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Synthesis and properties of novel aromatic polyamides containing 2-methyl-4,5-oxazolediyl structure

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Novel aromatic polyamides having 2-methyl-4,5-oxazolediyl units in the main chains were synthesized. The polyamides were prepared from 4,5-di(4-aminophenyl)-2-methyloxazole (DAPMO) and/or 4,4′-[4,5-(2-methyl)oxazole]dibenzoic acid (MODBA) by the direct polycondensation method. The polyamides, the inherent viscosities of which ranged from 0.64 to 1.95 dl g^{-1}, were obtained almost quantitatively. The polyamides indicated high thermal properties: glass transition temperatures were found in the range between 280 and 354°C, and thermal decomposition temperatures ranged from 376 to 421°C. The polyamides exhibited good solubility in many organic solvents such as *m*-cresol, *N,N*-dimethylacetamide, 1-methyl-2-pyrrolidone, *N,N*-dimethyl formamide and conc. H_2SO_4 at 2.0% (w/v). All the polyamides showed amorphous nature. The introduction of the zigzag, rigid and polar 2-methyl-4,5-oxazolediyl structure into the main chains of polyamides was effective in improving the solubility without lowering the high thermal properties. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: aromatic polyamides; solubility; thermal properties)

INTRODUCTION

Wholly aromatic polyamides are well known to be high-performance engineering thermoplastics, and they have been used in various industries owing to their high thermal stability and inert behaviour towards many organic solvents[1]. However, their high softening temperatures and poor solubility in many organic solvents, caused by their rigid structures, make their fabrication difficult. Therefore, a means of improving their processability is required without lowering the high thermal properties. It is known that one of the most effective methods of improving processability is the introduction of a polar, rigid and zigzag structure, such as the 1,2-heteroarylene unit, into the main chains of polyamides[2–7]. We reported previously that polyamides having 1,2-heteroarylene structure, such as 2,3-quinoxalinediyl[8–11], 1,2,4-triazine-5,6-diyl[12,13] and 2-phenyl-4,5-imidazolediyl[14] units, exhibit good solubility and high thermal resistance.

In this study, novel aromatic polyamides containing the 2-methyl-4,5-oxazolediyl structure, which is a rigid and zigzag structure having a heterocycle, in the main chains were synthesized from 4,5-di(4-aminophenyl)-2-methyloxazole (DAPMO) and/or 4,4′-[4,5-(2-methyl)oxazole]dibenzoic acid (MODBA) as the monomer (*Scheme 1*), and their properties were investigated. As for polymers having 4,5-oxazolediyl structure, Carter *et al.* reported poly(arylene ether)s containing 2-(4-sulfonylphenyl)-4,5-oxazolediyl structure[15], but the other polymers have not been reported.

EXPERIMENTAL

4,4′-Di(methoxycarbonyl)benzoin acetate (**6**)

4,4′-Dimethoxycarbonylbenzoin, **5** (Midori Kagaku Co., Ltd) (25.58 g, 0.078 mol), was dissolved in a mixture of acetic anhydride (39 ml) and acetic acid (39 ml) with heating. Conc. sulfuric acid (1.5 ml) was added, and the reaction mixture was stirred at 80°C for 30 min. After cooling to room temperature, the mixture was poured into water (200 ml) for precipitation. The product was collected by filtration, dried under reduced pressure, and recrystallized from ethanol to give pale yellow needles (87% yield), melting point (m.p.) 121.5–122.5°C. Infra-red (i.r.) (KBr, cm^{-1}): 1742, 1720 and 1700 (C=O). Mass spectrometry (MS) (*m/e*): 371 (M^+). Analysis calculated for $C_{22}H_{18}O_7$ (370.4): C, 64.87; H, 4.86. Found: C, 64.87; H, 4.95.

Dimethyl 4,4′-[4,5-(2-methyl)oxazole]dibenzoate (**7**)

6 (2.02 g, 5.95 mmol), ammonium acetate (0.8 g) and acetic acid (5 ml) were placed in a flask, and the mixture was refluxed for 1 h. After cooling, the precipitate formed was collected by filtration, washed with water, and dried under reduced pressure. The product was recrystallized from acetone to give white needles (51% yield), m.p. 177.8–178.3°C. I.r. (KBr, cm^{-1}): 1728 (C=O). MS (*m/e*): 351 (M^+). ^1H nuclear magnetic resonance (n.m.r.) spectroscopy ($CDCl_3$, ppm): 2.58 (s, 3H, $-CH_3$), 3.93 (s, 6H, $-COOCH_3$), 7.50–8.25 (m, 8H, Ar). Analysis calculated for $C_{20}H_{17}O_5N$ (351.4): C, 68.37; H, 4.88; N, 3.99. Found: C, 68.21; H, 4.86; N, 4.12.

