

# Preparation of Polyamides Containing *para*-Linked Dimethylbiphenylene Moieties

AKINORI SHIOTANI, KATSUTOSHI WASHIO

Chiba Research Laboratory, UBE Industries Ltd., 8-1 Goi-Minamikaigan, Ichihara city, CHIBA, 290 Japan

Received 23 July 1997; accepted 28 October 1997

**ABSTRACT:** A series of wholly aromatic polyamides containing 3,3'-dimethylbiphenyl-4,4'-dicarboxylic acid (P-DMBA) and 3,4'-dimethylbiphenyl-4,3'-dicarboxylic acid (Q-DMBA) was prepared by the direct polycondensation method using triphenylphosphite and pyridine. Most of the polymers are readily soluble in polar aprotic solvents such as *N*-methyl-2-pyrrolidone (NMP), *N,N'*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), pyridine (py), and *m*-cresol and could be cast into tough and flexible films. The solubilities of copolyamides containing P-DMBA and Q-DMBA as acid components were remarkably improved. These were characterized by inherent viscosity, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical spectrometry (DMS) measurements. The glass transition temperatures of these polymers were in the range of 200–300°C and the 5% weight loss temperatures were 430–470°C. Films prepared by casting from polymer solutions exhibited good tensile properties. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 847–853, 1998

**Key words:** polyamides; 3,3'-dimethylbiphenyl-4,4'-dicarboxylic acid; 3,4'-dimethylbiphenyl-4,3'-dicarboxylic acid; polycondensation

## INTRODUCTION

Aromatic polyamides (PAs) are well known as high-temperature-resistant materials and have been widely used in aerospace, military, and civilian applications.<sup>1–3</sup> Poly(*p*-phenylene terephthalamide) was commercialized in the 1970s (Kevlar fiber, DuPont Co.), as it possesses excellent properties such as high tensile strength and modulus, chemical resistance, and low flammability. However, the solubility of this polymer is limited and it is only soluble in strong acids, such as sulfuric acid or hydrofluoric acid. To improve solubility in aprotic media, many synthetic strategies have been reported and numerous aramid compositions have been investigated.<sup>4–21</sup> By introducing bulky substituents as pendant groups at the polymer chain, solubility and processability have indeed

been improved. However, this attempt brings about an effect only at the expense of thermal and mechanical properties. The synthesis of rodlike aramids containing noncoplanar 2,2'-disubstituted biphenylene moieties has been reported, and the solubility was found to be greatly enhanced, but the thermal stability of rodlike aramids containing noncoplanar 2,2'-disubstituted biphenylene moieties was remarkably reduced, especially when the substituents are aliphatic groups.<sup>22–24</sup> In this contribution, we report the preparation of a series of wholly aromatic, *para*-linked polyamides containing 3,3'-dimethylbiphenyl-4,4'-dicarboxylic acid (P-DMBA) and 3,4'-dimethylbiphenyl-4,3'-dicarboxylic acid (Q-DMBA), which are readily soluble in polar aprotic solvents and still have good thermal and mechanical properties.

## EXPERIMENTAL

### Materials

P-DMBA and Q-DMBA were prepared according to published procedures.<sup>25</sup> Other chemicals were

Correspondence to: A. Shiotani.

