

## Syntheses and Properties of Polyamides Containing Indolocarbazole Moiety in the Main Chain

Shusei Nakama<sup>1</sup>, Kazuki Yamashita<sup>1</sup>, Masaji Akimoto<sup>2</sup>,  
Masuki Kawamoto<sup>3</sup> and Yu Nagase<sup>1,2\*</sup>

<sup>1</sup>Graduate School of Engineering, <sup>2</sup>Graduate School of Science and Technology, Tokai University,

4-1-1 Kitakaname, Hiratsuka, Kanagawa, 259-1292, Japan,

<sup>3</sup>RIKEN, 2-1 Hirosawa, Wako, Saitama, 351-0198, Japan

\*Tel: +81-463-58-1211, Fax: +81-463-51-2012, E-mail: yunagase@tokai-u.jp

In this study, we have attempted to prepare novel aromatic polyamides containing indolo[3,2-*b*]carbazole (INC) moiety in the main chain. For this purpose, the synthesis of an aromatic dicarboxyl compound containing INC moiety was carried out. Novel aromatic polyamides containing INC moiety in the main chain were prepared by the polycondensation of the dicarboxyl INC monomer with the four kinds of diamine monomers. The obtained polymers were soluble in aprotic polar solvents such as *N,N*-dimethyl acetamide and *N*-methyl-2-pyrrolidone. According to the thermal gravimetric analysis, the obtained polyamides exhibited the relatively high thermal stability and the high char yield nearly 50 % at 1000 °C in the thermal degradation. Furthermore, it was found from the evaluation of the photonic property that the UV-Vis absorption and fluorescence spectra of these polyamides showed the similar tendency of the photonic property of INC.

**Key words:** indolocarbazole / aromatic polyamide / thermal property / photoluminescence

### 1. INTRODUCTION

Organic  $\pi$ -conjugated compounds have been known to show interesting optical and electrical properties and extensively studied in several applications such as memory devices, light-emitting diodes, transistors and solar cells [1-4]. Among them, we have focused on indolo[3,2-*b*]carbazole (INC), which possesses a low HOMO level and showed the blue fluorescence by the irradiation of UV light and exhibited the highly thermal stability. In addition, INC has been known to show a strong blue emission by the irradiation of UV light. In recent years, there have been some reports on the preparation and characterization of INC derivatives [5,6]. For example, Li et al. synthesized a new class of polyindolocarbazole via the coupling polymerization of 4,10-dichloroindolo[3,2-*b*]carbazole derivatives, a film of which could be manufactured by spin coating and exhibited the mobility of  $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in a field-effect transistor [7]. However, only few studies have been reported on the synthesis of INC-containing polymers.

In our previous study, the preparations of several polymers containing INC moiety in the main chain or side chain were investigated and the thermal and photonic properties of these polymers were estimated [8-11]. 1-(4-vinylbenzyl)-7-octylindolo[3,2-*b*]carbazole (VINC-C8), and the copolymers of VINC-C8 with styrene or methyl methacrylate were prepared by a radical polymerization. Then, it was found that the obtained copolymers showed the amorphous state and the thermal stability of the copolymers increased as the INC content increased [8]. Therefore, it is considered that the INC moiety would be effective to increase the thermal stability of polymer materials.

In this study, we have attempted to prepare novel aromatic polyamides containing INC moiety in the main chain as a thermally stable polymer material. For this purpose, the synthesis of a novel INC derivative containing dicarboxyl groups was carried out. Thereafter, the polycondensations of dicarboxylated INC monomer with aromatic diamine compounds were conducted, and the

thermal and photonic properties of the obtained polyamides were investigated to reveal the thermal and photonic performance.

