Synthesis and Properties of Polyamides and Copolyamides Based on 2,6-Naphthalene Dicarboxylic Acid

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SYNOPSIS

A number of polyamides based on 2,6-naphthalene dicarboxylic acid (NDA) and various aromatic diamines were synthesized in N-methyl pyrrolidone (NMP) containing lithium chloride (LiCl) or calcium chloride (CaCl₂) by direct polycondensation using triphenyl phosphite and pyridine. The best reaction conditions for polycondensation were determined in terms of factors such as the amount of the solvency-promoting reagent such as LiCl or CaCl₂ and the initial reactant concentration. Thus, almost all polyamides were obtained with inherent viscosities above 1.0 and up to 3.28 dL/g. Similarly, high molecular weight copolyamides with inherent viscosities of 1.76–3.61 dL/g were prepared from 4,4'-oxydianiline (ODA) and mixed dicarboxylic acids of NDA/terephthalic acid (TPA) or NDA/isophthalic acid (IPA). The solubility of NDA homopolyamides depended on the diamine components. The polyamides derived from meta-, sulfone-, or alkylene-linked diamine showed increased solubility. Copolymerization of ODA with NDA/IPA led to a significant increase in solubility, whereas with NDA/TPA, it gave a limited improvement. All the homopolyamides and copolyamides showed an amorphous X-ray diffraction pattern. Almost all the polymers soluble in aprotic solvents can be solution-cast into strong and tough films. Glass transition shifts of some NDA polyamides can be observed in the differential scanning calorimetry (DSC) curves ranging from 243 to 345°C. Most NDA/IPA–ODA copolyamides also showed clear transitions in the range of 255–268°C. In nitrogen, all the polymers showed no significant weight loss up to 400°C, and their 10% weight loss temperatures were recorded in the range of 434–541°C. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Wholly aromatic polyamides exhibit a number of useful properties such as high thermal stability and chemical resistance, low flammability, and excellent mechanical properties. They are of considerable interest as flame-resistant and ultrahigh-strength/high-modulus fibers and high-performance engineering plastics.[1,2]

Some very high melting polyesters such as poly(1,4-phenylene terephthalate) (polymer melting temperature [PMT] > 500°C) can be modified with the rodlike comonomer, 2,6-naphthalene dicarboxylic acid (NDA), to reduce their melting points, but not their degree of crystallinity. The crankshaft conformation of the 2,6-naphthalene ring structure does not appear to reduce the liquid crystallinity of these polyesters.[3] Less is known about the polyamides and copolyamides of NDA. Earlier, Starr[4] demonstrated the preparation of wholly aromatic polyamides from 2,6-naphthalene dicarboxylic acid chloride and m-phenylenediamine by the interfacial polycondensation technique. However, the resulting polyamides were of relatively low molecular weight. High molecular weight wholly aromatic polyamides were developed by various workers at DuPont[5-10] in the 1960s using low-temperature solution polycondensation with diacid chlorides and diamines. Some dopes comprising NDA polyamides in suitable liquid media were found to be optically anisotropic. These were used in preparing fibers of exceptionally high tensile properties.

In 1975, Yamazaki and co-workers[11] reported an

elegant synthesis for aromatic polyamides that involved the direct polycondensation of aromatic amino acids or aromatic dicarboxylic acids with aromatic diamines in the presence of an aryl phosphite and an organic base. This technique has been widely used for the syntheses of novel aromatic polyamides.[12-14] An aromatic polyamide[15] has already been prepared from NDA and p-phenylenediamine using this type of reaction; however, a systematic study on this type of polyamide is absent. In this article, we have extended this technique to the preparation of a series of NDA polyamides and two 4,4'-oxydianiline series of copolyterephthalamides and copolyisophthalamides. Solubility, thermal behavior, and other properties of these naphthalene ring-containing polyamides are also described.

EXPERIMENTAL

Materials

Reagent-grade aromatic dicarboxylic acids consisting of 2,6-naphthalene dicarboxylic acid (NDA), terephthalic acid (TPA), and isophthalic acid (IPA) were supplied by Tokyo Chemical Industry (TCI) Co. p-Phenylenediamine (I_a) and m-phenylenediamine (I_b) were distilled under vacuum prior to use. 2,5-Bis(4-aminophenyl)-3,4-diphenylthiophene (I_n) was synthesized from tetraphenylthiophene,[16] which, in turn, was easily obtained by the reaction of benzyl chloride with powdered sulfur at an elevated temperature. 9,9-Bis[4-(p-aminophenoxy)phenyl]fluorene (I_o) was prepared starting from the condensation of 9,9-bis(4-hydroxyphenyl)fluorene with p-chloronitrobenzene,[17] followed by the reduction of the dinitro compound. Other diamines were of high purity as received from the manufacturers and were used without any further purification. They include 2,4-diaminotoluene (I_c) (TCI); 4,4'-oxydianiline (I_d) (TCI); 3,4'-oxydianiline (I_e) (from Teijin Ltd., Tokyo); 4,4'-thiodianiline (I_f) (TCI); 4,4'-methylenedianiline (I_g) (TCI); 1,4-bis(4-aminophenyl)benzene (I_h); (TCI); 1,3-bis(4-aminophenoxy)benzene (I_i) (Chriskev); 2,2-bis[4-(4-aminophenoxy)phenyl]sulfone (I_j) (Chriskev); 2,2-bis(4-aminophenyl)hexafluoropropane (I_l) (Chriskev); and 9,9-bis(4-aminophenyl)fluorene (I_m) (Chriskev). Commercially obtained anhydrous lithium chloride and calcium chloride were dried under vacuum at 150°C for 6 h and at 180°C for 10 h, respectively. N-Methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular seives. Triphenyl phosphite (TCI) was purified by distillation under reduced pressure.