*Journal of Applied Polymer Science*, Vol. 68, 847–853 (1998)  
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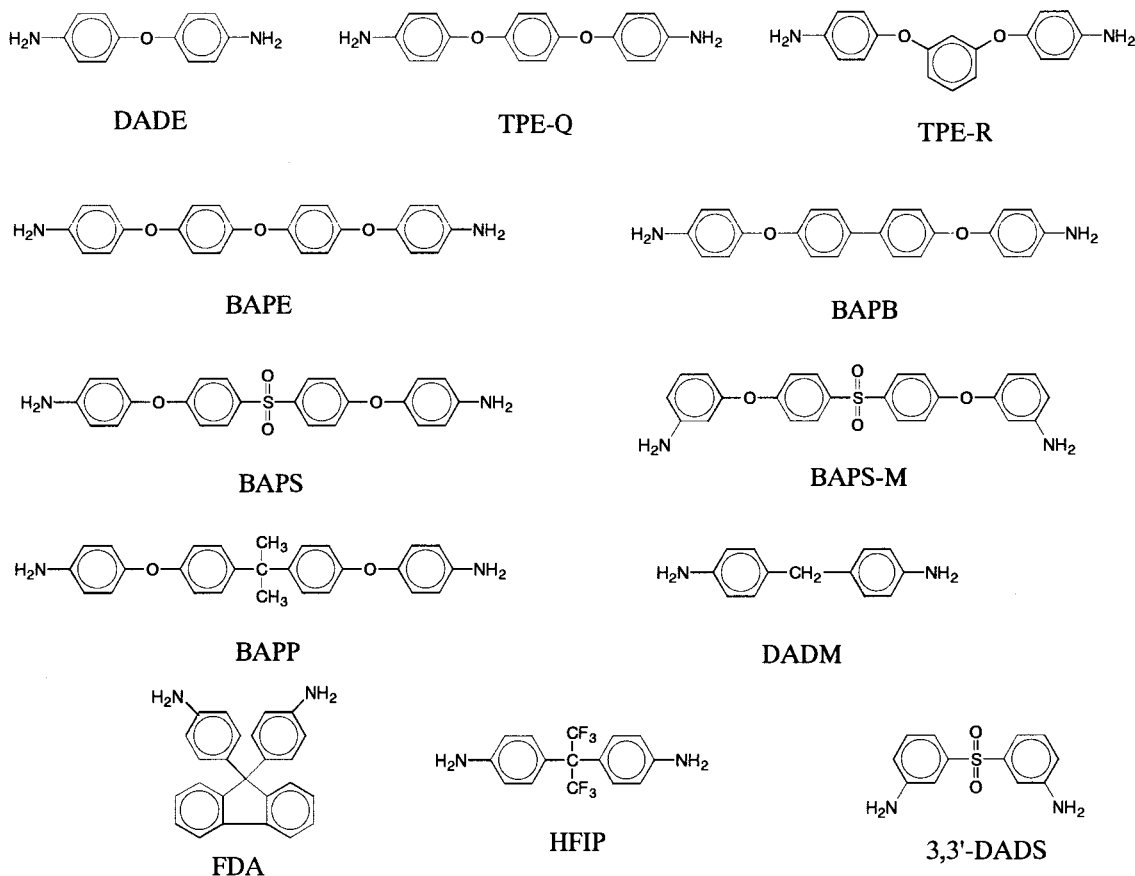


Figure 1 Diamines used in the polycondensation.

commercially available. The aromatic diamines used were 4,4'-diaminodiphenylether (DADE), 1,4-bis(4-aminophenoxy)benzene (TPE-Q), 1,3-bis(4-aminophenoxy)benzene (TPE-R), 4,4'-bis(4-aminophenoxy)biphenylether (BAPE), 4,4'-bis(4-aminophenoxy)biphenyl (BAPB), bis[4-(4-aminophenoxy)phenyl]sulfone (BAPS), bis[4-(3-aminophenoxy)phenyl]sulfone (BAPS-M), 2,2-bis(4-aminophenoxy)propane (BAPP), 4,4'-diaminodiphenylmethane (DADM), 5,5-bis(4-aminophenyl)fluorene (FDA), 2,2-bis(4-aminophenyl)-1,1,1,3,3,3-hexafluoropropane (HFIP), and 3,3'-diaminodiphenylsulfone (3,3'-DADS). These diamines as shown by their formulas in Figure 1 were used without further purification. *N*-Methyl-2-pyrrolidone (NMP), *N,N'*-dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO) were purified by distillation under reduced pressure. Pyridine (py) was distilled prior to use.