MODBA

In a four-necked flask equipped with a dropping funnel, **7** (4.72 g, 1.34 mmol) was dissolved in ethanol (290 ml) on

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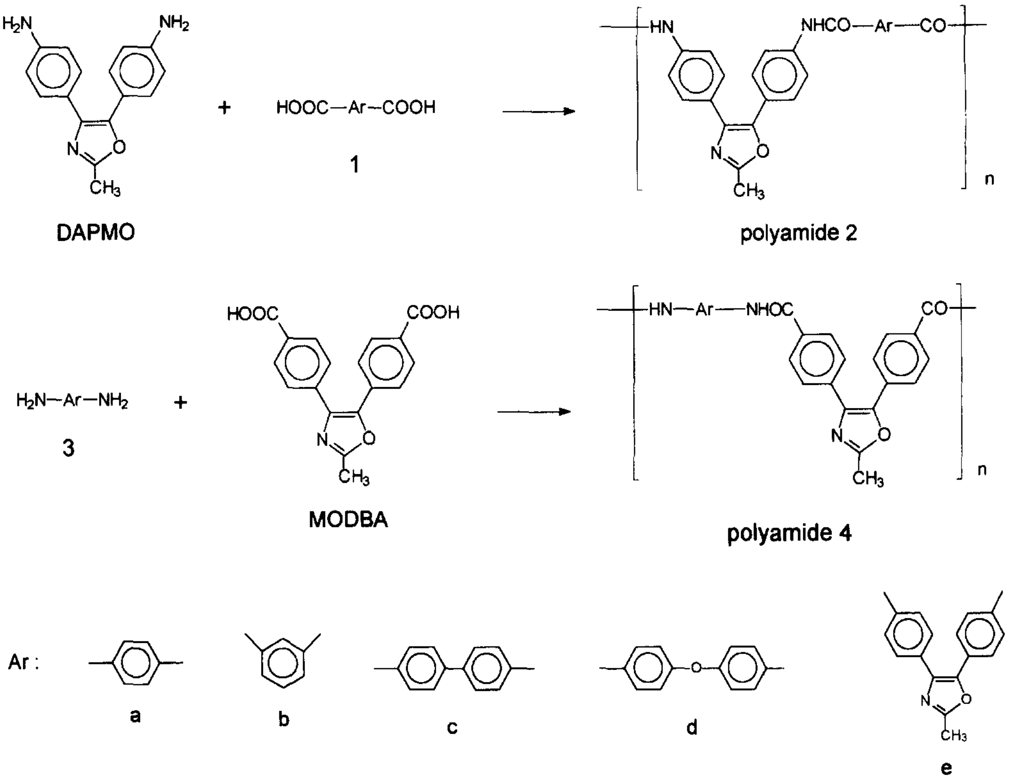


Scheme 1

heating. A solution of potassium hydroxide (2.5 g) in aqueous ethanol (20 ml, 1:1 by volume) was added dropwise, and then refluxed for 3 h. A pale yellow precipitate formed during reflux. After cooling to room temperature, the reaction mixture was acidified with 2 M HCl for further precipitation. The precipitate was filtrated, washed with water, and dried under reduced pressure. The product was dissolved in 1 wt% aqueous potassium hydroxide solution. The solution was filtrated, acidified with 2 M HCl for precipitation again to obtain a white powder (93% yield), m.p. 303°C (d.t.a.). I.r. (KBr, cm^{-1}): 3400–2500 (broad, O–H), 1718, 1686 (C=O). Analysis calculated for $C_{18}H_{13}O_5N$ (323.3): C, 66.87; H, 4.05; N, 4.33. Found: C, 66.92; H, 4.05; N, 4.29.

DAPMO

DAPMO was prepared by the nitration of 2-methyl-4,5-diphenyloxazole[12], followed by the reduction reported by Van Es and Backberg[17], and recrystallized from methanol/water under a nitrogen atmosphere, m.p. 181.0–181.5°C (literature value[13] 178.0–180.0°C). I.r. (KBr, cm^{-1}): 3436, 3360 (N–H). ^{1}H n.m.r. (dimethylsulfoxide-d_6, ppm): 2.40 (s, 3H, $-CH_3$), 5.52 (s, broad, $-NH_2$), 6.57 (m, 4H, Ar–H) 7.17 (d, J = 8.3 Hz, 2H, Ar–H), 7.24 (d, J = 8.5 Hz, 2H, Ar–H). Analysis calculated for $C_{16}H_{15}ON_3$ (265.3): C, 72.43; H, 5.70; N, 15.84. Found: C, 72.26; H, 5.75; N, 15.75.

