Synthesis and Properties of the Aromatic Polyamides Containing the 2,4′-Biphenyldiyl Structure

Fumihiko Akutsu*, Norihisa Sugiyama, Nobuyuki Ando,
Yoshio Kasashima, Mari Inoki, and Kiyoshi Naruchi

*Department of Applied Chemistry, Faculty of Engineering, Chiba University,
Yayoi-cho 1–33, Inage-ku, Chiba-shi 263, Japan*

ABSTRACT: Novel aromatic polyamides were synthesized from 2,4′-biphenyldiamine by low-temperature solution polycondensation. The polyamides were soluble in pyridine, *m*-cresol, *N,N*-dimethylacetamide, 1-methyl-2-pyrrolidone, hexamethylphosphoric triamide, *N,N*-dimethylformamide, dimethylsulfoxide, and conc. H_2SO_4. The glass-transition temperatures (T_gs) were found in the 248—284°C range. The temperatures at 5% weight loss in nitrogen atmosphere (T_ds) were 435—459°C, and residual weights at 600°C were 43—56%. The introduction of 2,4′-biphenyldiyl structure to the backbones of aromatic polyamides improves solubility without lowering high thermal stability. In addition, brominated aromatic polyamides were synthesized from *N,N′*-bis(trimethylsilyl)-5-bromo-2,4′-biphenyldiamine, and their properties were compared with those of none-brominated polyamides. The brominated aromatic polyamides indicated higher solubility, though their T_gs were as high as those of none-brominated polyamides. As concerns thermal decomposition behavior, the introduction of a bromo-group to the structures of aromatic polyamides lowered T_ds, but heightened residual weight.
    KEY WORDS   2,4′-Biphenyldiamine / Aromatic Polyamide / Solubility / Thermal Property / 5-Bromo-2,4′-biphenyldiamine / *N,N′*-Bis(trimethylsilyl)-5-bromo-2,4′-biphenyldiamine /

Wholly aromatic polyamides are well known as high-performance polymers. Their rigid structures induce not only high thermal stability, but poor solubility in many organic solvents[1] with consequently low processability. Thus, it is necessary to improve the solubility of aromatic polyamides without lowering high thermal resistance in order to apply to industry. It was found that the introduction of rigid and zigzag structures, *e.g.*, 2,3-quinoxalinediyl,[2-5] 1,2,4-triazine-5,6-diyl,[6,7] 2-phenyl-4,5-imidazolediyl,[8] and 4,4″-*o*-terphenyldiyl[9,10] structures, to the main chains of polyamides improved solubility with keeping high thermal stability, and the effect produced by heterocycles on the improvement of the solubility is larger than that by 4,4″-*o*-terphenyldiyl structure. Glass-transition temperatures (T_gs) of the polyamide having the heterocycles were higher than that of the corresponding polyamide containing the 4,4″-*o*-terphenyldiyl structure. The introduction of a polar substituent to the zigzag structures of aromatic polyamides may thus be effective for improving solubility and heightening T_g.

This study investigates the synthesis and properties of novel aromatic polyamides introduced rigid and zigzag 2,4′-biphenyldiyl structure to backbones in order to improve solubility without lowering highly thermal properties. Novel aromatic polyamides having 5-bromo-2,4′-biphenyldiyl structure were

---

* To whom correspondence should be addressed.

studied. Kuze *et al.* reported that the introduction of the chloro-group as a side substituent to the structures of poly(*m*-phenyleneisophthalamide) and poly(*m*-phenyleneterephthalamide) improves solubility and lowers T_gs.[11] The main chains of these polyamides were linear, but those of polyamides containing 2,4′-biphenyldiyl structure were zigzag. Effects on the solubility and T_g of the zigzag polyamides produced by the introduction of the halogeno-group as the polar substituent have not been investigated. Aromatic polyimide prepared from the diamine 1 with 3,3′,4,4′-benzophenonetetracarboxylic dianhydride has been reported[11] by Bell *et al.*, but there has been no reports on polyamide containing 2,4′-biphenyldiyl structure yet.

