

Synthesis of poly(acryl amide) containing indolo[3,2-*b*]carbazole moiety in the side chain

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Poly(acryl amide)s containing INC moiety in the side chain were prepared by radical polymerization using 6-(4-acryloylamino benzoylamino)-1,7-dioctylindolo[3,2-*b*]carbazole (AAINC) as a novel monomer. The obtained polymers exhibited the good solubility and the high thermal stability, where T_g and T_d5 of the homopolymer of AAINC were over 200°C and 400°C, respectively. In addition, T_g of copolymers of AAINC with *N*-(*p*-tolyl)acrylamide increased as the INC content increased. It was found that the HOMO, LUMO levels and the energy gap of AAINC and polymers showed the similar values as those of INC, and the UV-Vis absorption and fluorescence spectra of these polymers were also similar to the tendency of photonic property of INC. Furthermore, the fluorescence intensity of these polymers was higher than that of the monomer, AAINC. Especially, the copolymer having 5% INC content showed the higher fluorescence intensity than the copolymers having the higher INC content.

Key words: indolo[3,2-*b*]carbazole / poly(acryl amide) / thermal property / photonic property

1. INTRODUCTION

Organic π -conjugated compounds have been known to show interesting optical and electrical properties and extensively studied for 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 exhibits the blue fluorescence by the irradiation of UV light and 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 cm² V⁻¹ 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 [8-12]. 1-(4-vinylbenzyl)-7-octylindolo[3,2-*b*]carbazole (VINC-C8), and the copolymers of VINC-C8 with styrene or MMA were prepared by radical polymerizations, and the thermal and photonic properties were investigated. 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, the synthesis of a new pendant type poly(acryl amide) containing INC moiety was carried out, and the characterization of the obtained polymers was investigated. Interestingly, it was found that amino-INC, 6-amino-1,7-dioctylindolo[3,2-*b*]carbazole (**2**), was selectively produced, when the reduction of 6,12-dinitro-1,7-dioctylindolo[3,2-*b*]carbazole (**1**) was carried out with

hydrogen in the presence of Pd catalyst, as shown in Scheme 1. The reactivity of **2** is thought to be useful for the synthesis of poly(acryl amide) containing INC moiety. At first, we attempted to synthesize 6-acryloylamino-INC from **2** as an acryl amide monomer, however, a radical polymerization of 6-acryloylamino-INC did not proceed. It would be due to that the steric hindrance caused by long alkyl groups at *N*- position of INC would prevent the addition polymerization. Therefore, as a novel monomer, the spacer was introduced between INC unit and polymerizable group to avoid the steric hindrance to obtain AAINC in Scheme 1. Then, the desired homopolymer PAAINC and copolymer CPAAINC were obtained by radical polymerization using AAINC. The thermal and photonic properties of the obtained compounds were investigated.