Other monomers

Aromatic dicarboxylic acids, such as terephthalic acid (**1a**), isophthalic acid (**1b**) and 4,4′-biphenyldicarboxylic acid (**1c**), were used after recrystallization (**1a** and **1b**, from hexane; **1c**, from benzene). *p*-Phenylenediamine (**3a**) was used after recrystallization under a nitrogen atmosphere from dry isopropyl alcohol. *m*-Phenylenediamine (**3b**) was used after distillation under reduced pressure with zinc dust. 4,4′-Diaminodiphenylether (**3d**) was used after recrystallization under a nitrogen atmosphere from dry ethanol with an activated charcoal.

Direct polycondensation

A typical procedure (**4e**) is as follows. Into a four-necked, 10 ml reaction tube equipped with a refluxed condenser, a mechanical stirrer and a nitrogen gas inlet having a calcium chloride tube, were placed lithium chloride (0.082 g), calcium chloride (0.242 g), pyridine (0.8 ml) and 1-methyl-2-pyrrolidone (NMP) (1.8 ml). The mixture was heated with stirring under a nitrogen atmosphere until the salts were dissolved. After the mixture was cooled to room temperature, MODBA (0.647 g, 2.00 mmol), triphenyl phosphite (1.05 ml, 4.00 mmol), DAPMO (0.531 g, 2.0 mmol) and NMP (1.6 ml) were added. The reaction mixture was heated at 115°C for 5 h with stirring. It was then cooled and diluted with NMP (48 ml). The mixture was poured into aqueous methanol (1:1 by volume). The precipitate formed was collected on a glass filter, washed with methanol under reflux and dried under reduced pressure. The obtained polymer was purified by reprecipitation (DMAc/aqueous methanol), and dried under reduced pressure at 100°C [87% yield, η_{inh} = 1.20 dl g^{-1} (0.5 g dl^{-1} in conc. sulfuric acid at 30°C)]. I.r. (KBr, cm^{-1}): 1666, 1518 (amide I, II). Analysis calculated for $(C_{34}H_{24}N_4O_4)_n$ $(552.6)_n$: C, 73.90; H, 4.38; N, 10.14. Found: C, 72.30; H, 4.61; N, 9.91.

Other polyamides were synthesized by a similar procedure.

Measurements

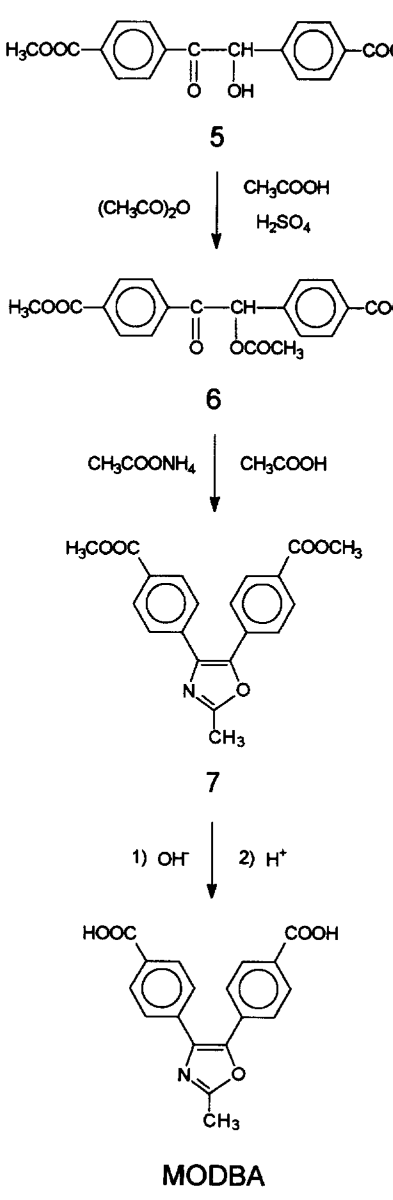
Glass transition temperature (T_g), thermal decomposition temperature (T_d), temperature at 10% weight loss (T_{d10}) and weight residue at 600°C were obtained by thermogravimetric analysis (t.g.a.)–differential scanning calorimetry (d.s.c) (Rigaku TG-DSC 8055D1) under the following conditions: heating rate = 10 K min^{-1}, nitrogen atmosphere.