Polymerization

A typical example of polymerization is as follows: A mixture of 0.27 g (1.25 mmol) of NDA, 0.25 g (1.25 mmol) of ODA (i.e., diamine I_d), 0.15 g of lithium chloride, 0.25 g of calcium chloride, 0.7 mL of pyridine, 0.8 mL of triphenyl phosphite, and 4 mL of NMP was heated with stirring at 100°C under nitrogen. The polymer solution was too viscous to stir after 1 h and was diluted gradually with an additional 10 mL of NMP to maintain smooth stirring for a further 3 h. The polymer solution obtained was trickled into 500 mL methanol, giving a stringy yellow precipitate that was washed thoroughly with methanol and hot water, collected by filtration, and dried. The yield was 0.50 g (98%). Inherent viscosity of the polymer in DMAc + 5 wt % LiCl was 3.28 dL/g.

ANAL: Calcd for $(C_{24}H_{16}N_2O_3)_n$ (380.39): C, 75.77%; H, 4.24%; N, 7.37%.
Found: C, 72.27%; H, 4.77%; N, 7.0%.

All other polymers were prepared by a similar procedure.

Measurements

Elemental analyses were run in a Perkin-Elmer Model 240 C, H, N analyzer. IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. The inherent viscosities were measured with a Cannon-Fenske viscometer thermostated at 30°C.

The DSC traces were measured on a Sinku-Riko 7000 differential scanning calorimeter coupled to a Sinku-Riko TA 7000 thermal analyzer at the rate of 20°C/min in flowing nitrogen (30 cm³/min). Thermogravimetry (TG) was conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen (50 cm³/min) at a heating rate of 20°C/min.

The wide-angle X-ray measurements were performed at room temperature (about 25°C) with film (or powder) specimens of about 0.1 mm thick on a Rigaku Geiger Flex D-Max IIIa X-ray diffractometer, using Ni-filtered CuKα radiation (40 kV, 15 mA). The scanning rate was 2°/min.

An Instron universal tester Model 1130 with a load cell 5 kg was used to study the stress–strain behavior of the samples. A gauge of 2 cm and a strain rate of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.1 mm thick) and an average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Polymer Synthesis

Aromatic polyamides (aramids) of 2,6-naphthalene dicarboxylic acid (NDA) were synthesized by the direct polycondensation technique, which was carried out under 100°C by reacting NDA with aromatic diamines in the solvent NMP with triphenyl phosphite/pyridine (TPP/Py) as the condensing agent and calcium chloride or lithium chloride as the solvency-promoting agent. To obtain polymers of high molecular weight in this polycondensation reaction, although the reaction conditions required may be different due to the different kinds of diamines used, the optimum polymerization condition seems to depend upon two main factors: The first is the monomer concentration during the initial period of reaction; the second is the amount of calcium chloride or lithium chloride. Take the reaction of NDA with 4,4'-oxydianiline (ODA; I_d) as an example. The reaction conditions and results are tabulated and shown in Table I. The reactions were carried out

with a reaction scale of 2.5 mmol of each monomer and the solvent dosage of 6–8 mL, and the effect of adding $CaCl_2$ to the polymerization was investigated. With the $CaCl_2$ addition below 0.5 g, the reaction solution was milky throughout the reaction and the inherent viscosity (η_{inh}) of the product could not be over 1.0 dL/g. As the $CaCl_2$ addition was increased to 0.8 g, the reaction system was homogeneously transparent, and 1 h after the reaction, the viscosity of the solution increased to gelation (a state of non-agitability). If some additional NMP was added gradually before gelation, a degree of agitation could be maintained (the addition was about 20 mL or higher) and the inherent viscosity of the resultant polymer could be increased to 3.12 dL/g. However, if more solvent was used at the initial period, e.g., 16 mL, the inherent viscosity was much lower than in the case of increasing the solvent gradually. When $CaCl_2$ was replaced with LiCl, the situation was similar: The solution might become turbid (whitened) at low LiCl concentration, and as the LiCl addition was increased to 0.75 g, the inherent viscosity might attain 2.66 dL/g. The result was also very good when adding $CaCl_2$ and LiCl simultaneously, e.g., when adding 0.5 g of $CaCl_2$ and 0.3 g of LiCl, and by increasing the solvent dosage gradually, polymers of even higher inherent viscosity (η_{inh} = 3.28 dL/g) could be obtained.