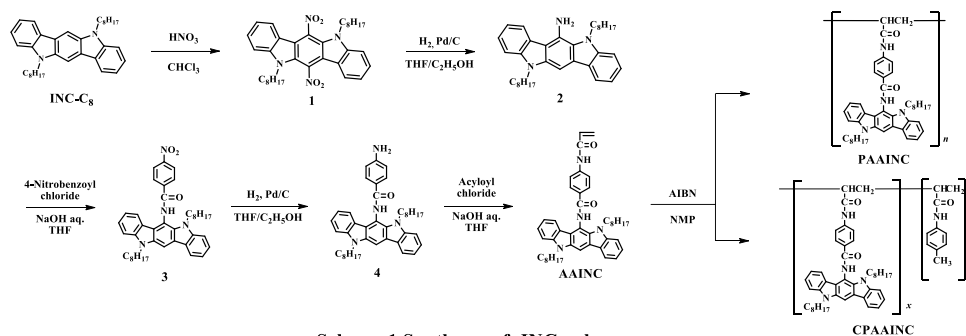
2. EXPERIMENTAL

2.1 Materials

1,7-dioctylindolo[3,2-*b*]carbazole (INC-C₈) was prepared according to the procedure described in our previous paper [8]. Nitric acid, triethylamine, 5% Pd on charcoal powder were purchased from Wako Pure Chemical, Co. Ltd., and used as received. 4-Nitrobenzoyl chloride, acryloyl chloride, 2,2'-azobis(isobutyronitrile) (AIBN) were purchased from Tokyo Chemical Industry, Co. Ltd. AIBN was purified by recrystallization from ethanol. Other chemical reagents were used without further purification.

2.2 Synthesis of 6,12-dinitro-1,7-dioctylindole[3,2-*b*]carbazole (**1**)

Under an argon atmosphere, INC-C₈ (6.50 g, 13.5 mmol) was dissolved in 40 mL of CHCl₃. Nitric acid (2.96 g, 32.5 mmol) was added slowly to the mixture, and it was stirred at room temperature overnight. The crude product was extracted with chloroform, washed with brine solution, and purified by column chromatography on silica gel with hexane and chloroform to obtain compound **1** as a red solid. Yield : 93.6 %



Scheme 1 Syntheses of INC polymers.

¹H-NMR (500 MHz, DMSO-*d*₆, ppm): 0.85 (6H, t, *J* = 7.9 Hz), 1.10-1.45 (20H, m), 1.77 (4H, quin, *J* = 7.9 Hz), 4.23 (4H, t, *J* = 8.0 Hz), 7.31 (2H, t, *J* = 7.6 Hz), 7.49 (2H, d, *J* = 8.2 Hz), 7.62 (2H, t, *J* = 7.6 Hz), 7.90 (2H, d, *J* = 8.3 Hz).

2.3 Synthesis of 6-amino-1,7-dioctylindolo[3,2-*b*]carbazole (2)

Compound 1 (2.00 g, 3.51 mmol) and triethylamine (18 mL) was dissolved in 18 mL of THF and 7.8 mL of ethanol. 5% Pd on charcoal powder (0.373 g, 0.176 mmol) was added to the solution. The mixture was degassed under reduced pressure at -78 °C, and the vessel was filled with hydrogen gas. After stirring at 40 °C for 24 h, the charcoal powder was filtered off, and the solvents and triethylamine were evaporated under reduced pressure. Then, the product was washed with hexane to obtain compound 3 as a yellow powder. Yield: 91.9 %

¹H-NMR (500 MHz, DMSO-*d*₆, ppm): 0.79 (6H, t, *J* = 7.2 Hz), 1.10-1.23 (16H, m), 1.27-1.39 (4H, m), 1.66 (2H, quin, *J* = 7.3 Hz), 1.82 (2H, quin, *J* = 7.3 Hz), 4.40 (2H, t, *J* = 7.1 Hz), 4.63 (2H, t, *J* = 7.1 Hz), 5.40 (2H, s), 7.17 (2H, dt, *J* = 8.0, 7.8 Hz), 7.44 (2H, dt, *J* = 8.0, 7.8 Hz), 7.49 (2H, d, *J* = 8.1 Hz), 7.55 (2H, d, *J* = 8.1 Hz), 7.61 (1H, s), 8.16 (1H, d, *J* = 7.7 Hz), 8.36 (2H, d, *J* = 7.7 Hz).