T_gs were determined by second scannings. I.r. spectra were recorded on a Hitachi 270-30 spectrophotometer. Wide-angle X-ray diffraction patterns were obtained for specimens on a Rigaku KG X-ray diffraction apparatus with Cu K_α radiation (25 kV, 10 mA) on virgin samples. ^1H n.m.r. spectra (400 MHz) were recored on a JEOL JNM-LA 400 FT-NMR spectrometer.

RESULTS AND DISCUSSION

Syntheses of monomers

DAPMO, as the diamine monomer for the polyamide synthesis, was prepared by the nitration of 2-methyl-4,5-diphenyloxazole[16], followed by reduction using stannous chloride and hydrochloric acid according to the method reported by Van Es and Backberg[17]. MODBA, as the novel dicarboxylic acid monomer, was prepared from 4,4′-dimethoxycarbonylbenzoin (**5**) as the starting material as follows: acetylation of **5**, then the formation of an oxazole ring, followed by hydrolysis, as shown in *Scheme 2*. The product was identified by spectroscopic data and elemental analysis as MODBA.



Scheme 2

Table 1 Results of preparations of polyamides

Polymer	Yield (%)	η_{inh} (dl g^{-1})^a	Colour	Appearance^b
2a	99	0.73	pale yellow	H
2b	99	0.64	white	H
2c	98	1.14	pale yellow	H
4a	97	1.01	yellow	H
4b	94	1.00	white	H
4d	92	1.95	yellow	G
4e	87	1.20	yellow	G

^{a}Inherent viscosity, measured in conc. sulfuric acid (0.50 g dl^{-1}) at 30°C
^{b}H, homogeneous system; G, gelation

Synthesis of polyamides

Polyamides **2** were prepared from DAPMO and aromatic dicarboxylic acids **1**. Polyamides **4** were prepared from aromatic diamines **3** and MODBA. Polyamide **4e** was synthesized from **3e** (DAPMO) and MODBA. All polyamides were synthesized by the direct polycondensation method by using lithium chloride, calcium chloride, triphenyl phosphite and pyridine as condensation agents, as reported by Higashi *et al.*[18–20]. Some polycondensations caused gelation during the reaction, others proceeded in a homogeneous system. I.r. spectra of the products showed characteristic amide absorptions near 1670 and 1520 cm^{-1}. The inherent viscosities of the polyamides were middle or high. Those of polyamides **2** were found in the range from 0.73 to 1.14 dl g^{-1}, and those of polyamides **4** ranged between 1.00 and 1.95 dl g^{-1}. The inherent viscosities of polyamides **4** were higher than those of the corresponding polyamides **2**. These results were attributed to the activation of a carboxyl group at the 4-position by the polar oxazole group at the 1-position. The results are summarized in *Table 1*.

Thermal properties of polyamides

T_gs were determined by d.s.c. Polyamides **2** and **4** possessed high T_gs: those of polyamides **2** were found in the range from 293 to 354°C, and those of polyamides **4** ranged from 280 to 321°C. These T_g values were compared with those of the corresponding polyamides having 4,4″-*o*-terphenyldiyl units[21,22]. In the *o*-terphenyl structure, there is the non-polar 1,2-phenylene unit instead of the 2-methyl-4,5-oxazolediyl unit. Therefore, the 4,4″-*o*-terphenyldiyl structure is similar to 2-methyl-4,5-diphenyloxazole structure, but has lower polarity. The T_gs of polyamides **2** and **4** were higher than those of the corresponding polyamides containing 4,4″-*o*-terphenyldiyl structure. This suggested that introduction of the zigzag, rigid and polar 2-methyl-4,5-oxazolediyl structure into the backbones of polyamides maintained high T_g because of the rigidity as well as the intermolecular dipole–dipole interaction owing to the polarity of the oxazole ring.

T_ds, T_{d10}s and weight residues at 600°C were determined by t.g.a. T_ds of polyamides **2** were found in the range from 400 to 415°C, and those of **4** ranged between 376 and 417°C. The weight residues at 600°C of **2** were in the 64–71% range, and those of **4** ranged between 73 and 84%. Thus, the polyamides having 2-methyl-4,5-oxazolediyl structure exhibited high thermal stability. The thermal behaviour of the polyamides **2** and **4** is shown in *Table 2*.