Polyamides of different molecular structures synthesized through the direct polycondensation by reacting NDA with aromatic diamines (I_{a-o}) of various structures are shown in Scheme 1. Synthesis conditions and inherent viscosities of the produced

Table I   Effect of Reaction Conditions on the Preparation of Polyamides II_d from 2,6-Naphthalene Dicarboxylic Acid (NDA) and 4,4'-Oxydianiline (ODA)[a]

| Run | Amount of Reagents[b] | | | | | | Polymer | |
	Initial NMP (mL)	CaCl₂ (g)	LiCl (g)	Py (mL)	TPP (mL)	Additional NMP (mL)	η_{inh}[c] (dL/g)	Remark[d]
1	6	0.25	—	1.6	1.5	—	0.70	P
2	8	0.50	—	1.6	1.5	—	0.80	P
3	8	0.80	—	1.6	1.5	20–24	3.12	S
4	16	0.80	—	1.6	1.5	12	2.20	S
5	8	—	0.50	1.4	1.5	—	0.70	P
6	6	—	0.75	1.4	1.5	20–28	2.66	S
7	8	0.50	0.30	1.4	1.5	20	3.28	S
8	16	0.50	0.20	1.6	1.5	—	1.81	S

[a] In each polymerization, 2.5 mmol monomers were used, i.e., 0.54 g of NDA and 0.51 g of ODA. Reaction temperature = 100°C; reaction time = 3 h.

[b] Py: pyridine; TPP: triphenyl phosphite.

[c] Measured at a polymer concentration of 0.5 g/dL in DMAc + 5 wt % LiCl at 30°C.

[d] Appearance of the reaction mixtures: S, homogeneous solution throughout the reaction, P, precipitation occurred during the reaction.

HOOC—⬡⬡—COOH + NH₂–Ar–NH₂ $\xrightarrow{- H_2O}$ II

I_{a-o}

II_{a-o}

Ar :