RESULTS AND DISCUSSION

Monomer and Polymer Synthesis

2,4′-Biphenyldiamine (diphenyline) 1 was obtained by the reduction of 2-amino-4′-nitrobiphenyl.[13] The synthesis of 5-bromo-2,4′-biphenyldiamine 4 was attempted according to the method using benzidine-rearregement from 4-bromoazobenzene[14] reported Jacobson *et al.*, but the attempt was unsuccessful due to reduction of the bromo-group accompanying the reduction of the azobenzene. There have not been any other reports on brominated diamine 4. Diamine 4 was thus synthesized by reduction of 2- amino-5-bromo-4′-nitrobiphenyl 8 using a Fe–HCl system. The boiling point of diamine 4 was so high that the crude products could not be purified by distillation under reduced pressure. Thus, acetylation was carried out. Diacetamide 9 was purified by recrystallization, and then hydrolyzed. The hydrolyzate, a clear yellow oil, was identified as diamine 4 by spectroscopic data as well as by elemental analysis.

Polyamides 3 were prepared by low-temperature solution polycondensation[15] of diamine 1 with several aromatic dicarbonyl dichlorides 2. Methyloxirane was used as the

hydrogen chloride acceptor. The results are shown in Table I. All polycondensations proceeded to homogeny. The IR spectra of the polymers showed characteristic amide absorptions near 1660 and 1520 cm^{-1}. All polyamides were obtained in quantitative yields. The inherent viscosities of polyamides 3 were in the range of 0.42—0.72 dl g^{-1}.

Polyamide 6a was synthesized from diamine 4 by a similar procedure, but the inherent viscosity of the produced polyamide was a low 0.13 dl g^{-1}. It was assumed that a slight impurity contained by diamine 4 influenced the degree of polymerization. Therefore, N-trimethylsilylation[16] of diamine 4 was performed because the boiling point was lowered and the reactivity of diamine was heightened. After the N-silylated product was distilled under reduced pressure, the distillate was identified as N,N′-bis(trimethylsilyl)-5-bromo-2,4′-biphenyldiamine 5 by spectroscopic data and elemental analysis. Polyamides 6 were prepared by low-temperature solution polycondensation[17,18] of N-silylated diamine 5 with several aromatic dicarbonyl dichlorides 2. The results are summarized in Table I. The inherent viscosities of polyamides 6 were improved, but were not high, ranging from 0.20 to 0.26 dl g^{-1}. It was

Table I. Data of prepared polyamides

Polymer	Diamines	Yield %	η_{inh}[a] dl g^{-1}	Color
3a	1	91.8	0.72	White
3b	1	98.6	0.49	White
3c	1	99.5	0.59	White
3d	1	99.1	0.41	White
3e	1	90.7	0.45	White
6a	4	97.1	0.13	White
6a	5	99.3	0.22	White
6b	5	96.1	0.22	White
6c	5	100.2	0.21	White
6d	5	99.9	0.26	White
6e	5	99.6	0.20	White

[a] Inherent viscosity measured in conc. sulfuric acid (0.50 g dl^{-1}) at 30°C.

considered that the low reactivity of the formed oligomers by steric hindrance contributed to the low inherent viscosities of polyamides **6**.

Thermal Properties of Polyamides

T_gs were determined by differential scanning calorimetry (DSC). The temperatures at 5% weight loss (T_ds) and weight residues at 600°C were determined by thermogravimetry (TG). Thermal behavior of polyamides are summarized in Table II. T_g of polyamide **3d** and that of **6d** were not observed by DSC. T_gs of polyamides **3** were found in the range of 248—284°C, and those of polyamides **6** ranged from 249 to 288°C. It was expected that T_gs of polyamides **6** were lower due to their low inherent viscosities. However, T_gs of **6** are as high as those of **3**. This indicated that polyamides **6** have enough inherent viscosities to investigate their physical and chemical properties. The results of those T_gs were attributed to a bulkiness of the bromo-group as the side substituent and to the dipole–dipole interactions between the polymer chains by the polarity of the bromo-group.

T_ds of polyamides **3** were found in the 435—459°C range. T_ds of polyamides **6** ranged from 364 to 403°C, which were lower than those of corresponding polyamides **3**. The weight residues at 600°C of polyamides **3** were in the 43—56% range. However, those of polyamides **6** ranged between 59 and 71%, which were higher than those of corresponding polyamides **3**. Figure 1 shows the typical TG-curves of polyamide **3d** and corresponding brominated polyamide **6d** in nitrogen atmosphere. T_d of **6d** was 403°C, which was 49°lower than that of **3d**. On the contrary, the residual weight at 600°C of **6d** was high; the value was 71%, which was 15% higher than that of **3d**. In addition, while the thermal degradation of polyamide **3d** occurred in one step, **6d** pyrolyzed in two steps; the first drop was 11% decrease at the 384—430°C range. It was considered that the first decrease of the pyrolysis of **6d** corresponded to the scission of the C–Br bond. The thermal