Solubility of polyamides

Solubilities in several organic solvents at 2.0% (w/v) are summarized in *Table 3*. Polyamides **2** indicated good solubility for aromatic polyamides. In particular, polyamide

Table 2 Thermal properties of polyamides

Polymer	T_g (°C)[a]	T_d (°C)[b]	T_{d10} (°C)[c]	Weight residue at 600°C (%)[d]
2a	325	400	486	64
2b	293	403	500	71
2c	354	415	512	71
4a	321	417	513	78
4b	284	376	537	84
4d	280	403	528	80
4e	298	384	506	73

[a] Measured by d.s.c. in a nitrogen atmosphere; heating rate, 10 K min^{-1}

[b] Thermal decomposition temperature, observed by t.g.a. in a nitrogen atmosphere

[c] Temperature at 10% weight loss, observed by t.g.a. in a nitrogen atmosphere

[d] Observed by t.g.a.

2b 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 at room temperature. Polyamides **4** also exhibited good solubility. **4b** and **4d** were soluble in conc. H_2SO_4, DMSO, DMF, HMPA, NMP, DMAc, *m*-cresol and pyridine at room temperature. The introduction of 2-methyl-4,5-oxazolediyl structure improved the solubility of the aromatic polyamide remarkably. The X-ray diffraction patterns showed that polyamides **2** and **4** are all amorphous polymers. One of the factors contributing to the improved solubility was the characteristic amorphous nature induced by the introduction of zigzag 2-methyl-4,5-oxazolediyl structure.

The solubility of polyamides **2** and **4** was compared with that of the corresponding polyamides having 4,4″-*o*-terphenyldiyl moieties. Polyamides **2** and **4** indicated as good solubility as the corresponding polyamides having 4,4″-*o*-terphenyldiyl structure, although the T_gs of **2** and **4** were higher. It was considered that the dipole–dipole interaction between the molecular chains of polyamides heightened the T_g; on the other hand, the amorphous nature and the interaction between the molecular chains and the polar solvent improved the solubility.

We reported previously that polyamides having a rigid and zigzag structure, such as 2,3-quinoxalinediyl and 4,4″-*o*-terphenyldiyl units, in the diamine moiety show properties differing from those of the corresponding polyamides having the rigid and zigzag structure in the dicarboxylic acid moiety[11,21]. Therefore, the properties of polyamides **2** were compared with those polyamides **4**. Polyamides **2** have 2-methyl-4,5-oxazolediyl structure in the diamine unit while polyamides **4** contain this structure in the dicarboxylic acid unit. The solubility of **2a** and **2b** was as good as that of **4a** and **4b**, respectively. T_gs of **2a** and **2b** were also as high as those of **4a** and **4b**, respectively. Thus, a wide difference between the properties of **2** and those of **4** did not appear.

Polyamide **4e**, containing 2-methyl-4,5-oxazolediyl structure in the diamine unit as well as in the dicarboxylic acid unit, indicated high T_g (298°C) and improved solubility. The T_g of **4e** was higher than that of **4b**, which has has both oxazolediyl and *m*-phenylene structures. The solubility of **4e** was lower than that of **4b**, although the main chain of **4e** is more zigzag. These properties of **4e** may be influenced by the stronger intermolecular dipole–dipole interaction between polyamide molecules of **4e**.

CONCLUSION

It is concluded that introduction of the 2-methyl-4,5-oxazolediyl structure, which is rigid, zigzag and polar, into the backbones of aromatic polyamides improves their solubility without lowering the high thermal properties. The improved solubility was a consequence of the amorphous nature of the polyamides and the dipole–dipole interaction between the molecular chains of the polyamides and the polar solvent. The rigidity and polarity of the 2-methyl-4,5-oxazolediyl structure maintained the high thermal stability of the polyamides.

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Table 3 Solubilities[a] of polyamides

Polymer	Cy	Py	*m*-Cre	DMAc	NMP	HMPA	DMF	DMSO	H_2SO_4
2a	±	±	+	+	+	+	(+)	±	+
2b	±	+	+	+	+	+	+	+	+
2c	±	±	+	±	+	+	+[b]	±	+
4a	−	±[b]	+	+	+	+	+[b]	+	+
4b	−	+	+	+	+	+	+	+	+
4d	−	+	+	+	+	+	+	+	+
4e	−	+[b]	+	+	+[b]	±	+[b]	±	+

[a] Measured at 2.0% (w/v). Data in parentheses were obtained during heating. The symbols have the following meanings: +, soluble; ±, partially soluble; −, insoluble; SW, swelling

[b] Addition of lithium chloride

Cy, 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

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