a   b   c   d   e   f

g   h   i

j   k

l   m

n   o
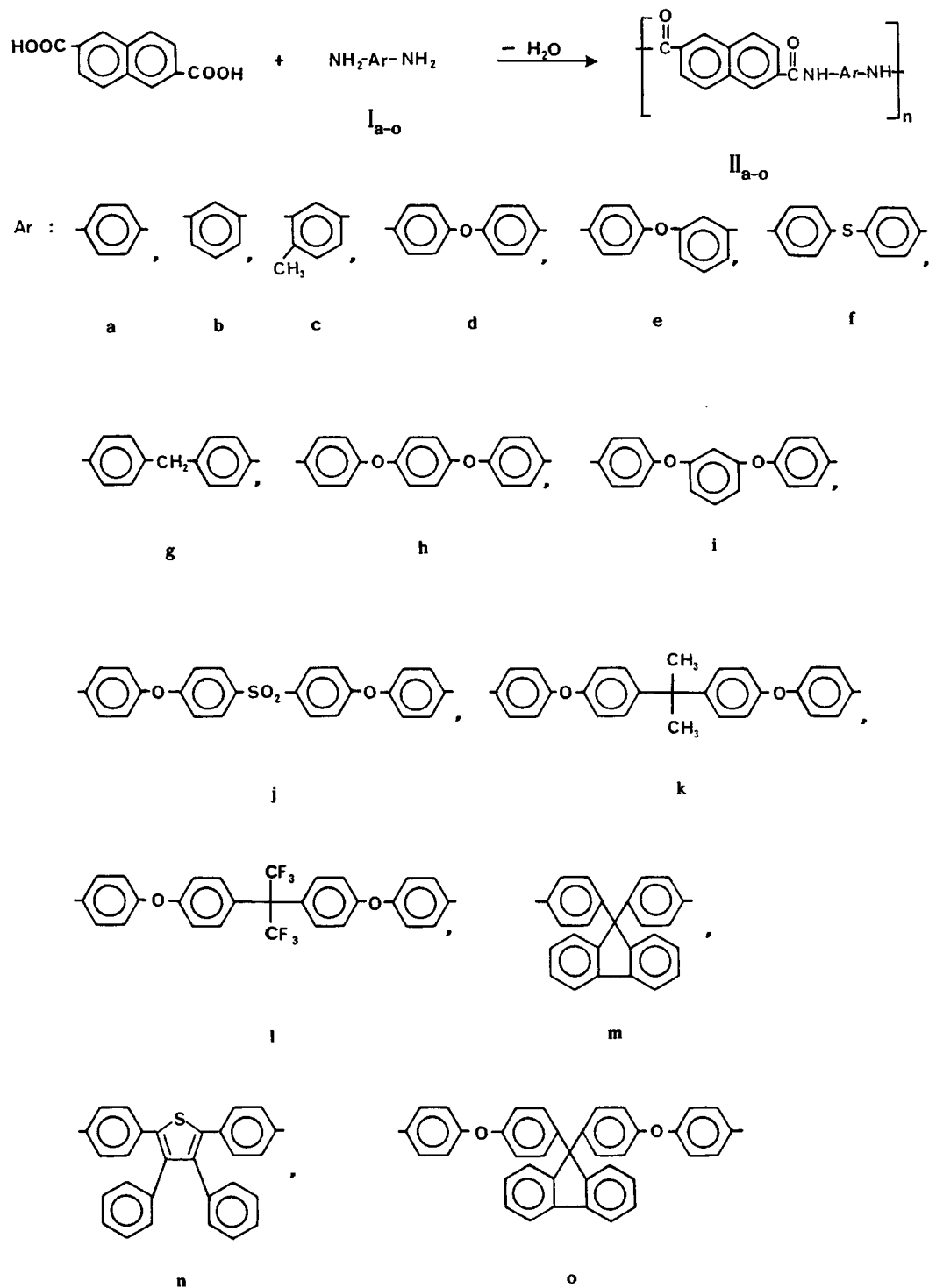
Scheme 1

polymers are shown in Table II. In each case, 1.25 mmol of monomers was used; except for diamines I_a and I_n, the initial dosage of NMP was 3–4 mL for all diamines and the dosage of $CaCl_2$ or LiCl was 0.3–0.4 g. Under these conditions, except for the case

of polymer II_a, the reaction solution was homogeneously transparent, and the inherent viscosity of polyamides obtained was above 1.00 dL/g for almost all other cases. For such polymers, η_{inh} values higher than 1.00 dL/g are usually indicative of high mo-

Table II Preparation of Polyamides from NDA and Diamines I$_{a-o}$

Polymer	Reaction Condition[a]						η_{inh}[b] (dL/g)
	Initial NMP (mL)	CaCl$_2$ (g)	LiCl (g)	Py (mL)	TPP (mL)	Additional NMP (mL)	
II$_a$	4.0	—	0.40	0.8	0.8	—	1.66[c]
	8.0	0.50	0.10	1.0	0.8	—	1.12[c]
II$_b$	3.0	—	0.40	0.6	0.8	—	1.36[d]
II$_c$	3.0	—	0.40	0.8	0.8	—	1.03
	3.0	0.30	—	0.7	0.8	2.5	1.80
II$_d$	4.0	0.25	0.15	0.7	0.8	10.0	3.28[e]
II$_e$	4.0	—	0.40	0.7	0.8	—	1.09
	3.5	0.40	—	0.7	0.8	3.0	1.70
II$_f$	4.0	—	0.40	0.7	0.8	—	1.21[e]
	3.0	0.22	0.08	1.0	0.8	2.0	1.99[e]
II$_g$	4.0	—	0.40	0.7	0.8	—	1.36[e]
II$_h$	3.5	—	0.40	0.6	0.8	2.5	1.57[e]
II$_i$	4.0	—	0.40	0.7	0.8	2.0	2.77[e]
II$_j$	4.0	—	0.40	0.7	0.8	2.0	1.06
	3.5	0.40	—	0.6	0.8	1.0	1.28
II$_k$	4.0	—	0.40	0.7	0.8	–	0.94
	3.5	0.40	—	0.7	0.8	3.0	1.60
II$_l$	3.5	0.40	—	0.7	0.8	3.0	1.39
II$_m$	4.0	0.40	—	0.8	0.8	4.0	1.39
II$_n$	6.0	—	0.60	0.8	0.8	3.0	1.99
II$_o$	3.0	0.30	—	0.8	0.8	4.0	1.08

[a] In each polymerization, 1.25 mmol monomers were used, i.e., 0.27 g of NDA and the equivalent quantities of diamines. Reaction temperature = 100°C; time = 3 h.
[b] Measured in DMAc at a polymer concentration of 0.5 g/dL at 30°C.
[c] In concd H$_2$SO$_4$.
[d] In NMP.
[e] In DMAc + 5 wt % LiCl.

lecular weights. Even though the purpose of adding inorganic chlorides is, in general, to promote solvency, the results shown in Tables I and II show that the chloride addition also affects the degree of polymerization, and it is observed that for the direct preparation of polyamides of such a series, the addition of CaCl$_2$ seems to show a better effect on the degree of polymerization than does the sole addition of LiCl. Under the above-mentioned reaction conditions, the polyamide II$_a$ formed by the polycondensation of NDA with p-phenylenediamine precipitated, giving rise to a milky reaction solution, but its inherent viscosity attained was 1.66 dL/g. However, if the initial solvent dosage increased, say, to 8 mL, then homogeneously transparent polymerization solutions could be acquired, but the inherent viscosity did not increase and, instead, decreased.

Despite the fact that the direct polycondensation between NDA and ODA (I$_d$) may produce aramids of a high degree of polymerization, for the time being NDA is not in mass production and its price is high.