Table II. Thermal properties of polyamides

Polymer	T_g[a]	T_d[b]	White residue at 600°C/%[c]
	°C	°C	
3a	248	435	43
3b	275	445	49
3c	251	442	47
3d	—[d]	452	56
3e	284	459	56
6a	253	379	69
6b	285	383	63
6c	249	380	69
6d	—[d]	403	71
6e	288	364	59

[a] Measured by differential scanning calorimetry (DSC) (heating rate 10 k min^{-1} in nitrogen atmosphere). [b] Temperature at 5% weight loss was determined by thermogravimetry (TG) (heating rate 10 K min^{-1} in nitrogen atmosphere). [c] Determined by TG. [d] Not observed by DSC.
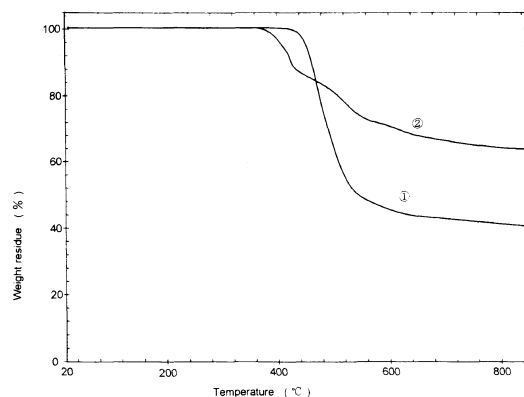

Figure 1. TG curves at a heating rate of 10 K min^{-1} in nitrogen atmosphere for polyamide **3d** (①) and for brominated polyamide **6d** (②).

degradation of aromatic polyamides proceeds crosslinking and condensation reaction with elimination of gases such as water, carbon monoxide, carbon dioxide, hydrogen cyanide, hydrogen, and methane.[19,20] Nara *et al.* reported that, in the thermal degradation of the tetrabrominated epoxy resin, hydrogen bromide produced by the initial thermal decomposition promotes crosslinking or con-

densation reaction of residual polymer.[21] Therefore, it is suggested that the pyrolysis of **6d** causes the cleavage of the C–Br bond initially, and hydrogen bromide formed promotes crosslinking or condensation reaction of the residual polymer.

Solubility of Polyamides

Solubilities in several organic solvents are summarized in Table III. Polyamides **3** showed high solubility. In particular, polyamide **3a** was soluble in conc. H_2SO_4, dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), hexamethylphosphoric triamide (HMPA), 1-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *m*-cresol, and pyridine. Polyamides **6** exhibited higher solubilities than polyamides **3**; **6a**, **6b**, **6c**, and **6e** were soluble in conc. H_2SO_4, DMSO, DMF, HMPA, NMP, DMAc, *m*-cresol, pyridine, and cyclohexanone. Polyamides **6** indicated higher solubilities than polyamides **3** though T_gs of **6** were as high as those of **3**. This was attributed to the effect of the introduction of a polar and bulky bromo-group into the structures of polyamides.

Conclusion

It is concluded that the introduction of 2,4'-biphenyldiyl structure, which is rigid and zigzag, to the backbones of aromatic polyamides improves the solubility without lowering high thermal stability, and that the introduction of a bromo-group to the structures of aromatic polyamides containing 2,4'-biphenyldiyl structure improves solubility keeping high T_gs, but influences thermal decomposition behavior, lowers T_ds, and heightens residual weight.

EXPERIMENTAL

Material

2-Amino-4'-nitrobiphenyl was prepared by the nitration[13] of 2-aminobiphenyl (Tokyo Kasei Kogyo Co.), and purified by recrystallization from methanol/water mixture (methanol : water = 1 : 20 in volume). mp 157.0—159.0°C (lit.[13] 156.0—158.5°C). 2-Amino-5-bromobiphenyl **7** was synthesized from 2-aminobiphenyl according to the method[22] reported by Scarborough *et al.* mp 57.0—58.0°C (lit.[22] 57.5°C).

