

Synthesis of Polyamide Dendrons Bearing Pyridine Groups as Multiple Hydrogen Bonding Parts on the Periphery

Takayuki KOUKETSU, Masa-aki KAKIMOTO,[†] Mitsutoshi JIKEI,* and Sang Youl KIM**

*Department of Organic and Polymeric materials, Tokyo Institute of Technology,
2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552, Japan*

**Department of Material-process Engineering and Applied Chemistry for Environments, Akita University,
1-1, Tegata, Gakuen-machi, Akita 010-8502, Japan*

***Department of Chemistry, Korea Advanced Institute of Science and Technology,
373-1, Kusong-dong, Yusong-gu, Taejeon 305-701, Korea*

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ABSTRACT: Aromatic polyamide dendrons (G0–G2) having amino groups on the periphery were prepared by divergent method. Reaction of G0 aromatic polyamide dendron with isonicotinoyl chloride hydrochloride gave polyamide dendron (G0-2Py) bearing two pyridine groups. The structures of polyamide dendrons were confirmed by IR, ¹H, ¹³C NMR, MALDI-TOF mass spectroscopy. A hydrogen-bonded G0-2Py/poly(acrylic acid) (PAA) 1/2 complex was prepared by mixing G0-2Py with PAA in methanol, followed by removing the solvent. IR spectrum of G0-2Py/PAA 1/2 complex showed characteristic absorptions at 2550 and 1950 cm⁻¹ due to hydrogen bonding. A glass transition temperature (*T*_g) of G0-2Py/PAA 1/2 complex was observed at 121 °C by DSC measurement, whereas *T*_gs of G0-2Py (137 °C) and PAA (87 °C) disappeared. *T*_g of the G0-2Py/PAA complex was dependent on the molar ratio ([Donor]/[Acceptor]). Maximum *T*_g at 121 °C was observed at a ratio of 1. [DOI 10.1295/polymj.36.513]

KEY WORDS Polyamide Dendron / Pyridine Group / Multiple Hydrogen Bonding /

Self-assembly based on selective control of non-covalent interactions provides a powerful tool for the creation of structured systems at the molecular level. Hydrogen bonding is one of the important non-covalent interactions in nature because of its stability, dynamics, and directionality. Meijer and co-workers recently reported stable complexes formed by quadruple hydrogen bonding between 2-ureido-4[1*H*]-pyrimidone (UPy) units attached to various spacers.^{1–4} Self-assembled molecules containing multiple hydrogen bonding units exhibited polymer-like properties such as shear thinning in the melt phase, viscoelastic behavior in the solid state, and glass transition temperatures. Initial supramolecular systems based on multiple hydrogen bonding were reported by Lehn,⁵ Kato and Fréchet,^{6–8} and Whitesides.^{9–12} These diverse efforts focused on the selective formation of discrete supramolecules from complementary receptor-substrate hydrogen bonding pairs, such as barbituric acid and triaminopyrimidine units, 2,6-diaminopyridine and 2,6-pyridinedi-carbonyl units, and carboxylic acid and pyridine units.

Dendritic macromolecules such as dendrimers and hyperbranched polymers have received much attention in recent years. These polymers have unique properties such as low viscosity, high solubility, amorphous nature, and multi-functionality, due to unique architecture. In particular, dendrimers have well-controllable structure and size with perfect branching.

Number of functional groups on the periphery of dendrimers can be controlled precisely by the number of generations. Tomalia and co-workers^{13–15} and Kabanov *et al.*^{16,17} reported polyion complexes formed by DNA and poly(amideamine) starburst dendrimers or Astramol poly(propyleneimine) dendrimers. These complexes could be used in gene delivery strategies or interpolyelectrolyte complexes. Zhang *et al.* recently reported the formation of a microporous film by alternating the deposition of poly(4-vinylpyridine) and carboxyl-terminated polyether dendrimers *via* hydrogen bonding in a cyclic fashion.¹⁸ Using the ends of dendrimers for multiple hydrogen bonding expects obtaining a stable complex.