### 2. EXPERIMENTAL

#### 2.1 Materials

1,7-dioctylindolo[3,2-*b*]carbazole (**1**) was prepared according to the procedure described in our previous paper [8]. Chloroacetyl chloride and potassium hypochlorite aqueous solution (Cl content: 5 - 7 %) were purchased from Wako Pure Chemical, Co. Ltd., and used as received. Aluminum chloride ( $\text{AlCl}_3$ ), pyridine (Py) and triphenyl phosphite (TPP) were purchased from Tokyo Chemical Industry, Co. Ltd., and used without further purification.

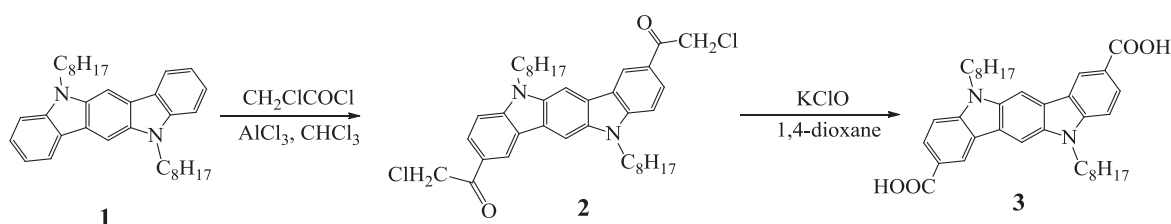
#### 2.2 Synthesis of 1,7-dioctyl-3,9-di(chloroacetyl)indolo[3,2-*b*]carbazole (**2**)

Under an argon atmosphere, chloroacetyl chloride (2.34 g, 20.8 mmol) was added slowly to a suspension of  $\text{AlCl}_3$  (2.77 g, 20.8 mmol) in 21.5 mL of chloroform, and the mixture was stirred at 0 °C for 1 h. 1,7-dioctylindolo[3,2-*b*]carbazole (4.17 g, 8.67 mmol) was then added slowly to the mixture, and it was refluxed for 6 h. After cooling, the reaction mixture was poured into iced water and the mixture was extracted with chloroform. The combined organic phase was washed with brine solution, dried over  $\text{Na}_2\text{SO}_4$ , and filtered. The product was purified by recrystallization with chloroform and hexane to obtain 3.43 g of compound **2** as a pale yellow powder. Yield: 62.2 %.

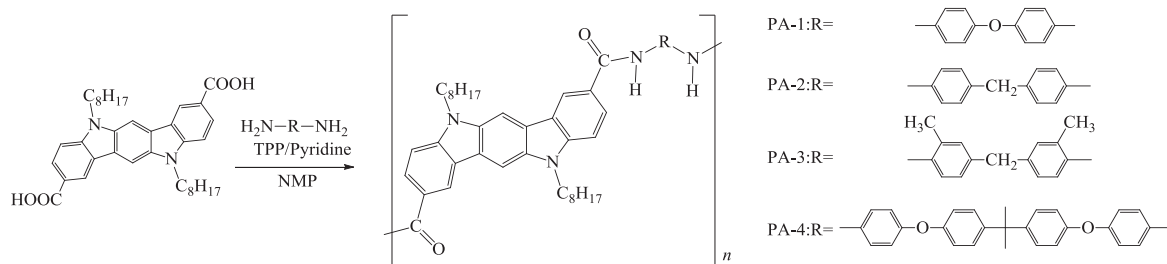
<sup>1</sup>H-NMR,  $\delta$  (DMSO-*d*<sub>6</sub>, ppm): 0.75 - 0.77 (6H, m), 1.16 - 1.31 (20H, m), 1.89 (4H, m), 4.56 (4H, t,  $J = 6.83 \text{ Hz}$ ), 5.30 (4H, s), 7.73 (2H, d,  $J = 8.78 \text{ Hz}$ ), 8.12 (2H, d,  $J = 8.78 \text{ Hz}$ ), 8.62 (2H, s), 9.07 (2H, s).

IR,  $\nu$  (KBr,  $\text{cm}^{-1}$ ): 2943, 2855, 1674 (C=O), 1609, 1512, 1470, 1320, 1240, 1115, 845, 679.