Therefore, the following is the synthesis of copolyamides by reacting ODA with mixed diacids of NDA and terephthalic acid (TPA) or isophthalic acid (IPA) for investigating their properties. The copolymer compositions, reaction conditions, and polymerization results are summarized in Table III. Under the conditions of Table III, the copolymers (III$_{a-e}$) of the NDA/TPA-ODA series have higher inherent viscosities; η_{inh} is greater than 3.00 dL/g, whereas the copolymers (IV$_{a-f}$) of the NDA/IPA-ODA series have relatively lower inherent viscosities and have a tendency to decreasing inherent viscosities with increasing IPA content. Because the solubilities of the copolymers (IV) of such a series are better, the quantities of metal chlorides and solvents need not be high during the polycondensation reaction, and polymers of a high degree of polymerization can still be obtained.

The elemental analysis results of these polyamides showed that the found values of carbon were lower than the calculated ones for the proposed

structures. This may be attributed to the hygroscopic characteristics of the amide group. The moisture uptakes for polyamides II_{a-n} were in the range of 2.51–5.88%. The corrected values were in good agreement with the calculated ones after deducting the amount of moisture uptake.

Properties of Polymers

Solubility

The qualitative solubility behavior of all the NDA homopolyamides (II_{a-o}) is shown in Table IV. These solubilities vary with the structures of the diamines. If the aromatic diamines for the polycondensation reaction with NDA are of asymmetrical structures, e.g., m-phenylene (I_b), 2,4-tolylene (I_c), and those containing the isopropylidene (I_k), sulfonyl (I_j), fluorenylidene (I_m), or bisphenoxyfluorene (I_o) group, the resultant polyamides show better solubility and are readily soluble in DMAc, NMP, etc. If the aromatic rings of diamines are of symmetric disubstituted structures, e.g., those of p-phenylene diamine (I_a), 4,4'-diaminodiphenyl sulfide (I_f), 4,4'-diaminodiphenyl methane (I_g), and diamines I_d and I_h (containing the p-phenoxy group), they cannot easily dissolve in the polar solvents without a metal salt also dissolved. However, except for the p-

phenylenediamine (I_a)-derived polyamide II_a, they are all soluble in DMAc or NMP containing LiCl; this is because salts such as LiCl or $CaCl_2$, etc., have a promoting action for solubility of polyamides in amide-type polar solvents. However, polymer II_a can be dissolved only in concentrated sulfuric acid.

The solubilities of copolyamides of the NDA/TPA–ODA (III_{a-e}) series and the NDA/IPA–ODA (III_{a-f}) series, together with TPA–ODA (III_f) and IPA–ODA (IV_g) homopolyamides, are also summarized in Table V. These solubilities depend upon the kinds of dicarboxylic acids copolymerized and the quantities used. As for the NDA/TPA–ODA series, those containing TPA of 20–50 mol % increase solubility and can dissolve in NMP, whereas solubilities of the rest do not change significantly and show a tendency to decrease as the TPA content increases. The solubilities of copolyamides of the NDA/IPA–ODA series increase with increasing IPA content. When the IPA content increases to 80%, the copolyamide can dissolve in DMAc, NMP, DMF, and DMSO and also in m-cresol and pyridine.

Tensile Properties of Polymer Films

Some films of homopolyamides and copolyamides were prepared with 10% polymer solutions of DMAc or NMP and prepared in DMAc or NMP containing

Table III   Preparation of Copolyamides from 4,4'-Oxydianiline (ODA) and Mixed Diacids[a]

Polymer	Mole Ratio[b] of NDA/TPA or NDA/IPA	Reaction Conditions					
		$CaCl_2$ (g)	LiCl (g)	Py (mL)	TPP (mL)	NMP[c] (mL)	η_{inh}[d] (dL/g)
II_d	(100/0)	0.50	0.30	1.25	1.5	8 + 10	3.28
III_a	(80/20)	0.50	0.25	1.25	1.5	8 + 8	3.16
III_b	(70/30)	0.50	0.25	1.25	1.5	8 + 8	3.51
III_c	(50/50)	0.25	—	1.25	1.5	6 + 6	3.46
III_d	(30/70)	0.25	—	1.25	1.5	6 + 6	3.15
III_e	(20/80)	0.50	0.25	1.25	1.5	8 + 8	3.36
III_f	(0/100)	0.50	0.30	1.25	1.5	6 + 6	2.91
IV_a	(80/20)	0.50	0.30	1.25	1.5	8 + 8	2.98
IV_b	(70/30)	0.50	0.30	1.25	1.5	6 + 0	2.29
IV_c	(60/40)	0.25	—	1.25	1.5	6 + 0	2.34[e]
IV_d	(50/50)	0.25	—	1.25	1.5	6 + 0	1.97[e]
IV_e	(40/60)	0.25	—	1.25	1.5	6 + 0	2.10[e]
IV_f	(20/80)	0.25	—	1.25	1.5	6 + 0	1.76[e]
IV_g	(0/100)	0.25	—	1.25	1.5	6 + 0	1.05[e]

[a] In each case, 0.5 g of ODA (2.5 mmol) and equivalent quantities of diacid or mixed diacids were used. Reaction temperature = 100°C; time = 3 h.

