Non	P.C.	Non	P.C.
	Non <sup>c</sup>	P.C. <sup>b,c</sup>	Non	P.C.				
PPBP-20	42	72.6	9.4	64.5	309.5	391.1	345.3	413.5
PPBP-25	21.4	75.3	5.4	47.3	282.7	389.1	316.3	389.1

<sup>a</sup> Retention of storage modulus ( $G'$ ).  
<sup>b</sup> Temperature at the peak of curve.  
<sup>c</sup> Non, non-postcured; P.C., postcured.

ment in thermal and mechanical properties of the resulting PMR matrix resin containing pyrrolone structure, as well as PPBP matrix resin using 3,5-DPPD. This is explained by the fact that the pyridine monomer has better thermostability and dynamic mechanical property than those of monomers that use 2,6-DPPD. Consequently, the 3,5-PPBP-20 molded plate showed that the initial decomposition temperature could be over 620°C and its  $T_g$  would reach 413.5°C, found from the peak temperature in its  $\tan \delta$  curve.

The authors acknowledge the financial support from the Research Foundation of the State Key Laboratory of Engineering Plastics (SKLEP0061).

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