#### 2.3 Synthesis of 1,7-dioctyl-3,9-dicaroxylindolo[3,2-*b*]carbazole (**3**)



Scheme 1 Synthesis of INC-containing dicarboxyl monomer.



Scheme 2 Syntheses of INC-containing polyamides.

Under an argon atmosphere, compound **2** (2.00 g, 2.05 mmol) was suspended in 100 ml of 1,4-dioxane, and potassium hypochlorite (40.0 g, 30.5 mmol) was added. After the mixture was stirred at 50 °C for 15 min, the reaction mixture was poured into an excess solution of sodium hydrogen sulfite dissolved in water, and the product was collected by filtration. Then, the product was washed with water, methanol and tetrahydrofuran (THF) to obtain 1.17 g of compound **3** as a white powder. Yield: 67.2 %  
<sup>1</sup>H-NMR,  $\delta$  (DMSO-*d*<sub>6</sub>, ppm): 0.76 - 0.79 (6H, m), 1.17 - 1.35 (20H, m), 1.84 - 1.89 (4H, m), 4.52 (4H, t, *J* = 6.83 Hz), 7.64 (2H, d, *J* = 10.2 Hz), 8.05 (2H, d, *J* = 7.32 Hz), 8.60 (2H, s), 8.96 (2H, s).  
 IR,  $\nu$  (KBr, cm<sup>-1</sup>): 3051 (OH), 2924, 2851, 1651 (C=O), 1612, 1508, 1470, 1416, 1327, 1227, 1153, 833, 741.

#### 2.4 Polycondensation (PA-1 – PA-4)

Under an argon atmosphere, compound **3** (0.25 g, 0.44 mmol) and 4,4'-diaminodiphenyl ether (0.080 g, 0.44 mmol) were dissolved in 2.6 ml of *N*-methylpyrrolidone (NMP), and TPP (0.27 g, 0.88 mmol) and Py (0.07 g, 0.88 mmol) were added to this solution. Then, the mixture was stirred at 100 °C for 24 h. The reaction mixture was poured into an excess amount of methanol to precipitate the polymer. The reprecipitation was carried out by pouring the NMP solution into excess methanol to obtain 0.53 g of PA-1 as a yellow powder. Yield: 49.0 %.

IR,  $\nu$  (KBr, cm<sup>-1</sup>): 3429 (N-H), 3051, 2924, 2851, 1651 (C=O), 1612, 1497, 1470, 1404, 1315, 1219, 1170, 1123, 833.

In the above reaction, 4,4'-diaminodiphenylmethane, 4,4'-diamino-3,3'-dimethyldiphenylmethane and 4,4'-diamino-2,2-di(4-phenoxyphenyl)propane were used instead of 4,4'-diaminodiphenyl ether to obtain PA-2, PA-3 and PA-4, respectively.

PA-2 (66.1 % yield): IR,  $\nu$  (KBr, cm<sup>-1</sup>): 2924, 2850, 1651 (C=O), 1612, 1575, 1510, 1469, 1373, 1301, 1230, 1171, 1120, 1087.

PA-3 (46.9 % yield): IR,  $\nu$  (KBr, cm<sup>-1</sup>): 2923, 2850, 1651 (C=O), 1612, 1573, 1508, 1469, 1373, 1303, 1230, 1172, 1122, 1087.

PA-4 (19.1 % yield): IR,  $\nu$  (KBr, cm<sup>-1</sup>): 2924, 2850, 1651 (C=O), 1612, 1575, 1499, 1469, 1408, 1314, 1222, 1171, 1120, 1065.