[b] TPA: terephthalic acid; IPA: isophthalic acid. Copolymers of the IV series were derived from mixed diacids NDA/TPA, and those of the V series were obtained from NDA/IPA.

[c] First number refers to an initial amount of NMP and second number refers to an additional amount of NMP.

[d] Measured in DMAc + 5 wt % LiCl at a polymer concentration of 0.5 g/dL at 30°C.

[e] DMAc.

Table IV Solubility of Polyamides and Copolyamides[a]

Polymer	Solvent[b,c]					
	DMAc	DMF	NMP	DMSO	m-Cresol	Py
II$_a$	−	−	−	−	−	−
II$_b$	+	−	+	−	−	−
II$_c$	+	−	+	+	−	−
II$_d$	−	−	−	−	−	−
II$_e$	+	+	+	+	+	+
II$_f$	−	−	−	−	−	−
II$_g$	−	−	−	−	−	−
II$_h$	−	−	−	−	−	−
II$_i$	+	−	+	−	−	−
II$_j$	+	+	+	+	+	+−
II$_k$	+	−	+	+	+	+
II$_l$	+	+	+	+	+	+
II$_m$	+	+	+	+	+	+
II$_n$	+	−	+	−	−	−
II$_o$	+	+	+	+	+	+
III$_a$	−	−	+	−	−	−
III$_b$	−	−	+	−	−	−
III$_c$	−	−	+	+−	−	−
III$_d$	−	−	−	−	−	−
III$_e$	−	−	−	−	−	−
III$_f$	−	−	−	−	−	−
IV$_a$	−	−	+	−	−	−
IV$_b$	+	−	+	+−	−	−
IV$_c$	+	−	+	+	−	−
IV$_d$	+	+−	+	+	−	−
IV$_e$	+	+	+	+	−	−
IV$_f$	+	+	+	+	+	+
IV$_g$	+	+	+	+	+	+

[a] Solubility: (+) soluble at room temperature, (+−) partially soluble, and (−) insoluble.

[b] DMAc, N,N-dimethylacetamide; DMF, N,N-dimethylformamide; NMP, N-methyl-2-pyrrolidone; DMSO, dimethyl sulfoxide; and Py, pyridine.

[c] All the polymers were soluble in concd H_2SO_4; all were soluble in DMAc + 5% LiCl except for **II**$_a$.

1% LiCl for those insoluble in the pure solvents. Their mechanical properties were tested with an Instron machine. The results are shown in Table V. As a whole, tensile strengths at the breaking point of all films are in the range of 44–111 MPa. The elongation rate at the breaking point is between 7–46%, and the initial modulus is between 1.0 and 2.9 GPa. Those homopolyamides derived from 3,4'-oxydianiline (**I**$_e$) and the diamines containing the sulfonyl (**I**$_j$), isopropylidene (**I**$_k$), or hexafluoroisopropylidene (**I**$_l$) group and all the copolyamide films show obvious yielding points, and their breaking-point strengths are all greater than 55 MPa and have moderate elongation rates (as shown in Table VI). The polyamide **II**$_b$ synthesized by the direct polycondensation of NDA with m-phenylenediamine shows a higher degree of polymerization and better

mechanical properties than does the same polymer synthesized by interfacial polycondensation described in the reference article.[4]

Even though polymer **II**$_d$ of NDA and ODA has a very high inherent viscosity, it does not dissolve in pure DMAc or NMP, so that its film is not easily made. Polymer **II**$_d$ is soluble in hot NMP containing LiCl (1–2%) and can be cast into film; however, due to the effects of salts, the film shrinks, causing its mechanical properties to become worse. Nevertheless, copolymer **III**$_a$ prepared by adding 20% of TPA shows better solubility and mechanical properties: Tensile strength increases from 44 to 78 MPa, elongation at break also from 7 to 36%, and a yield point also appears. At the molar ratio of TPA/NDA equal to 1, the polymer film (**III**$_c$) shows excellent tensile properties: tensile strength 111 MPa, elongation to

Table V Tensile Properties of Aramid Films

Polymer[a]	Strength at Yield (MPa)	Strength at Break (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
II_{b_b}	—	66	9	2.3
II_{c_c}	—	92	9	1.8
II_d	—	44	7	1.0
II_{e_b}	85	93	20	2.2
II_{f_b}	—	83	25	1.5
II_h	—	79	7	1.4
I_i	—	75	9	1.2
I_j	61	62	13	1.4
II_k	72	76	23	1.7
II_l	73	76	14	2.1
II_m	—	78	6	1.9
II_n	—	71	16	1.8
II_o	—	99	11	2.5
III_a	76	78	36	1.9
III_b	67	99	39	2.0
III_c	110	111	42	2.9
IV_a	70	73	46	1.5
IV_c	54	55	16	1.0
IV_e	66	65	17	1.7
IV_f	68	70	18	2.1
IV_g	—	79	20	1.7

[a] The polymer samples of III_c, III_e, III_f, III_j, and III_k with the higher inherent viscosity (as shown in Table II) were chosen for film casting. The polymer films were cast from polymer solutions in DMAc, unless otherwise indicated.