Previously, we reported the preparation and properties of complexes between polyamide dendrons bearing carboxyl groups as hydrogen bonded donors and poly(4-vinylpyridine) as hydrogen bonded acceptor.¹⁹ Polyamide dendrons having carboxyl groups on the periphery were mixed with poly(4-vinylpyridine) to form complexes *via* multiple hydrogen bonding. It was found that complexes were obtained by DSC and ¹H NMR spin–lattice relaxation time (*T*₁) measurements. This paper reports the synthesis of various polyamide dendrons bearing pyridine groups as hydrogen bonded acceptors, and the preparation of the complexes from these dendrons and poly(acrylic acid) *via* multiple hydrogen bonding.

[†]To whom correspondence should be addressed (E-mail: mkakimoto@o.cc.titech.ac.jp).

EXPERIMENTAL

Materials

3,5-Dinitrobenzoyl chloride (DNBC) was used as received from Tokyo Chemical Industry Co., Ltd. 1,3-Phenylenediamine (*m*-PD), isonicotinoyl chloride hydrochloride (INC), and poly(acrylic acid) ($M_w = 2000$) were used as received from Aldrich. *N,N*-Dimethylacetamide (DMAc) was purified by vacuum distillation over calcium hydride. Methanol and 10% palladium on activated carbon (Pd-C) were used as received.

G1-4NO₂. In a flask equipped with a magnetic stirrer and nitrogen inlet were placed 1,3-phenylenediamine (2.16 g, 20.0 mmol) and DMAc (150 mL). 3,5-Dinitrobenzoyl chloride (11.1 g, 48 mmol) was added. The solution was stirred at room temperature for 3 h. The reaction mixture was then poured into water. The crude product was filtered and washed with hot methanol. The product was filtered and dried at 80 °C *in vacuo*. The yield was 99%. ¹H NMR (DMSO-*d*₆): δ 10.94 (s, 2H, amide H), 9.18 (s, 4H), 9.00 (s, 2H), 8.40 (s, 1H), 7.57 (d, 2H), 7.42 (t, 1H).

G1-4NH₂. In a flask equipped with a magnetic stirrer and hydrogen inlet were placed G1-4NO₂ (1.99 g, 4.0 mmol), DMAc (120 mL), and 10% Pd-C (0.851 g, 5 mol %). The flask was degassed and purged with hydrogen several times and then stirred at room temperature for 2 d. The mixture was filtered using Celite-545. The solution was concentrated and poured into CH₂Cl₂. The product was filtered and dried at 50 °C *in vacuo*. The yield was 92%. ¹H NMR (DMSO-*d*₆): δ 9.91 (s, 2H, amide H), 8.18 (s, 1H), 7.37 (d, 2H), 7.20 (t, 1H), 6.28 (s, 4H), 5.98 (s, 2H), 4.93 (s, 8H, NH₂).

G2-8NO₂. In a flask equipped with a magnetic stirrer and nitrogen inlet were placed G1-4NH₂ (0.565 g, 1.5 mmol) and DMAc (15 mL). 3,5-Dinitrobenzoyl chloride (2.08 g, 9.0 mmol) was added. The solution was stirred at room temperature for 12 h. The reaction mixture was then poured into water. The crude product was filtered and washed with hot methanol. The product was filtered and dried at 80 °C *in vacuo*. The yield was 95%. ¹H NMR (DMSO-*d*₆): δ 11.15 (s, 4H, amide H), 10.51 (s, 2H, amide H), 9.23 (s, 8H), 9.03 (s, 4H), 8.71 (s, 2H), 8.34 (s, 1H), 8.11 (s, 4H), 7.52 (d, 2H), 7.32 (t, 1H).

G2-8NH₂. In a flask equipped with a magnetic stirrer and hydrogen inlet were placed G2-8NO₂ (1.50 g, 1.3 mmol), DMAc (100 mL), and 10% Pd-C (0.553 g, 5 mol %). The flask was degassed and purged with hydrogen several times and then stirred at room temperature for 2 d. The mixture was filtered using Celite-545. The solution was concentrated and poured into

CH₂Cl₂. The product was filtered and dried at 50 °C *in vacuo*. The yield was 81%. ¹H NMR (DMSO-*d*₆): δ 10.35 (s, 2H, amide H), 10.13 (s, 4H, amide H), 8.38 (s, 2H), 8.29 (s, 1H), 7.91 (s, 4H), 7.49 (d, 2H), 7.30 (t, 1H), 6.33 (s, 8H), 6.00 (s, 4H), 4.95 (s, 16H, NH₂).