#### 2.5 Polycondensation (PA-r)

Under an argon atmosphere, terephthalic acid chloride (1.00 g, 6.01 mmol) and 4,4'-diamino-3,3'-dimethyldiphenylmethane (1.36 g, 6.01 mmol) were dissolved in 10.4 ml of NMP, and TPP (3.73 g, 12.0 mmol) and Py (0.95 g, 12.0 mmol) were added to this solution. Then, the mixture was stirred at 100 °C for 24 h. The reaction mixture was poured into an excess amount of methanol to obtain 2.03 g of PA-r as a white powder. Yield: 87.5 %.

#### 2.5 Characterizations

<sup>1</sup>H-NMR spectroscopy was conducted with a BRUKER AVANCE-500 NMR spectrometer (500 MHz). IR spectra were recorded with a Shimadzu FTIR-8400 spectrometer. The molecular weights of polymers were estimated with the two gel permeation chromatography (GPC) systems. One of them is a Tosoh HLC-8320 equipped with three columns of TSK gels, Super Multipore HZ-H, using THF as an eluent. The second is a Tosoh GPC system equipped with four columns of TSK gels, Multipore HXL-M, and RI detector of RI-8010 using *N,N*-dimethyl formamide (DMF) as an eluent. The average molecular weights were calibrated based on polystyrene standards.

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were carried out on Seiko Instruments DSC-6200 and TG/DTA-6200, respectively, at a heating rate of 10 °C/min under a nitrogen atmosphere. Ultraviolet-visible adsorption and photoluminescence spectra were conducted with a JASCO V-550 and SHIMADZU RF-5300PC, respectively.

## RESULTS AND DISCUSSION

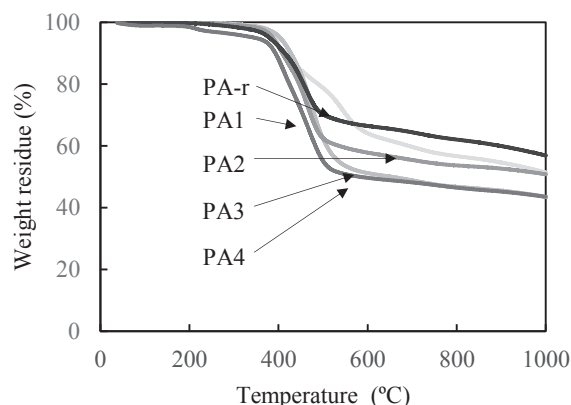
### 3.1 Preparation of a monomer and polymers

The synthetic routes of a monomer and polymers are shown in Scheme 1 and 2, and the molecular weights of the obtained polyamides are listed in Table 1. The solubility of polymers is summarized in Table 2.

As shown in Scheme 1, compound **3** was synthesized by using Friedel-Crafts reaction of compound **2** with chloroacetyl chloride. Then, a novel dicarboxylated INC monomer was synthesized by using haloform reaction of compound **2**. As shown in Scheme 2, polyamides containing INC were successfully prepared from the dicarboxylated INC monomer with the four kinds of diamine monomers by using TPP/Py catalyst as a polycondensation reagent. On the other hand, a reference polyamide, PA-r, was prepared by the similar polycondensation of terephthaloyl chloride with 4,4'-diamino-3,3'-dimethyldiphenylmethane

The molecular weights of the obtained polyamides were determined by GPC using THF and DMF. The weight-average molecular weights of obtained polymers were over  $10^4$ . The molecular weights of PA-1 and PA-r could not be determined, because they were insoluble in both of DMF and THF.

The obtained INC-containing polyamides were soluble in aprotic polar solvents, such as *N,N*-dimethyl acetamide (DMAc) and NMP. In particular, PA-3 was soluble in DMF, and PA-4 was soluble in DMF and THF. On the other hand, PA-r was insoluble in all solvents. Thus, INC-containing polyamides showed superior solubility as compared with PA-r, which would be due to the long alkyl chain at the *N*-position of INC component. Especially, PA-3 and PA-4 showed the improved solubility, due to the bulky structure of the diamine monomers.