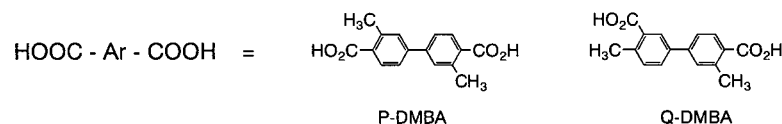
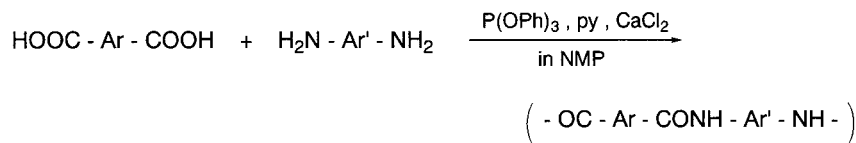
### Polycondensation

As a typical experiment, the polycondensation of P-DMBA with DADE under nitrogen was con-

ducted as follows: In a 100 mL three-necked round flask equipped with a mechanical stirrer, a condenser, and a nitrogen inlet were combined P-DMBA (1.351 g, 5 mM), DADE (1.001 g, 5 mM),  $\text{CaCl}_2$  (2.22 g), NMP (30 mL), pyridine (5 mL), and  $\text{P(OPh)}_3$  (3 mL). The reaction mixture was heated in an oil bath to 120°C to afford a clear solution within 5 min. The reaction temperature was maintained at 120°C for 3 h. The resulting viscous solution was poured into 1 L of water under rapid stirring, and the precipitated product was pulverized with a cooking mixer. The product was washed with 0.5 L of water and 0.5 L of methanol and dried in vacuum at 120°C for 3 h. Yield 2.00 g (92%).

### Measurements

The films used for the thermal measurements were prepared by casting NMP solutions containing 20% polymer by weight onto a glass plate and drying at 80°C for 10 min, 80–200°C for 30 min, 200°C for 15 min, 200–300°C for 15 min, and 300°C for 15 min.

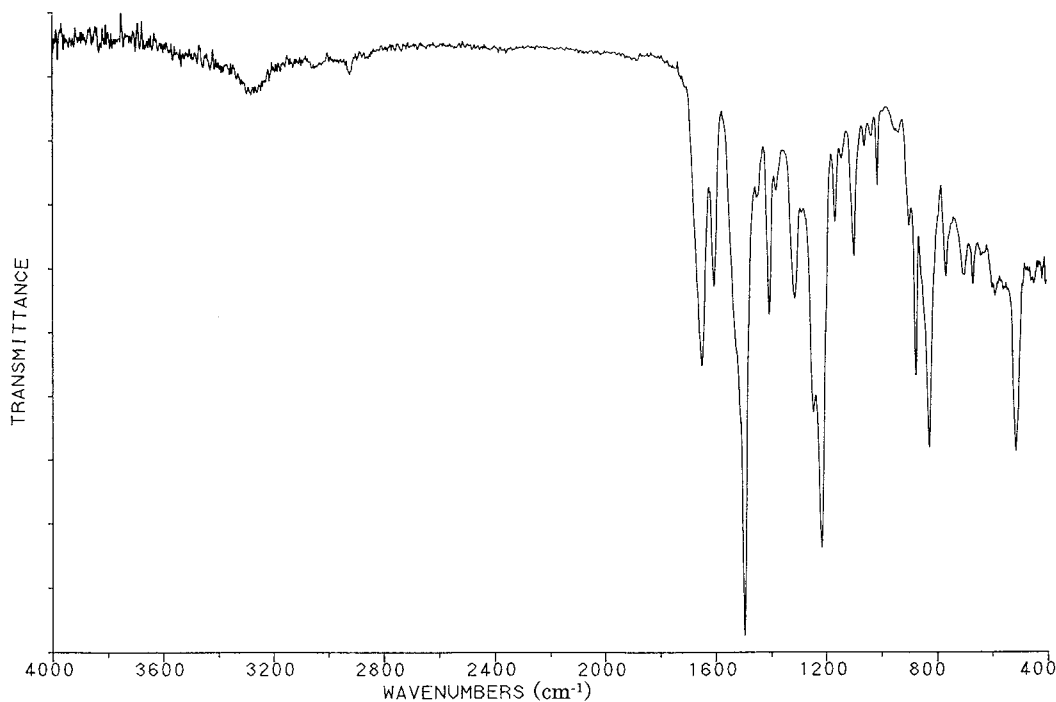


$\text{H}_2\text{N} - \text{Ar}' - \text{NH}_2$  = Diamines indicated in Figure 1