2,4'-Biphenyldiamine (1)

Diamine **1** was obtained by the reduction of 2-amino-4'-nitrobiphenyl using a $SnCl_2$–HCl system. The reduction products were purified by distillation twice under reduced pressure
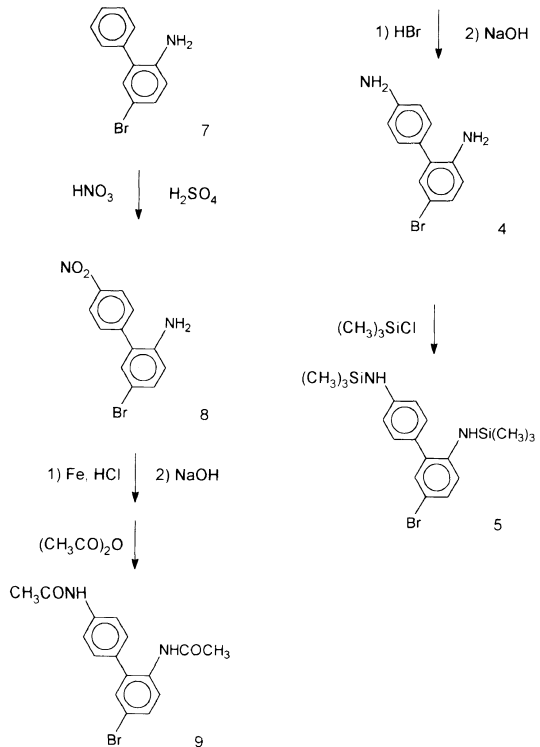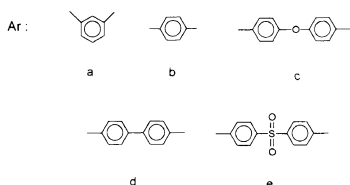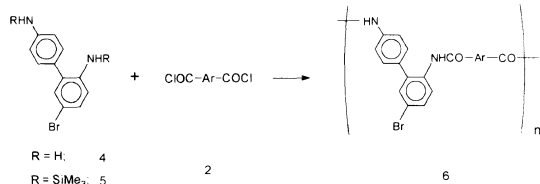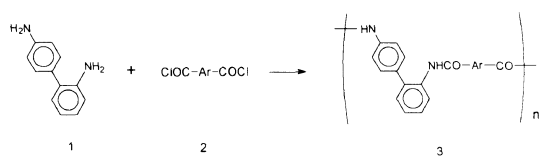
Table III. Polyamide solubilities[a]

Polymer	CHO	Py	*m*-Cre	DMAc	NMP	HMPA	DMF	DMSO	H_2SO_4
3a	(±)	+	+	+	+	(+)	+	+	+
3b	−	±	+	+	+	(+)	SW	+	+
3c	(±)	+	+	+	+	(+)	±	+	+
3d	−	−	(±)	(±)	+	+	(±)	+	+
3e	(±)	±	±	±	+	(+)	−	±	+
6a	(+)	+	+	+	+	+	+	+	+
6b	(+)	+	+	+	+	+	+	+	+
6c	(+)	+	+	+	+	(+)	+	+	+
6d	(±)	(±)	+	+	+	+	+	+	+
6e	+	+	+	+	+	+	+	+	+

[a] Measured at 2.0% (w/v). Data in parentheses were obtained during heating. CHO, Cyclohexanone; Py, pyridine; *m*-Cre, *m*-cresol; DMAc, *N,N*-dimethylacetamide; NMP, 1-methyl-2-pyrrolidone; HMPA, hexamethylphosphoric triamide; DMF, *N, N*-dimethylformamide; DMSO, dimethylsulfoxide.

+, Soluble; ±, partially soluble; −, insoluble; SW, swelling.

Ar: a b c d e

R = H; 4
R = SiMe₃; 5

1) HBr   2) NaOH

HNO₃ | H₂SO₄

(CH₃)₃SiCl | (CH₃)₃SiNH

1) Fe, HCl | 2) NaOH

(CH₃CO)₂O

7, 8, 9

with zinc dust (bp 161.0—163.0°C/1 mmHg). The distillate was a clear oil, but slowly crystallized. mp 56.0—57.0°C (lit.[11,22] 54.0—54.5°C), pale yellow crystals.

IR (KBr disk) 3456 and 3384 cm^{-1} (N–H).