G0-2Py. In a flask equipped with a magnetic stirrer and nitrogen inlet were placed 1,3-phenylenediamine (2.16 g, 20.0 mmol) and DMAc (100 mL). Isonicotinoyl chloride hydrochloride (8.54 g, 48 mmol) was added. The solution was stirred at room temperature for 3 h. The solution was then poured into dilute NaOH water. The product was filtered and dried at 80 °C *in vacuo*. The yield was 94%. IR (KBr, cm⁻¹): 1687, 1615, 1556, 1440. ¹H NMR (DMSO-*d*₆): δ 10.58 (s, 2H, amide H), 8.78 (d, 4H), 8.35 (s, 1H), 7.86 (d, 4H), 7.52 (d, 2H), 7.36 (t, 1H). ¹³C NMR (DMSO-*d*₆): δ 164.1, 150.3, 141.9, 138.9, 128.9, 121.7, 116.6, 112.9. MALDI-TOF MS: *m/z* calcd for C₁₈H₁₄N₄O₂ 319.3 (M + H⁺), found 319.9 (M + H⁺).

G1-4Py. In a flask equipped with a magnetic stirrer and nitrogen inlet were placed G1-4NH₂ (0.753 g, 2.0 mmol) and DMAc (20 mL). Isonicotinoyl chloride hydrochloride (1.71 g, 9.6 mmol) was added. The solution was stirred at room temperature for 3 h. The solution was then poured into dilute NaOH water. The product was filtered and dried at 80 °C *in vacuo*. The yield was 90%. IR (KBr, cm⁻¹): 1664, 1605, 1553, 1447. ¹H NMR (DMSO-*d*₆): δ 10.82 (s, 4H, amide H), 10.47 (s, 2H, amide H), 8.81 (d, 8H), 8.60 (s, 2H), 8.32 (s, 1H), 8.07 (s, 4H), 7.92 (d, 8H), 7.50 (d, 2H), 7.33 (t, 1H). ¹³C NMR (DMSO-*d*₆): δ 165.7, 164.3, 150.4, 141.7, 139.4, 139.0, 136.4, 128.8, 121.7, 116.1, 116.0, 115.6, 112.8. MALDI-TOF MS: *m/z* calcd for C₄₄H₃₂N₁₀O₆ 819.7 (M + Na⁺), found 820.3 (M + Na⁺).

G2-8Py. In a flask equipped with a magnetic stirrer and nitrogen inlet were placed G1-4NH₂ (0.456 g, 0.5 mmol) and DMAc (10 mL). Isonicotinoyl chloride hydrochloride (1.07 g, 6.0 mmol) was added. The solution was stirred at room temperature for 3 h. The solution was then poured into dilute NaOH water. The product was filtered and dried at 80 °C *in vacuo*. The yield was 87%. IR (KBr, cm⁻¹): 1665, 1605, 1553, 1448. ¹H NMR (DMSO-*d*₆): δ 10.82 (s, 8H, amide H), 10.68 (s, 4H, amide H), 10.46 (s, 2H, amide H), 8.80 (d, 16H), 8.58 (s, 4H), 8.53 (s, 2H), 8.35 (s, 1H), 8.13 (s, 8H), 8.03 (s, 4H), 7.91 (d, 16H), 7.50 (d, 2H), 7.32 (t, 1H). ¹³C NMR (DMSO-*d*₆): δ 170.0, 166.2, 166.1, 164.5, 150.5, 141.8, 139.6, 139.5, 139.2, 136.6, 136.3, 128.9, 121.8, 116.2, 116.0, 115.7, 112.9. MALDI-TOF MS: *m/z* calcd for C₉₆H₆₈N₂₂O₁₄ 1776.7 (M + Na⁺), found 1778.7 (M + Na⁺).

Preparation of Polyamide Dendron/PAA Complexes

The polyamide dendron/PAA complexes were prepared by evaporation from methanol or DMAc solution containing equimolar amounts of hydrogen bonding acceptor and donor moieties followed by drying *in vacuo* at 60 °C. For example, the G1-4Py/PAA 1/4 complex (*i.e.* donor/acceptor = 1/1) was prepared by the mixture of G1-4Py (0.0398 g, 0.05 mmol) and PAA (0.0144 g, 0.2 mmol) in DMAc (50 mL), followed by drying *in vacuo* at 60 °C after it was concentrated DMAc.