**Scheme 1** Polycondensation of polyamides.

Differential scanning calorimetry (DSC) measurements were conducted on a Seiko-Denshi DS2000 instrument in aluminum pans at a heating rate of 20°C/min under nitrogen. Glass transition temperatures ( $T_g$ 's) were determined from the endothermic peak in the second heating run of the DSC curves. The  $T_g$ 's of the copolymers (Table III) could not be unambiguously determined from the DSC measurements. Thermogravimetric analysis (TGA) measurements were conducted at a heating rate of 10°C/min under nitrogen. The

5% weight loss temperatures ( $T_d^5$ 's) were determined from the TGA curve. Inherent viscosities were measured with a Cannon Fenske viscosimeter in 5% LiCl-containing DMAc solution or a neat DMAc solution (0.5 g/dL, 30°C). Infrared spectra were recorded on a Nihondenshi JIR-5500 Fourier transform infrared spectrometer. Dynamic mechanical spectrometry (DMS) measurements were performed on a Rheometrics RSA-II mechanical spectrometer in the plate geometry using 0.04-mm plates at 10 Hz (62.8 rad/s). Dynamic



**Figure 2** FTIR spectrum of PA-I.

**Table I Conditions for the Polycondensation and Inherent Viscosities of PAs**

| Polymer | Diamine   | Temp (°C) | Yield (%) | $\eta_{inh}^a$ (dL/g) |
|---------|-----------|-----------|-----------|-----------------------|
| I       | DADE      | 120       | 92        | 3.96 (3.79)           |
| I       | DADE      | 100       | 91        | 3.90 (3.73)           |
| II      | TPE-Q     | 100       | 88        | 3.48                  |
| III     | TPE-R     | 100       | 85        | 3.25                  |
| IV      | BAPE      | 100       | 88        | 2.67                  |
| V       | BAPB      | 100       | 89        | 3.30                  |
| VI      | BAPS      | 100       | 97        | 1.87 (1.70)           |
| VI      | BAPS      | 120       | 92        | 1.94 (1.81)           |
| VII     | BAPS-M    | 120       | 89        | 1.51 (1.18)           |
| VIII    | BAPP      | 100       | 87        | 2.29 (1.97)           |
| IX      | DADM      | 120       | 89        | 2.99 (2.61)           |
| X       | FDA       | 100       | 87        | 0.91                  |
| XI      | HFIP      | 100       | 87        | 1.03                  |
| XII     | 3,3'-DADS | 100       | 85        | 0.73                  |

Reaction conditions: 5 mmol of P-DMBA and 5 mmol of diamine, 3 mL of triphenylphosphite, 2.22 g of calcium chloride, 5 mL of pyridine in 30 mL of NMP, at 100°C (or 120°C) for 3 h.

<sup>a</sup> Inherent viscosity in DMAc containing 5% LiCl of 0.5 g/dL, at 30°C. Inherent viscosity in neat DMAc in parentheses.

data were recorded at a step of 3°C in the range of strain of 0.05%. Test pieces (6 cm long, 0.4 mm wide, and 0.02 mm thick) for the mechanical measurements were prepared by a casting method as described above and the tensile data were obtained according to the ASTM D882 standard.

**Table II Properties of PAs**

| Polymer        | Solubility <sup>a</sup> |      |      |    |             | Film <sup>b</sup> | $T_g^c$ (°C) | $T_d^{5d}$ (°C) |
|----------------|-------------------------|------|------|----|-------------|-------------------|--------------|-----------------|
|                | NMP                     | DMAc | DMSO | py | <i>m-cr</i> |                   |              |                 |
| I              | ○                       | ○    | △    | ×  | ×           | Tough             | 256          | 447             |
| II             | ○                       | △    | ×    | ×  | ×           | Tough             | 219          | 456             |
| III            | ○                       | ○    | △    | ×  | ×           | Tough             | 213          | 454             |
| IV             | ○                       | △    | ×    | ×  | ×           | Tough             | 200          | 456             |
| V <sup>e</sup> | △                       | ×    | ×    | ×  | ×           |                   |              |                 |
| VI             | ○                       | ○    | ○    | △  | ○           | Tough             | 251          | 447             |
| VII            | ○                       | ○    | ○    | ○  | ○           | Tough             | 220          | 449             |
| VIII           | ○                       | ○    | ○    | ○  | ○           | Tough             | 230          | 462             |
| IX             | ○                       | ○    | ○    | ×  | ○           | Tough             | <sup>f</sup> | 440             |
| X              | ○                       | ○    | ○    | ○  | ○           | Tough             | 293          | 435             |
| XI             | ○                       | ○    | ○    | ○  | ○           | Tough             | 289          | 451             |
| XII            | ○                       | ○    | ○    | ○  | ×           | Brittle           | 260          | 439             |