^{13}C-NMR (CDCl₃, 100 MHz, ppm) 115.3 (C₃′, C₅′), 115.4 (C₃), 118.6 (C₅), 127.8 (C₁), 127.9 (C₄), 129.4 (C₁′), 130.0 (C₂′, C₆′), 130.4 (C₆), 143.8 (C₂), and 145.5 (C₄′).

Analysis. Calcd for C₁₂H₁₂N₂ (184.2): C, 78.23%; H, 6.56%; N, 15.20%. Found : C, 78.32%; H, 6.51%; N, 15.34%.

2-Amino-5-bromo-4'-nitrobiphenyl (8)

In a 50-ml four-necked flask equipped with a reflux condenser and thermometer were placed 4.82 g of **7**, 29.0 ml of conc. sulfuric acid, and a magnetic stirrer bar. The mixture was stirred to dissolve the solids, cooled to 0°C, and a mixture of 2.15 ml conc. sulfuric acid and 0.81 ml fuming nitric acid was added dropwise for 50 min. The mixture was stirred below 0°C for 1h, poured into crushed ice, and neutralized with aqueous NaOH solution. The precipitates were filtrated, washed with water, and dried under reduced pressure at 60°C. Crude products were recrystallized from ethanol. Yield 59.8%. mp 149.4°C (DTA).

IR (KBr disk) 3476, 3384, 1624 cm^{-1} (N–H), 1512 and 1350 cm^{-1} (N–O).

Analysis. Calcd for C₁₂H₉N₂O₂Br (293.1): C, 49.17%; H, 3.09%; N, 9.56%. Found: C, 49.10%; H, 2.96%; N, 9.50%.

5-Bromo-2,4'-diacetamidebiphenyl (9)

In a 50-ml four-necked flask equipped with a reflux condenser and thermometer were placed 10.0 g of **8**, 37.2 ml of methanol, 19.0 ml of hydrochloric acid, and a magnetic stirrer bar. Powdered iron (5.8 g) was added for 50 min. The mixture was refluxed for 3 h, and poured into 100 ml 50% aqueous solution of citric acid. The aqueous solution was made basic to litmus with 10% NaOH aqueous solution. The precipitates were filtered and washed with ether three times. The filtrate was

1029

extracted with three portions of ether. The combined ether layer was dried with anhydrous sodium sulfate over night. Ether was removed by evaporation and dark black oil was obtained.

The oil was dissolved in 11.5 ml benzene, and poured into a Erlenmeyer-flask. After acetic anhydride (5.9 ml) was added dropwise, the reaction mixture was allowed to stand over night. The precipitates were filtrated, washed with water, and dried under reduced pressure at 60°C over night. Crude products were purified by recrystallization from ethanol. Yield 60.7%. mp 230.1°C (DTA).

IR (KBr disk) 3280 cm^{-1} (N–H), 1656 and 1528 cm^{-1} (amides -I, -II).

Analysis. Calcd for $C_{16}H_{15}N_2O_2Br$ (347.2): C, 55.35%; H, 4.35%; N, 8.07%. Found: C, 55.21%; H, 4.19%; N, 8.11%.

5-Bromo-2,4'-biphenyldiamine (**4**)

In a 300-ml flask equipped with a reflux condenser were placed 3.02 g of **9**, 60.0 ml of ethanol, and a magnetic stirrer bar. The mixture was stirred on heating to dissolve the solids. Then, 140 ml hydrobromic acid was added. The reaction mixture was refluxed for 10 h, cooled to room temperature. After removal of ethanol with an evaporator, aqueous NaOH solution was added to the residue. The aqueous solution was extracted with three portions of ether and the combined ether-layer was dried with anhydrous sodium sulfate over night. A pale yellow clear oil was obtained by removal of ether with an evaporator. The oil was dried under reduced pressure at 60°C over night. Yield 97.4%.

IR (KBr neat) 3476, 3396, and 1622 cm^{-1} (N–H).

^{13}C-NMR (CDCl$_3$, 125 MHz, ppm) 110.1 (C$_5$), 115.3 (C$_3$·, C$_5$·), 116.9 (C$_3$), 128.1 (C$_1$·), 129.7 (C$_1$), 129.9 (C$_2$·, C$_6$·), 130.4 (C$_6$), 132.7 (C$_4$), 142.8 (C$_2$), and 145.9 (C$_4$·).

Analysis. Calcd for $C_{12}H_{11}N_2Br$ (263.1): C, 54.77%; H, 4.21%; N, 10.65%. Found: C, 54.94%; H, 4.13%; N, 10.36%.