[b] Films were cast from polymer solution of DMAC containing 1 wt % LiCl.

[c] Films were cast from polymer solution of NMP containing 1 wt % LiCl.

break 42%, initial modulus 2.9 GPa, and yield strength 110 MPa. The copolymers of the **IV** series containing the IPA moiety did not only show better solubilities but also were easy to form into films, and they showed yield points and good toughness in tension. As a whole, copolymers of series **III** containing TPA moieties show better mechanical properties than those of series **IV** containing IPA moieties, but as regards solubility for processing, the latter are better. All the homopolyamides, except for II_a, and both of the NDA/TPA–ODA and NDA/IPA–ODA series copolyamides are amorphous in nature as revealed by the wide-angle X-ray diffractograms.

Thermal Properties

Thermal properties of all the homopolyamides and copolyamides were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results are summarized in Table VI. All the NDA homopolyamides showed no ob-

vious weight loss below 400°C, and their 10% weight loss temperatures in nitrogen were in the range of 472–532°C. They left a charcoal yield above 50% when heated to 800°C in nitrogen. The thermal stability of polymers depends upon the structure of diamine units; for example, II_a containing p-phenylene units and II_d and II_h containing symmetrical arylene ether chains are more stable, 10% weight loss temperatures are all close to 500°C, and the initial decomposition temperatures are also above 460°C, a little higher than II_b containing the m-phenylene unit and II_e and II_i containing meta-substituted arylene ether and the aliphatic chain, respectively. Typical TG curves in both air and nitrogen atmospheres of representative NDA homopolyamides II_a and II_b are shown in Figure 1. Above 500°C in air, an obvious decrease in weight occurred due to the heat and oxidation decomposition.

The glass transition temperature (T_g) was measured by DSC at the heating rate of 20°C/min. The polymers were heated to about 350°C and then quenched to room temperature to form more amor-

Table VI   Thermal Properties of Copolyamides

Polymer	DSC[a] T_g (°C)	TGA[b] Temp (°C) at 5 Wt % Loss	Residual Wt % at 800°C
II$_a$	—[c]	478	66.7
II$_b$	—	447	61.1
II$_c$	309	474	71.6
II$_d$	296	496	54.9
II$_e$	—	443	52.6
II$_f$	345	405	50.3
II$_g$	—	458	56.3
II$_h$	—	460	60.3
II$_i$	—	458	52.5
II$_j$	—	453	52.6
II$_k$	—	442	59.8
II$_l$	243	461	55.9
II$_m$	—	453	53.1
II$_n$	—	473	68.6
II$_o$	301	474	65.6
III$_a$	—	480	52.1
III$_b$	—	476	50.2
III$_c$	—	487	56.1
III$_d$	—	473	51.3
III$_e$	—	480	58.8
III$_f$	—	490	50.3
IV$_a$	—	480	51.3
IV$_b$	—	514	58.3
IV$_c$	268	453	50.9
IV$_d$	264	449	50.0
IV$_e$	256	457	63.5
IV$_f$	255	455	55.2
IV$_g$	235	435	46.8

[a] From DSC measurements conducted at a heating rate of 20°C/min in nitrogen.
[b] Thermogravimetric analysis conducted at a heating rate 20°C/min in nitrogen.
[c] No T_g was observed in DSC trace.

Figure 1   TG curves of polyamides II$_a$ and II$_b$, with a heating rate of 20°C/min (———) in nitrogen or (– – –) in air.

phous samples. The base-line shift was judged as T_g on the second DSC heating trace. However, it can be seen from Table VI that T_g's of most polymers of the NDA homopolyamides are difficult to measure from DSC. T_g values measured from polyamide II$_e$, II$_d$, II$_f$, and II$_l$ are in the range of 243–345°C.