Measurements

IR spectra were recorded on a Bomem Michelson series FT-IR spectrometer. ¹H and ¹³C NMR spectroscopic measurements were carried out on 300 MHz Bruker NMR spectrometers. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed at a heating rate of 10 °C/min under nitrogen on a TA 2200 thermal analyzer system, T_g was taken at the middle of the step transition in the second heating run.

RESULTS AND DISCUSSION

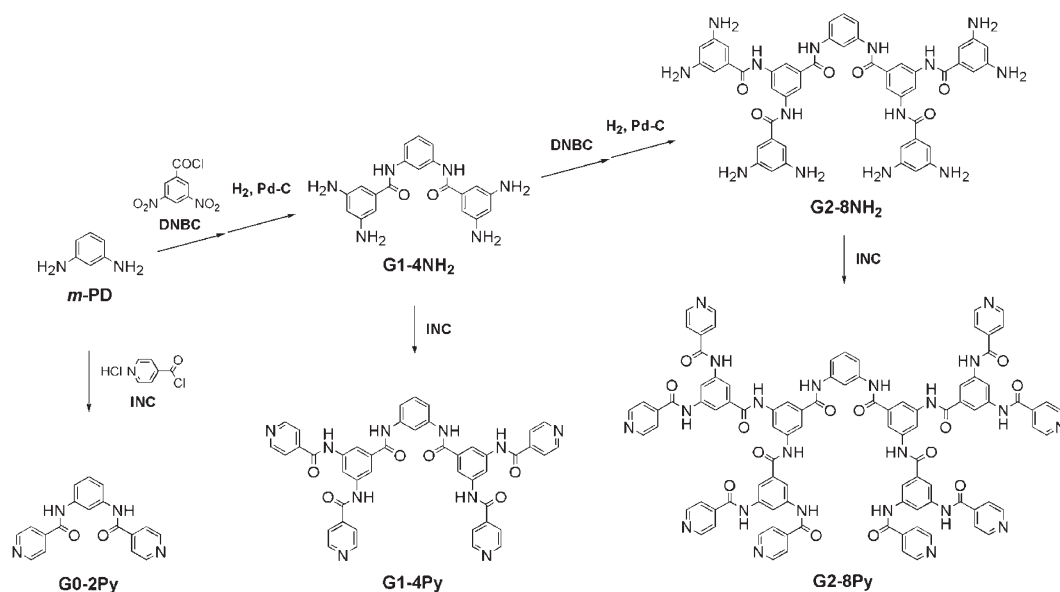
Synthesis of Polyamide Dendrons

The synthetic routes for aromatic polyamide dendrons are shown in Scheme 1.²⁰ G1-4NH₂ was prepared by the hydrogenation of G1-4NO₂ synthesized from 1,3-phenylenediamine and 3,5-dinitrobenzoyl chloride. The crude G1-4NO₂ was washed with hot methanol in order to remove excess 3,5-dinitrobenzoyl chloride and its hydrate. The structure of G1-4NO₂ was confirmed by ¹H NMR. G2-8NH₂ was also prepared by the hydrogenation of G2-8NO₂ prepared

from G1-4NH₂ and 3,5-dinitrobenzoyl chloride. The reaction of G1-4NH₂ or G2-8NH₂ with isonicotinoyl chloride hydrochloride (INC) was carried out at room temperature for 3 h in DMAc to give G1-4Py and G2-8Py bearing four and eight pyridine groups on the periphery. G0-2Py bearing two pyridine groups at the end was prepared by reaction of 1,3-phenylenediamine with INC. The structure of aromatic polyamide dendrons was confirmed by IR, ¹H, ¹³C NMR, and MALDI-TOF mass spectroscopies. Because the starting materials, 1,3-phenylenediamine, G1-4NH₂, and G2-8NH₂, can be isolated without column chromatography, these dendrons can be synthesized readily on a large scale.

Solubility of aromatic polyamide dendrons are shown in Table I. The aromatic polyamide dendrons bearing pyridine groups on the periphery were soluble in aprotic polar solvents, such as DMF, DMAc, NMP, and DMSO. G0-2Py was also soluble in methanol. Aromatic polyamide dendrons were also partially soluble in HCl water due to pyridine groups of the dendrons.