**Figure 1** Thermal gravimetric analysis curves of the polymers at 10 °C per min in N<sub>2</sub> flow.

### 3.2 Thermal properties of the polymers

The thermal properties of the obtained polyamides are also shown in Table 1. The thermal properties of the polymers were evaluated by TGA and DSC. By the DSC measurements, no transition temperature of these polymers was observed up to 200 °C. According to the TGA curves shown in Figure 1, the 10 % decomposition temperature,  $T_{d10}$ , of these polymers were nearly 400 °C. Interestingly, the decomposition temperatures of PA-3 and PA-r were almost same. In addition, the char yields of these polymers were in the range of 42 – 57 %. Although INC-containing polyamides possessed long alkyl chains in the each repeating unit, they exhibited the relatively high heat resistance and char yield.

Table 1 The molecular weights and the thermal property of the polymers.

code	$M_w \times 10^{-3}$	$M_w/M_n$	$T_{d10}$ (°C)	Char Yield (wt. %) (d)
PA-1	—	—	397	42.1
PA-2	12.1 (a)	1.31 (a)	413	56.8
PA-3	19.9 (a)	1.58 (a)	408	50.8
PA-4	15.1 (b)	1.42 (b)	423	43.5
PA-r	—	—	408	51.4

- a) Number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights were determined by gel permeation chromatography (GPC) using DMF as eluent.  
 b)  $M_n$  and  $M_w$  molecular weights were determined by GPC using THF as eluent.  
 d) The temperature at 10% weight loss,  $T_{d10}$ , was determined by TG-DTA.  
 e) Residual weight percentage at 1000 °C in nitrogen.

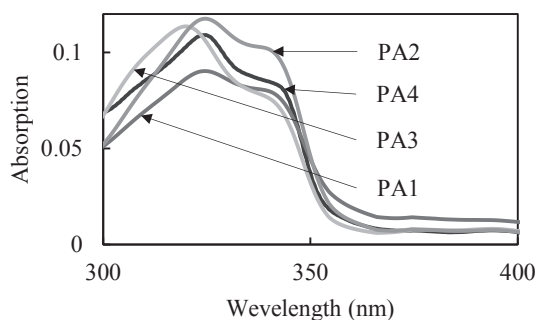
Table 2 Solubility of polymers.

code	Hexane	THF	Chloroform	DMSO	DMF	DMAc	NMP
PA-1	×	×	×	×	×	○	○
PA-2	×	×	×	×	△	○	○
PA-3	×	×	×	×	○	○	○
PA-4	×	○	×	△	○	○	○
PA-r	×	×	×	×	×	×	×

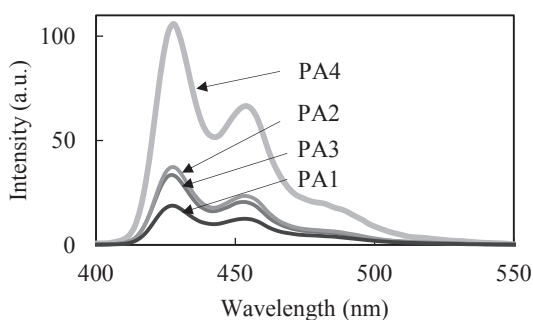
Abbreviations: DMSO; dimethyl sulfoxide

Symbols: ○; soluble, △; partially soluble, ×; insoluble.

The concentration of the solubility test was 1.0 wt% in each solvent.



**Figure 2** UV-Vis absorption spectra of the solutions of PA1-4, the concentration of which was  $1 \times 10^{-6}$  mol/L in NMP.



**Figure 3** Photoluminescence spectra of the solutions of PA1-4, the concentration of which was  $1 \times 10^{-6}$  mol/L in NMP. Excitation wavelength was 321nm for PA1 and 324nm for PA2, PA3 and PA4.

### 3.3 Photonic properties of the polymers

The photonic properties of the polymers were evaluated in the solutions dissolved in NMP. The UV-Vis absorption spectra of the polymer solutions are shown in Figure 2. The maximum absorption was observed at 321 - 324 nm.