Table VI also shows the results of TGA and DSC analysis in nitrogen of ODA-derived copolyamides. Initial decomposition temperatures of all copolymers are above 445°C, and the 10% weight loss temperatures are between 451 and 541°C. By observing the contents of NDA, TPA, and IPA of the copolymers of series III and series IV, the thermal stability of polymers containing naphthalene rings is better than for those containing benzene rings, especially
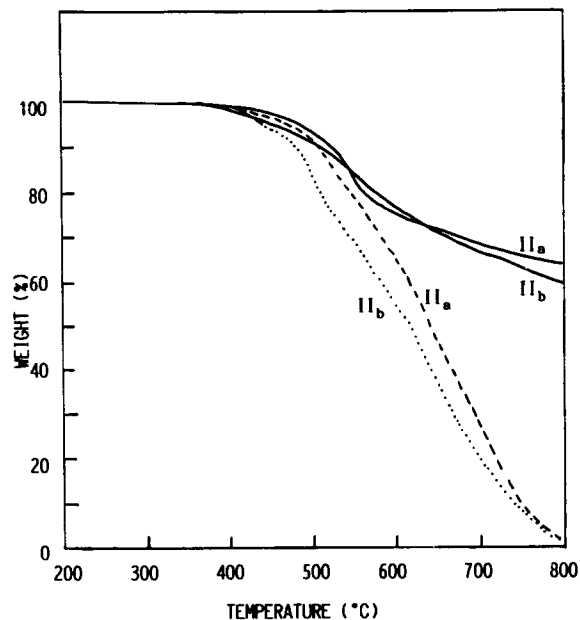
for series IV containing IPA. By comparing TGA diagrams of ODA polyamides II$_d$, II$_f$, and IV$_g$ only containing NDA, TPA, or IPA, the order of thermal resistance is NDA > TPA > IPA, as shown in Figure 2.
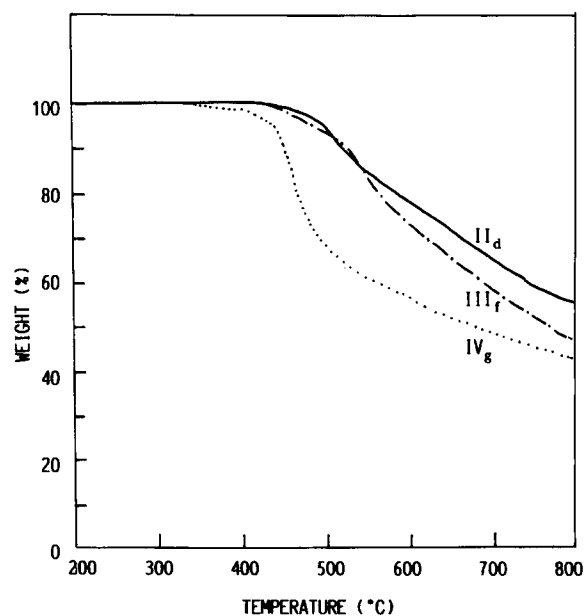

Figure 2   TG curves of homopolyamides II$_d$ (NDA–ODA), III$_f$ (TPA–ODA), and IV$_g$ (IPA–ODA), with a heating rate of 20°C/min in nitrogen.
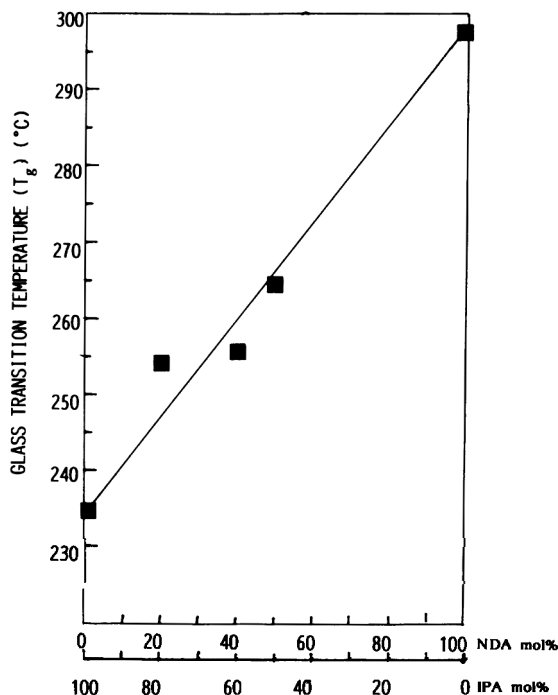
Figure 3 Relationship between glass transition temperature of NDA/IPA–ODA copolyamides and composition of mixed diacids.

In the measurements of T_g's by DSC, those of series **III** containing the TPA moiety were not easily determined, whereas those of series **IV** containing the IPA moiety over 40% were easily measurable. Comparing the T_g's from IPA–ODA homopolyamide (**IV$_g$**) (T_g = 235°C) to NDA/IPA (50/50)–ODA copolyamide (**IV$_d$**) (T_g = 264°C) and NDA–ODA homopolyamide (**II$_d$**) (T_g = 296°C), the change is nearly linear, as shown in Figure 3. The structure of the NDA moiety is more rigid, and the T_g of its derived polymers are higher; contrarily, T_g's of polymers derived from *meta*-substituted IPA are lower and the copolymers' T_g's lower as IPA content decreases.

CONCLUSIONS

1. High molecular weight polyamides (η_{inh} higher than 1.0 dL/g) could be easily obtained from direct polycondensation of NDA with various aromatic diamines by using triphenyl phosphite/pyridine as condensing agents in NMP.
2. Most NDA homopolyamides and NDA/TPA–ODA and NDA/IPA–ODA copolyam-

ides could be cast into tough and flexible films from polymer solutions in DMAc, NMP, or the amide-type polar solvents containing some LiCl (about 1 wt %). All the unstretched films revealed amorphous X-ray diffraction patterns.

3. The tensile test results showed that most of the polyamide films exhibited yield points, with tensile strength at break up to 111 MPa, elongation to break of 6–46%, and initial modulus ranging from 1.0 to 2.9 GPa.
4. Copolymerization of ODA with mixed NDA and TPA led to an increase in solubility and mechanical properties, especially in toughness, of TPA–ODA aramids.

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