Thermal properties of dendrons were examined by TGA and DSC (Table II). Although the molecular weight of G1-4Py is 797 g/mol, it has a high glass transition temperature (T_g) of 219 °C at second scan quenching with liquid nitrogen. T_g was dependent on the generation number of dendrons and increased to 263 °C for G2-8Py. DSC curves of G1-4Py showed an endothermic peak of 215 °C and an exothermic peak of 272 °C (Figure 2). It suggests that the endothermic peak was the T_g , and the exothermic peak was crystallization. The melting point of G1-4Py was observed at 360 °C by DTA measurement. In the case of G0-2Py and G2-8Py, properties similar



Scheme 1. Synthesis of aromatic polyamide dendrons bearing pyridine groups.

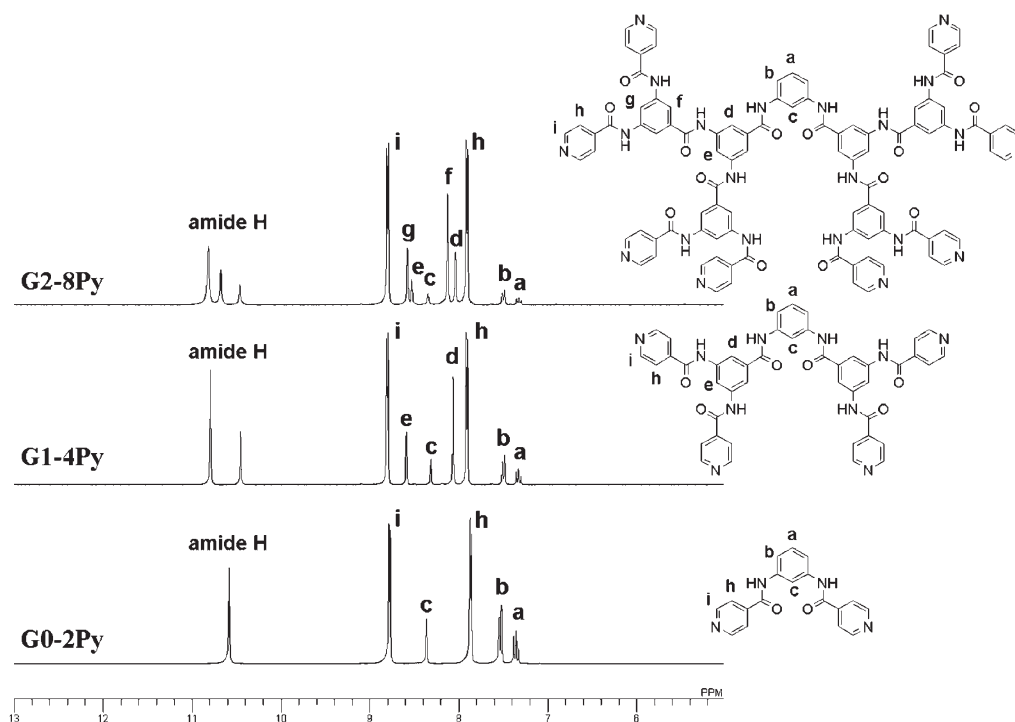


Figure 1. ^1H NMR spectra of aromatic polyamide dendrons; (a) G0-2Py, (b) G1-4Py, (c) G2-8Py.

Table I. Solubility of Polyamide Dendrons^a

	G0-2Py	G1-4Py	G2-8Py	PAA
<i>n</i> -Hexane	—	—	—	—
Acetone	—	—	—	—
MeOH	++	—	—	++
EtOAc	—	—	—	—
THF	—	—	—	++
CHCl_3	—	—	—	—
CH_2Cl_2	—	—	—	—
H_2O	—	—	—	++
aq HCl	++	+-	+-	++
DMAc	++	++	++	++
DMSO	++	++	++	++

^a++: soluble, +-: partially soluble, -: insoluble

to the case of G1-4Py were not observed. Thermal decomposition temperature (T_d) of G0-2Py, G1-4Py and G2-8Py was more than 300 °C.