N,N'-Bis(trimethylsilyl)-5-bromo-2,4'-biphenyldiamine (**5**)

In a 10-ml four-necked flask equipped with a reflux condenser having a calcium chloride tube, nitrogen gas inlet, thermometer, and dropping funnel were placed 9.75 ml of triethylamine, 5.97 g of diamine **4**, 42.6 ml of dry benzene and a magnetic stirrer bar. The mixture was stirred to dissolve the solids and trimethylsilyl chloride (6.70 ml) was added dropwise for 1 h. The reaction mixture was stirred at 60°C for 2 h, and refluxed for 25 h, and cooled to room temperature. Triethylamine hydrochloride that formed was removed by filtration with a G3 glass filter, and benzene was removed by distillation. The obtained products were purified by distillation under reduced pressure (169.0—169.2°C/1.8 mmHg). Yield 55.7% (pale yellow clear oil).

IR (neat): 3392, 1518 cm^{-1} (N–H), and 1254 cm^{-1} (Si–C).

Analysis. Calcd for $C_{18}H_{27}N_2BrSi_2$ (407.5): C, 53.05%; H, 6.68%; N, 6.87%. Found: C, 52.82%; H, 6.58%; N, 6.99%.

Aromatic Dicarbonyl Dichlorides (**2**)

Aromatic dicarbonyl dichlorides were synthesized from the corresponding aromatic dicarboxylic acids with thionyl chloride and DMF. 4,4'-Oxydibenzoic acid was prepared by the oxidation[23] of 4,4'-oxyditoluene obtained from Tokyo Kasei Kogyo Co., with potassium permangate in aqueous pyridine. 4,4'-Biphenyldicarboxylic acid was obtained from Tokyo Kasei Kogyo Co. and used as received. 4,4'-Sulfonyldibenzoic acid was obtained from New Japan Chemical Co., Ltd. and used as received. Isophthaloyl dichloride (**2a**) was recrystallized from dry ligroin. Terephthaloyl dichloride (**2b**) and 4,4'-oxydibenzoyl dichloride (**2c**) were recrystallized from dry *n*-hexane. 4,4'-Biphenyldicarbonyl dichloride (**2d**) and 4,4'-sulfonyldibenzoyl dichloride (**2e**) were recrystallized from dry benzene.

Low-Temperature Solution Polycondensation of Diamines with Aromatic Dicarbonyl Dichlorides

A typical procedure is as follows. In a 10-ml reaction tube equipped with a nitrogen gas inlet having a calcium chloride tube were placed 0.1500 g lithium chloride, 0.1842 g diamine **1**, and 2.0 ml NMP. The mixture was stirred to dissolve the solids, cooled to $-18°C$, and 0.2032 g of isophthaloyl dichloride and 0.78 ml of methyloxirane were added. The mixture was stirred at $-18°C$ for 2 h, and at room temperature for 5 h. The reaction mixture was poured into aqueous methanol (MeOH : $H_2O = 1 : 1$ in volume), and the precipitates were collected with a glass filter, washed with hot methanol and dried under reduced pressure at 60°C. Yield 91.8%.

$\eta_{inh} = 0.72 \, dl \, g^{-1}$ (0.5 g dl^{-1} conc. H_2SO_4 at 30°C). IR (KBr disk) 1656 and 1526 cm^{-1} (amides I, II).

Analysis. Calcd for $(C_{20}H_{14}N_2O_4)_n$ $(314.3)_n$: C, 76.42%; H, 4.49%; N, 8.91%. Found: C, 74.06%; H, 4.37%; N, 8.61%.

Other polyamides were synthesized by a similar procedure.

Low-Temperature Solution Polycondensation of N-Silylated Diamine 5 with Aromatic Dicarbonyl Dichlorides

A typical procedure is as follows. In a 10-ml reaction tube equipped with a nitrogen gas inlet having a calcium chloride tube were placed 0.4273 g of *N*-silylated diamine **5** and 1.5 ml of NMP. The mixture was stirred to dissolve the solids, cooled to $-18°C$, and then 0.2927 g of **2d** and 0.5 ml of NMP were added. The mixture was stirred at $-18°C$ for 2 h, and at room temperature for 5 h. The reaction mixture was poured into aqueous methanol (MeOH : $H_2O = 1 : 1$ in volume). The precipitates were collected with a glass filter, washed with hot methanol and dried under reduced pressure at 60°C. Yield 99.9%.