2.4 Synthesis of 6-(4-nitrobenzoylamino)-1,7-dioctylindolo[3,2-*b*]carbazole (3)

Compound 2 (3.50 g, 7.06 mmol) and triethylamine (1.43 g, 14.1 mmol) were dissolved in 65 mL of THF. 4-Nitrobenzoyl chloride (5.24 g, 28.2 mmol) was added slowly to the mixtures at 0 °C. The reaction mixtures were stirred at 40 °C for 30 min. The crude product was extracted with chloroform, washed with brine solution, and purified by recrystallization with THF and hexane to obtain compound 4 as an orange solid. Yield: 70.4 %

¹H-NMR (500 MHz, DMSO-*d*₆, ppm): 0.76 (3H, t, *J* = 7.2 Hz), 0.81 (3H, t, *J* = 7.2 Hz), 1.10 (8H, m), 1.13 (4H, m), 1.25 (8H, m), 1.35 (4H, m), 1.67-1.76 (2H, m), 1.87 (2H, quin, *J* = 7.1 Hz), 4.40-4.63 (4H, m), 7.02 (1H, t, *J* = 7.5 Hz), 7.23 (1H, t, *J* = 7.5 Hz), 7.45 (1H, t, *J* = 7.6 Hz), 7.48 (1H, t, *J* = 7.6 Hz), 7.58 (1H, d, *J* = 8.5 Hz), 7.61 (1H, d, *J* = 8.5 Hz), 7.90 (1H, d, *J* = 7.9 Hz), 8.36 (1H, d, *J* = 7.9 Hz), 8.46 (1H, s), 8.55 (4H, d, *J* = 2.8 Hz), 11.32 (1H, s). IR, ν (KBr, cm⁻¹): 3280, 2923, 2854, 1651, 1600, 1525, 1342, 738.

2.5 Synthesis of 6-(4-aminobenzoylamino)-1,7-dioctylindolo[3,2-*b*]carbazole (4)

Compound 3 (2.10 g, 32.6 mmol) was dissolved in 126 mL of THF and 5 mL of ethanol. 5% Pd on charcoal powder (0.347 g, 1.63 mmol) was added to the solution. The mixture was degassed under reduced pressure at -78 °C, and the vessel was filled with hydrogen gas. After stirring at 40 °C for 24 h, the charcoal powder was filtered

off, and the solvents were evaporated under reduced pressure. Then, the product was washed with hexane to obtain compound 4 as a yellow powder. Yield: 70.4%

¹H-NMR (500 MHz, DMSO-*d*₆, ppm): 0.70-0.89 (6H, m), 1.10 (8H, m), 1.21 (8H, m), 1.33 (4H, m), 1.67-1.76 (2H, m), 1.87 (2H, quin, *J* = 7.1 Hz), 4.40-4.63 (4H, m), 5.90 (2H, s), 6.70 (2H, d, *J* = 8.6 Hz), 7.08 (1H, t, *J* = 7.5 Hz), 7.28 (1H, t, *J* = 7.5 Hz), 7.45 (1H, t, *J* = 7.5 Hz), 7.48 (1H, t, *J* = 7.5 Hz), 7.59 (1H, d, *J* = 8.4 Hz), 7.61 (1H, d, *J* = 8.4 Hz), 8.01 (1H, d, *J* = 7.7 Hz), 8.02 (2H, d, *J* = 8.5 Hz), 8.38 (1H, d, *J* = 7.7 Hz), 8.41 (1H, s), 10.42 (1H, s). IR, ν (KBr, cm⁻¹): 3382, 3224, 2923, 2852, 1606, 1325, 736.

2.6 Synthesis of 6-(4-acryloylamino benzoylamino)-1,7-dioctylindolo[3,2-*b*]carbazole (AAINC)

Compound 4 (2.00 g, 3.25 mmol) and NaOH aq. (0.260 g, 6.50 mmol) were dissolved in 85 mL of THF. Acryloyl chloride (0.394 mL, 4.88 mmol) was added slowly to the mixtures at 0 °C. The reaction mixtures were stirred at room temperature for 15 min. The crude product was extracted with chloroform, washed with brine solution, and purified by column chromatography on silica gel with hexane and chloroform to obtain AAINC as a yellow solid. Yield: 96.8%