The photoluminescence spectra in the polymer solutions are shown in Figure 3. The maximum intensity of photoluminescence was observed at 427 - 428 nm. Thus, INC-containing polyamides showed photonic properties derived from INC component, and the structures of diamine comonomers didn't affect on the photonic properties. Interestingly, PA-4 which possessed the long bisphenol-A unit in the diamine component exhibited the highest intensity of emission. Akimoto *et al.* described that the photoluminescence intensity of INC containing copolymer solutions increased as the INC content decreased, because of the concentration quenching caused by the condensation of intermolecular interactions derived from INC components [8, 10, 11]. Namely, it was suggested that the photoluminescence intensity of INC-containing polyamides would be affected by weight percentage of INC content. The calculated values of INC content of PA-1, PA-2, PA-3 and PA-4 were 72.29%, 72.98%, 70.12%, 56.83%, respectively. Therefore, the INC content of PA-4 was the lowest among these polyamides, where the contents of PA-1, PA-2 and PA-3 were almost same. Consequently, it was suggested that the longer distance between INC components and the lower INC density would be effective to increase the intensity of emission in such polyamide system.

### 4. CONCLUSION

Aromatic polyamides containing INC moiety in the main chain were successfully prepared by polycondensation. The obtained polymers exhibited a good solubility and relatively high thermal stability. Especially, the solubility of PA-4 was better than others, which was soluble even in THF, and PA-4 exhibited the highest intensity of fluorescence. It was also found that the UV-Vis absorption and fluorescence spectra of these polyamides showed the similar tendency of the photonic property of INC. On the other hand, these INC-containing polyamides showed the relatively high char yield in the thermal degradation, therefore, these polymers are expected for the application as a precursor of carbon alloy.

### REFERENCES

- [1] W. Tang, L. Ke, L. Tan, T. Lin, T. Kietzke, Z. Chen, *Macromolecules*, **40**, 6164-6171 (2007).
- [2] G. Liou, S. Hsiao, H. Chen, *J. Mater. Chem.*, **16**, 1831-1842 (2006).
- [3] S. Park, K. Kim, J. C. Kim, W. Kwon, D. M. Kim, M. Ree, *Polymer*, **52**, 2170-2179 (2011).
- [4] O. Liu, M. Wang, C. Li, E. Jin, C. Du, J. Zhou, L. Li, Z. Bo, *Macromol. Rapid Commun.*, **33**, 2097-2102 (2012).
- [5] H. Jiang, H. Zhao, K. K. Zhang, X. Chen, C. Kloc, W. Hu, *Adv. Mater.*, **23**, 5075-5080 (2011).
- [6] Q. Peng, X. Liu, Y. Qin, J. Xu, M. Li, L. Dai, *J. Mater. Chem.*, **21**, 7714-7722 (2011).
- [7] Li, Y., Wu, Y. & Ong, B. S. *Macromolecules*, **39**, 6521-6527 (2006).
- [8] M. Akimoto, T. Kawano, Y. Iwasawa, Y. Takahashi, K. Yamashita, M. Kawamoto, Y. Nagase, *Polym J*, **43**, 959-965 (2011).
- [9] M. Akimoto, T. Kawano, Y. Nagase, M. Kawamoto, T. Wada, *Trans. Mater. Res. Soc. Jpn.*, **34**, 141-144 (2009).
- [10] M. Akimoto, Y. Takahashi, K. Yamashita, M. Kawamoto, Y. Nagase, *Kobunshi Ronbunshu*, **69**, 283-290 (2012).
- [11] K. Yamashita, M. Akimoto, M. Kawamoto, Y. Nagase, *Trans. Mater. Res. Soc. Jpn.*, **38**, 253-255 (2013).

(Received July 4, 2014; Accepted August 22, 2014)