PREPARATION AND PROPERTIES OF POLY-AMIDE DENDRON/PAA COMPLEXES

The pyridine groups of polyamide dendrons are hydrogen bonding acceptor, and carboxyl groups of poly(acrylic acid) (PAA) ($M_w = 2000$) are hydrogen bonding donor. The complexes were prepared by mixing polyamide dendrons with PAA in methanol or DMAc. A powdery complex was isolated after removing methanol or DMAc used as solvent, as described in Scheme 2. The IR spectrum of G0-2Py/PAA 1/2 (1/2 = molar ratio, *i.e.* [Donor]/[Acceptor] = 1/1)

Table II. Thermal Properties of Polyamide Dendrons

	Formula weight	T_g^a (°C)	T_d^b (°C)
G0-2Py	318.33	137	333
G1-4Py	796.79	219	390
G2-8Py	1753.71	263	411

^aDetermined by DSC at a heating rate of 10 °C/min in N_2 (second scan). ^bDetermined by TGA at a heating rate of 10 °C/min in N_2 .

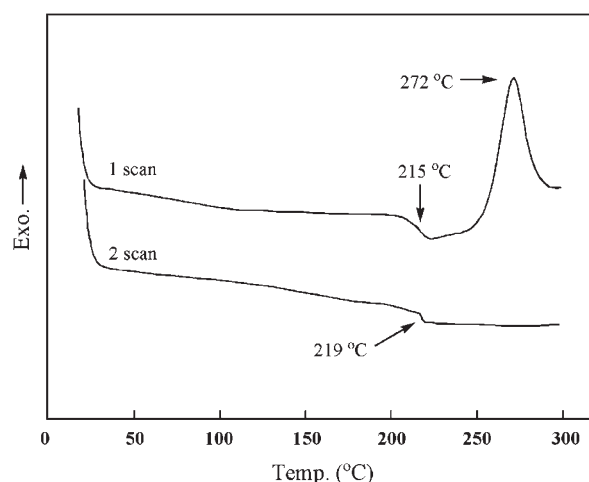


Figure 2. DSC curves of G1-4Py. Determined by DSC at a heating rate of 10 °C/min in N_2 .

complex showed characteristic absorptions at 2550 and 1950 cm^{-1} due to the hydrogen bond as shown in Figure 3.⁶⁻⁸ Absorption attributed to the stretching

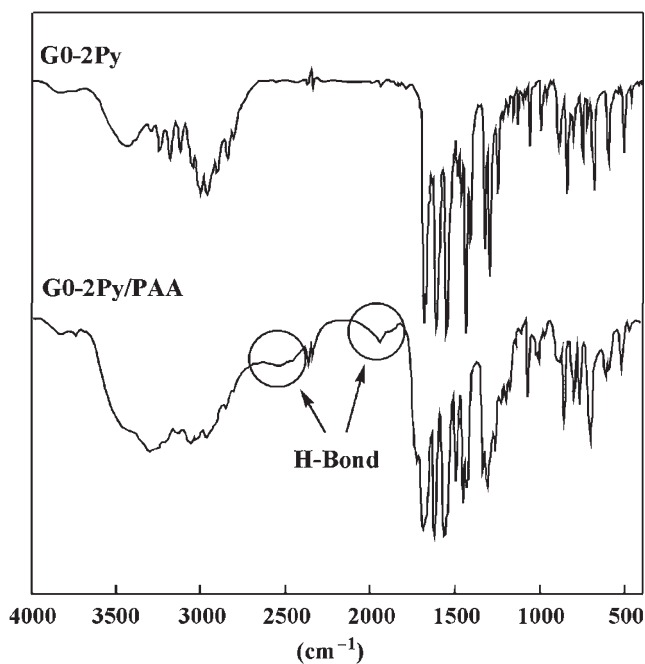
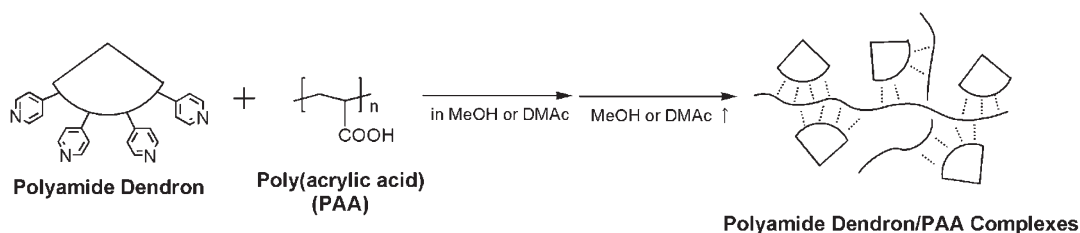


Figure 3. IR spectra of G0-2Py (a) and G0-2Py/PAA 1/1 complex (b).