¹H-NMR (500 MHz, DMSO-*d*₆, ppm): 0.70-0.89 (6H, m), 1.10 (6H, m), 1.13 (4H, q, *J* = 7.0 Hz), 1.21 (6H, m), 1.36 (4H, m), 1.67-1.76 (2H, m), 1.87 (2H, quin, *J* = 7.0 Hz), 4.40-4.63 (4H, m), 5.85 (1H, dd, *J* = 9.9, 1.8 Hz), 6.38 (1H, dd, *J* = 17.0, 1.8 Hz), 6.56 (1H, dd, *J* = 17.0, 10.2 Hz), 7.08 (1H, t, *J* = 7.5 Hz), 7.28 (1H, t, *J* = 7.5 Hz), 7.42 (1H, t, *J* = 7.5 Hz), 7.48 (1H, t, *J* = 7.5 Hz), 7.58 (1H, d, *J* = 7.3 Hz), 7.59 (1H, d, *J* = 7.3 Hz), 7.93 (1H, d, *J* = 8.6 Hz), 7.95 (2H, d, *J* = 8.7 Hz), 8.26 (2H, d, *J* = 8.7 Hz), 8.34 (1H, d, *J* = 8.6 Hz), 8.40 (1H, s), 10.55 (1H, s), 10.8 (1H, s). IR, ν (KBr, cm⁻¹): 3274, 2923, 2852, 1651, 1598, 979, 738.

2.7 Preparations of homopolymer (PAAINC) and copolymers (CPAAINC)

The radical polymerizations were carried out for AAINC and the mixtures of AAINC and *N*-(*p*-tolyl)acryl amide (TAA) to prepare a homopolymer and copolymers with different compositions of monomer units. The typical procedure of copolymerization is described below.

Under an argon atmosphere, AAINC (1.46 g, 3.01 mmol), TAA (5.70 g, 56.9 mmol) and AIBN (713 mg, 0.430 mmol) were dissolved in 60 mL of *N*-methylpyrrolidone (NMP). Then, the mixtures were stirred at 90 °C for 48 h, and the reaction mixtures were poured into an excess amount of methanol to precipitate the polymer. The obtained polymer was filtered and purified by reprecipitation from its NMP solution to excess methanol. Finally, the product was dried *in vacuo* to afford CPAAINC-5 as a pale yellow solid.

Table 1 Compositions, molecular weights and thermal property of polymers.

Code	Feed ratio of AAINC/TAA (mol%)	Composition, x/y^a (mol %)	$10^{-3} M_n^b$	$10^{-3} M_w^b$	M_w/M_n	T_g^c (°C)	$T_{d_5}^d$ (°C)
PAAINC	100/0	100/0	5.31	6.86	1.29	202	405
CPAAINC-80	80/20	60/40	6.40	7.00	1.09	197	394
CPAAINC-66	66/34	77/23	6.14	8.72	1.42	175	-
CPAAINC-30	30/70	43/57	5.32	9.04	1.70	168	366
CPAAINC-10	10/90	16/84	8.77	24.7	2.82	159	351
CPAAINC-5	5/95	5/95	14.0	29.2	2.09	159	340

a) The composition, x/y , was calculated from the ratio of peak intensities in $^1\text{H-NMR}$ spectra of copolymers.

b) Number and weight-average molecular weights (M_n and M_w) were determined by GPC based on polystyrene standards (eluent: THF).

c) T_g was determined by DSC at $10^\circ\text{C min}^{-1}$ on the second heating scan.

d) T_{d_5} was determined by TG-DTA at $10^\circ\text{C min}^{-1}$.

$^1\text{H-NMR}$ of CPAAINC-5: (500 MHz, DMSO- d_6 , ppm): 0.70-0.89 (m), 1.00-1.40 (m), 1.60-1.90 (m), 2.15 (m), 4.20-4.73 (m), 6.85 (m), 7.03 (m), 7.21 (m), 7.35 (m), 7.42-7.59 (m), 7.88 (m), 8.10 (m), 8.31 (m), 8.38 (m), 9.55 (m), 10.3-10.6 (m), 10.7 (m).