$\eta_{inh} = 0.26 \, dl \, g^{-1}$ (0.5 g dl^{-1} conc. H_2SO_4 at 30°C). IR (KBr) 1660 and 1516 cm^{-1} (amides I, II).

Analysis. Calcd for $(C_{26}H_{18}N_2O_2Br)_n$ $(469.3)_n$: C, 66.54%; H, 3.65%; N, 5.97%. Found: C, 65.11%; H, 3.49%; N, 5.89%.

Other polyamides were synthesized by similar procedures.

Measurements

T_gs were determined by DSC (Rigaku Denki 8230D). T_ds and residual weights were determined by TG (Mac Science TG-DTA 2000). IR spectra were recorded on a Hitachi 270-30 spectrophotometer. ^{13}C NMR spectra were obtained with FT-NMR spectrometer (JEOL JNM-GSX400 or JNM-GSX500).

REFERENCES

1. P. E. Cassidy, "Thermally Stable Polymers," Dekker, New York, N.Y., 1980.
2. F. Akutsu, H. Hirata, H. Hayashi, M. Miura, and K. Nagakubo, *Makromol. Chem., Rapid Commun.*, **6**, 215 (1985).
3. F. Akutsu, H. Hayashi, M. Miura, and K. Nagakubo, *Makromol. Chem., Rapid Commun.*, **6**, 407 (1985).
4. F. Akutsu, H. Hayashi, M. Miura, and K. Nagakubo, *Makromol. Chem., Rapid Commun.*, **6**, 475 (1985).
5. F. Akutsu, K. Matsuo, N. Naruchi, and M. Miura, *Polym. Commun.*, **30**, 182 (1987).
6. F. Akutsu, H. Takeyama, M. Miura, and K. Nagakubo, *Makromol. Chem.*, **186**, 483 (1985).
7. F. Akutsu, A. Suzuki, F. Saitoh, K. Naruchi, M. Miura, and K. Nagakubo, *Makromol. Chem.*, **188**, 1253 (1987).
8. F. Akutsu, T. Kataoka, K. Naruchi, M. Miura, and K. Nagakubo, *Polymer*, **28**, 1787 (1987).
9. Y. Kasashima, K. Yamamoto, N. Ando, F. Akutsu, K. Naruchi, and M. Miura, *Polym. J.*, **26**, 1298 (1994).
10. Y. Kasashima, H. Kumada, K. Yamamoto, F. Akutsu, K. Naruchi, and M. Miura, *Polymer*, **36**, 645 (1995).
11. K. Kuze and S. Miwa, *Kogyo Kagaku Zasshi*, **71**, 443 (1968); *Chem. Abstr.*, **69**, 36507j (1968).

12. V. L. Bell, B. L. Stump, and H. Gager, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2275 (1976).

13. G. D. Mendenhall and P. A. S. Smith, *Org. Syn.*, **46**, 85 (1966).

14. P. Jacobson and R. Grosse, *Justus Liebigs Ann. Chem.*, **303**, 319 (1898).

15. P. W. Morgan, "Condensation Polymers by Interfacial and Solution Methods," Interscience, New York, N.Y., (1965).

16. Y. Oishi, M. Padmanaban, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 3387 (1987).

17. Y. Oishi, M. Kakimoto, and Y. Imai, *Macromolecules*, **20**, 703 (1987).

18. Y. Oishi, M. Kakimoto, and Y. Imai, *Macro-molecules*, **21**, 547 (1988).

19. G. F. L. Ehlers, K. R. Fisch, and W. R. Powell, *J. Polym. Sci., A-1*, **8**, 3511 (1970).

20. H. H. G. Jellinek, "Degradation and Stabilization of Polymers," Vol. 1, Elsevier, Amsterdam, Oxford, New York, 1983.

21. S. Nara and K. Matsuyama, *J. Macromol. Sci. Chem.*, *A*, **5**, 1205 (1971).

22. H. A. Scarborough and W. A. Waters, *J. Chem. Soc.*, **130**, 89 (1927).

23. R. B. Carlin, R. G. Nelb, and R. C. Odioso, *J. Am. Chem. Soc.*, **73**, 1002 (1951).

24. M. Tomita and K. Kimura, *J. Pharm. Soc., Jpn.*, **70**, 44 (1950); *Chem. Abstr.*, **44**, 4448h (1950).