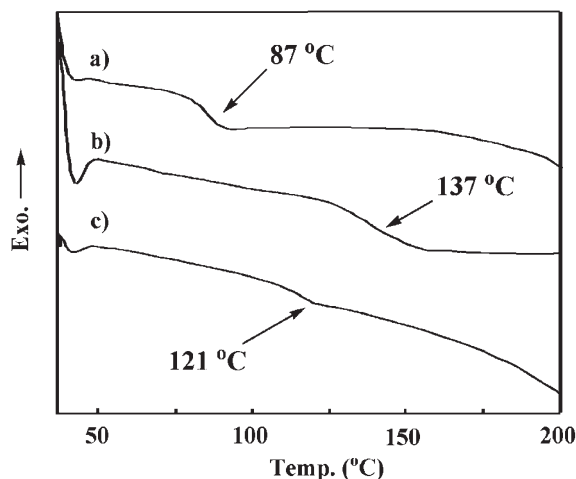


Figure 4. DSC curves of PAA (a), G0-2Py (b), and G0-2Py/PAA 1/2 complex (c). Determined by DSC at a heating rate of 10 °C/min in N₂ (second scan).

mode of pyridine ring also shifted from 997 to 1015 cm⁻¹. Other peaks such as amide bond of dendrons and carboxyl group of PAA did not change.

Table III. Relationship between T_g and PAA Content in G0-2Py/PAA Complex

[Donor]/[Acceptor]	T_g (°C) ^a
0.5	113
0.75	118
1	121
1.25	117
1.5	113
2	113
3	109
5	110
10	101

^aDetermined by DSC at a heating rate of 10 °C/min in N₂ (second scan).

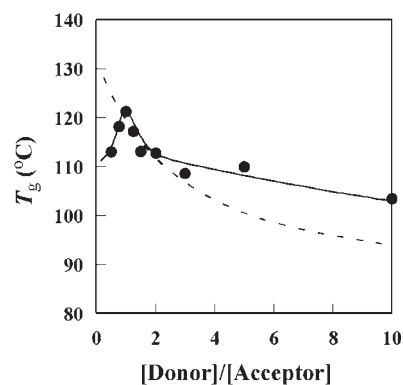


Figure 5. Effects of the donor/acceptor ratio of dendrons and PAA on T_g of a complex. The broken line (---) is determined by Fox equation ($1/T_g = w_1/T_{g1} + w_2/T_{g2}$).

DSC curves of G0-2Py, PAA, and its complex are shown in Figure 4. A single new T_g of G0-2Py/PAA 1/2 complex was observed at 121 °C as a single peak by DSC measurement, whereas T_g of G0-2Py at 137 °C and T_g of PAA at 87 °C disappeared. This suggests that G0-2Py and PAA are miscible. G1-4Py/PAA 1/4 and G2-8Py/PAA 1/8 complexes were prepared, and the IR spectrum of G1-4Py/PAA and G2-8Py/PAA complex showed characteristic absorption due to the hydrogen bonding. T_g s of G1-4Py/PAA 1/4 and G2-8Py/PAA 1/8 complexes were not observed at 30 °C to 200 °C. T_g s of complexes may be higher than 217 °C which is an onset thermal degradation temperature of PAA.

T_g s of G0-2Py/PAA were dependent on the ratio of [Donor]/[Acceptor] as shown in Table III and Figure 5. Maximum T_g at 121 °C was observed when the ratio was 1. It suggests that the maximum complex was obtained because of the formation of a strong network. T_g of the G0-2Py/PAA complex decreased with increase of the ratio. According to the Fox equation,²¹ T_g of the complex decreases with increase of the PAA ratio. As shown in Figure 5, T_g s of the G0-2Py/PAA complexes were higher than that of the Fox equation (broken line). This can be explained by multiple hydrogen bonding. Formation of hydrogen bonding suggests that the mobility of PAA decreases.