$^1\text{H-NMR}$ of PAAINC: (500 MHz, DMSO- d_6 , ppm): 0.70-0.89 (6H, m), 1.00-1.40 (20H, m), 1.60-1.90 (4H, m), 4.20-4.73 (4H, m), 7.03 (1H, m), 7.21 (1H, m), 7.42-7.59 (4H, m), 7.91 (3H, m), 8.30 (3H, m), 8.39 (1H, m), 10.3-10.6 (1H, m), 10.7 (1H, m).

2.8 Characterizations

$^1\text{H-NMR}$ 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 gel permeation chromatography (GPC) systems, which is a Tosoh HLC-8320 equipped with three columns of TSK gels, Super Multipore HZ-H, using THF 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 spectra with energy gaps and photoluminescence spectra were conducted with JEOL V-550 and SHIMADZU FP-6500PC, respectively, where the energy gaps were determined by diffuse reflectance spectra. HOMO levels were investigated by photo-electron spectrometer MODEL AC-3. LUMO levels were calculated from these results of the HOMO levels and the energy gaps.

3. RESULTS AND DISCUSSION

3.1 Preparation and thermal properties of polymers

The synthetic routes of a monomer and polymers are shown in Scheme 1. In the molecular design of the monomer, AAINC, the phenylene amide spacer was introduced between INC unit and acryl amide group to avoid the steric hindrance by the long alkyl groups of INC unit in the polymerization. In the copolymerization, the composition, x/y , was controlled by changing the monomer ratio of AAINC and TAA to obtain five copolymers with different compositions. The compositions were calculated from the ratio of peak intensities of the amide protons of AAINC at 10.7 ppm and TAA at 9.55 ppm in $^1\text{H-NMR}$ spectra. The compositions and the molecular weights of polymers are listed in Table 1. It was revealed that molecular weights of the copolymers increased with the decrease of INC content. It would be because the steric hindrance was reduced in the copolymerization by the decrease of INC content. The obtained monomer and polymers were soluble in chloroform, THF, *N,N*-

Table 2 Electrochemical, photophysical properties of INC- C_8 , AAINC and PAAINC.

Code	HOMO ^{a)} (eV)	LUMO (eV)	E_g^b (eV)	λ_{abs}^c (nm)	λ_{PL}^d (nm)
INC- C_8	-5.44	-2.68	2.76	340	427
AAINC	-5.48	-2.65	2.83	340	430
PAAINC	-5.35	-2.51	2.84	340	430

a) HOMO level was determined by photo-electron spectroscopy.

b) Energy gap (E_g) was determined by diffuse reflectance spectrum.

c) The maximum absorption peak in UV-vis absorption spectra.

d) The maximum emission peak in fluorescence spectra.

dimethylformamide (DMF) and NMP, but insoluble in alcohols such as methanol and ethanol.

Table 1 also shows the thermal properties, T_g and T_{d_5} , of the obtained polymers. It was found from DSC measurement that T_g of PAAINC was observed at around 200°C , and T_g 's of the copolymers increased with the increase of INC content. It would be due to the strong intermolecular interaction derived from amide bond and the planer structure of INC. Moreover, the 5% decomposition temperatures, T_{d_5} , of PAAINC was estimated by TGA at around 400°C . Therefore, these INC-containing polymers exhibited relatively high thermal stability, although the main chain consisted of aliphatic chain.

3.2 Photonic properties of the polymers

The UV-Vis absorption and photoluminescence spectra of AAINC, PAAINC and CPAAINC_s are shown in Figure 1. As shown in Figure 1(a) and (b), the maximum absorption and the photoluminescence peak of the monomer and the polymers were observed at 340 nm and 430 nm, respectively. In addition, the electrochemical and photonic properties of INC- C_8 , AAINC, PAAINC are summarized in Table 2. The HOMO levels of INC- C_8 , AAINC, and PAAINC were -5.44, -5.48 and -5.35 eV, and the energy gaps were 2.76, 2.83 and 2.84 eV, respectively. It was found that the optical properties of monomer and polymers were similar to those of INC- C_8 . Namely, the amide bond and the spacer in the polymer structure doesn't affect the photonic properties and electrochemical properties of INC component.