CONCLUSIONS

Aromatic polyamide dendrons bearing pyridine groups on the periphery were synthesized by the divergent method. The dendrons were mixed poly(acrylic acid) (PAA) to form complexes via multiple hydrogen bonding. IR spectra of G0-2Py/PAA, G1-4Py/PAA, and G2-8Py/PAA complexes suggested the formation of hydrogen bondings. A new T_g was observed for each complex and T_g was dependent on the molar ratio of the dendron and PAA. Maximum T_g at 121 °C was observed when donor (PAA) and acceptor (G0-2Py) ratio was 1. G0-2Py, G1-4Py, and G2-8Py afforded complexes with various polymers bearing carboxyl groups by multiple hydrogen bonding. Since multiple hydrogen bonding is potentially reversible by external stimuli, such as temperature, concentration and polarity of solvents, the properties of the complexes may be controlled by the formation or cleavage of multiple hydrogen bonding. In addition, there are little reports on dendrimers bearing pyridine groups at the periphery. Since pyridine groups are also used for coordination bonding in stead of hydrogen bonding, new soft-materials might be prepared.

REFERENCES

1. R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe, and E. W. Meijer, *Science*, **278**, 1601 (1997).
2. B. J. B. Folmer, R. P. Sijbesma, and E. W. Meijer, *J. Am. Chem. Soc.*, **123**, 2093 (2001).
3. B. J. B. Folmer, R. P. Sijbesma, H. Kooijman, A. L. Spek, and E. W. Meijer, *J. Am. Chem. Soc.*, **121**, 9001 (1999).
4. R. F. M. Lange, M. V. Gulp, and E. W. Meijer, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 3657 (1999).
5. C. Fouquey, J. M. Lehn, and A. M. Levelut, *Adv. Mater.*, **2**, 254 (1990).
6. T. Kato and J. M. J. Fréchet, *Macromolecules*, **22**, 3818 (1989).
7. T. Kato, H. Kihara, U. Kumar, T. Uryu, and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, **33**, 1644 (1994).
8. T. Kato and J. M. J. Fréchet, *Macromol. Symp.*, **98**, 311 (1995).
9. S. Palacin, D. N. Chin, E. E. Simanek, C. J. MacDonald, G. M. Whitesides, M. T. McBridge, and G. T. R. Palmore, *J. Am. Chem. Soc.*, **119**, 11807 (1997).
10. E. E. Simanek, L. Isaacs, C. C. C. Wang, and G. M. Whitesides, *J. Org. Chem.*, **62**, 8994 (1997).
11. M. Mammen, E. I. Shakhnovich, J. M. Deutch, and G. M. Whitesides, *J. Org. Chem.*, **63**, 3821 (1998).
12. I. S. Choi, X. Li, E. E. Simanek, R. Akaba, and G. M. Whitesides, *Chem. Mater.*, **11**, 684 (1999).
13. W. Chen, N. J. Turro, and D. A. Tomalia, *Langmuir*, **16**, 15 (2000).
14. M. F. Ottaviani, B. Sacchi, N. J. Turro, W. Chen, S. Jockusch, and D. A. Tomalia, *Macromolecules*, **32**, 2275 (1999).
15. M. F. Ottaviani, F. Furini, A. Casini, N. J. Turro, S. Jockusch, D. A. Tomalia, and L. Messori, *Macromolecules*, **33**, 7842 (2000).
16. V. A. Kabanov, A. B. Zezin, V. B. Rogacheva, Z. G. Gnlyara, M. F. Zansochova, J. G. H. Joosten, and J. Brackman, *Macromolecules*, **32**, 1904 (1999).
17. V. A. Kabanov, V. G. Sergeev, O. A. Pyshkina, A. A. Zinchenko, A. B. Zezin, J. G. H. Joosten, J. Brackman, and K. Yoshikawa, *Macromolecules*, **33**, 9587 (2000).
18. H. Zhang, Y. Fu, D. Wang, L. Wang, Z. Wang, and X. Zhang, *Langmuir*, **19**, 8497 (2003).
19. M. Jikei, T. Koketsu, K. Yokomachi, and M. Kakimoto, *Polym. Prepr.*, **44**, 581 (2003).
20. Y. Ishida, M. Jikei, and M. Kakimoto, *Macromolecules*, **33**, 3202 (2003).
21. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).