On the other hand, as shown in Figure 1(b), the fluorescence intensities of PAAINC, CPAAINC-5, CPAAINC-30 and CPAAINC-80 were extremely higher than that of the monomer, AAINC. Therefore, it was speculated that AAINC would aggregate in the solution to derive the concentration quenching, and the concentration quenching of INC components was restrained by keeping distance between INC moieties in copolymers. Moreover, in the case of homopolymer, it was suggested that the

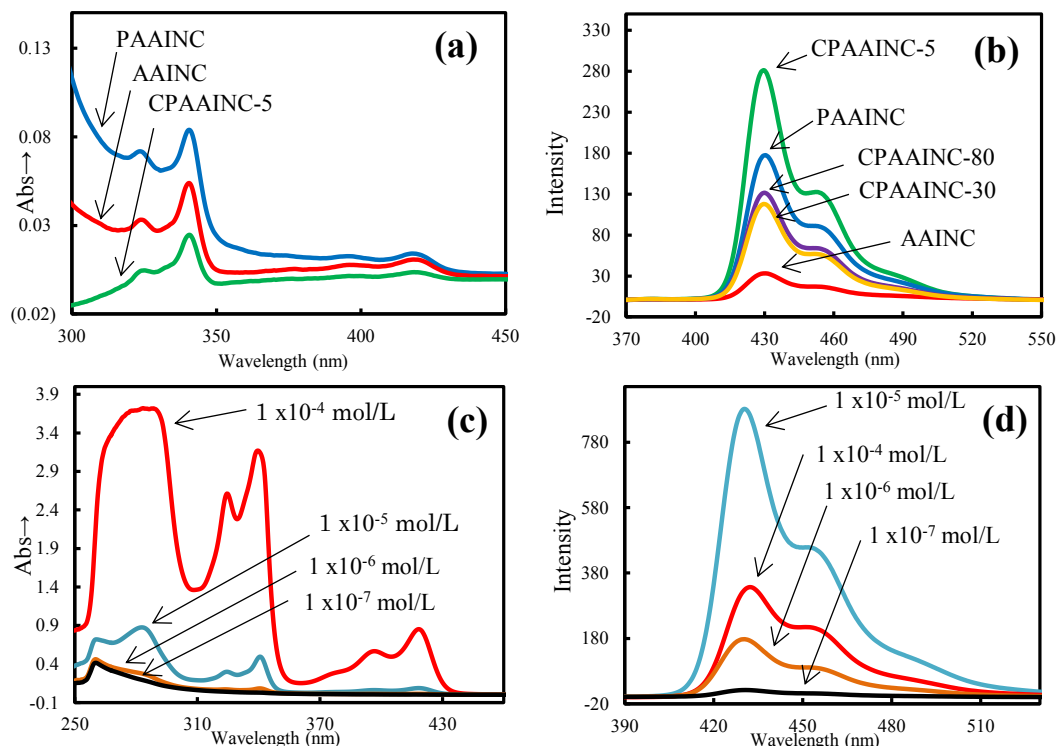


Figure 1 UV-vis absorption spectra (a, c) and fluorescence spectra (b, d) in NMP solutions. (a, b) The concentrations of AAINC, PAAINC, CPAAINC were 1×10^{-6} mol/L (c, d) The concentrations of PAAINC were adjusted to 1×10^{-4} , 1×10^{-5} , 1×10^{-6} , 1×10^{-7} mol/L.

regular conformation would be constructed in the solution to avoid the aggregation of INC moieties.

In addition, it was observed that CPAAINC-5 had the highest photoluminescence intensity in these copolymers, while CPAAINC-30 and CPAAINC-80 showed the similar intensities in photoluminescence spectra. Akimoto *et al.* described that the photoluminescence intensity of INC containing polymer solutions increased as the INC content decreased, because of the concentration quenching caused by the condensation of intermolecular interactions between INC components [8, 10, 11]. Therefore, to investigate the effect of INC concentration on the photoluminescence intensity, UV-Vis absorption and photoluminescence spectra of PAAINC were measured with changing the concentrations of polymer solutions, as shown in Figure 1(c) and (d). The absorption intensity increased as the increase of concentrations, however, the fluorescence intensity was increased in the order of concentrations at 1×10^{-7} , 1×10^{-6} , 1×10^{-4} and 1×10^{-5} mol/L, where the peak intensity at 1×10^{-5} mol/L was higher than that at 1×10^{-4} mol/L. From these results, it was considered that the suitable INC concentration existed to exhibit the highest intensity of photoluminescence of polymers.

4. CONCLUSION

Novel poly(acryl amide)s containing INC moiety in the side chain were successfully prepared by radical polymerization. The obtained polymers exhibited the good solubility and the high thermal stability, where T_g and T_d5 of the homopolymer, PAAINC, were over 200°C and 400°C , respectively. PAAINC and CPAAINC showed the higher strong fluorescence intensity derived from INC component than that of the monomer, AAINC. Furthermore, it was found that HOMO, LUMO levels and energy gap of the obtained compounds were similar to those of INC. The high thermal stability and the photonic

property of INC polymers might be applied to organic photonic devices.

REFERENCES

- [1] W. Tang, L. Ke, L. Tan, T. Lin, T. Kietzke, and Z. Chen, *Macromolecules*, **40**, 6164-6171 (2007).
- [2] G. Liou, S. Hsiao, and H. Chen, *J. Mater. Chem.*, **16**, 1831-1842 (2006).
- [3] S. Park, K. Kim, J. C. Kim, W. Kwon, D. M. Kim, and M. Ree, *Polymer*, **52**, 2170-2179 (2011).
- [4] O. liu, M. Wang, C. Li, E. jin, C. Du, J. Zhou, L. Li, and Z. Bo, *Macromol. Rapid Commun.*, **33**, 2097-2102 (2012).
- [5] H. Jiang, H. Zhao, K. K. Zhang, X. Chen, C. Kloc, and W. Hu, *Adv. Mater.*, **23**, 5075-5080 (2011).
- [6] Q. Peng, X. Liu, Y. Qin, J. Xu, M. Li, and L. Dai, *J. Mater. Chem.*, **21**, 7714-7722 (2011).
- [7] Y. Li, Y. Wu, and B. S. Ong, *Macromolecules*, **39**, 6521-6527 (2006).
- [8] M. Akimoto, T. Kawano, Y. Iwasawa, Y. Takahashi, K. Yamashita, M. Kawamoto, and Y. Nagase, *Polym. J.*, **43**, 959-965 (2011).
- [9] M. Akimoto, T. Kawano, Y. Nagase, M. Kawamoto, and T. Wada, *Trans. Mater. Res. Soc. Japan*, **34**, 141-144 (2009).
- [10] M. Akimoto, Y. Takahashi, K. Yamashita, M. Kawamoto, and Y. Nagase, *Kobunshi Ronbunshu*, **69**, 283-290 (2012).
- [11] K. Yamashita, M. Akimoto, M. Kawamoto, and Y. Nagase, *Trans. Mater. Res. Soc. Japan*, **38**, 253-255 (2013).
- [12] S. Nakama, K. Yamashita, M. Akimoto, M. Kawamoto, and Y. Nagase, *Trans. Mater. Res. Soc. Japan*, **39**, 407-410 (2014).

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