<sup>a</sup> NMP: *N*-methyl-2-pyrrolidone, DMAc: *N,N'*-dimethylacetamide, DMSO: dimethyl sulfoxide, py: pyridine, *m-cr*: *m*-cresol. (○) Soluble at room temp; (△) partially soluble; (×) insoluble.

<sup>b</sup> Polymer film cast on a glass plate and cured at 300°C.

<sup>c</sup> Glass transition temperature from DSC measurements at a heating rate of 20°C/min.

<sup>d</sup> 5% weight loss temperature from TGA measurements at a heating rate of 10°C/min.

<sup>e</sup> A small amount of particles remained undissolved; therefore, film casting was not attempted.

<sup>f</sup> Not clearly defined.

## RESULTS AND DISCUSSION

### Polymer Synthesis

3,3'-Dimethylbiphenyl-4,4'-dicarboxylic acid (P-DMBA) and 3,4'-dimethylbiphenyl-4,3'-dicarboxylic acid (Q-DMBA) were prepared from a Pd-catalyzed coupling reaction of methyl *o*-toluate. Dicarboxylic acids were obtained by the hydrolysis of the dimethyl esters.<sup>25</sup> A series of new PAs was prepared by the direct polycondensation method using triphenylphosphite and pyridine (Scheme 1). All the polymers were readily obtained in good yields in the combination of P-DMBA and diamines indicated in Figure 1. *p*-Phenylenediamine and *o*-tolidine did not afford the desired product because of a low solubility of polymers under these conditions, although the polymer has been successfully prepared from P-DMBA dichloride and *p*-phenylenediamine by an acid chloride method.<sup>26</sup>

The FTIR spectrum of polymer I showed the characteristic absorption bands (in Fig. 2): 3277 cm<sup>-1</sup> (N—H stretching vibration), 1651 cm<sup>-1</sup> (C=O stretching vibration), 1309 cm<sup>-1</sup> (C—N stretching and N—H bending vibrations), and 1215 cm<sup>-1</sup> (aromatic ether group stretching vibration) were observed and assigned.<sup>27</sup>

### Properties of Polymers

The results of the polycondensation reactions are summarized in Table I. The inherent viscosities

**Table III** Properties of PA Copolymers

| Polymer        | Acid   |        | Diamine | Solubility <sup>a</sup> |      |      |    |              | Film <sup>b</sup> | $T_g^c$<br>(°C) | $T_d^{5d}$<br>(°C) |
|----------------|--------|--------|---------|-------------------------|------|------|----|--------------|-------------------|-----------------|--------------------|
|                | P-DMBA | Q-DMBA |         | NMP                     | DMAc | DMSO | py | <i>m</i> -cr |                   |                 |                    |
| I              | 100    | 0      | DADE    | ○                       | ○    | △    | ×  | ×            | Tough             | 256             | 447                |
| XIII           | 75     | 25     | DADE    | ○                       | ○    | ○    | △  | ○            | Tough             | <sup>e</sup>    | 456                |
| XIV            | 50     | 50     | DADE    | ○                       | ○    | ○    | ○  | ○            | Tough             | <sup>e</sup>    | 454                |
| XV             | 25     | 75     | DADE    | ○                       | ○    | ○    | ○  | ○            | Tough             | <sup>e</sup>    | 456                |
| XVI            | 0      | 100    | DADE    | ○                       | ○    | ○    | ○  | ○            | Tough             | <sup>e</sup>    | 448                |
| II             | 100    | 0      | TPE-Q   | ○                       | △    | ×    | ×  | ×            | Tough             | 219             | 456                |
| XVII           | 50     | 50     | TPE-Q   | ○                       | ○    | ○    | △  | ○            | Tough             | <sup>e</sup>    | 456                |
| V <sup>f</sup> | 100    | 0      | BAPB    | △                       | ×    | ×    | ×  | ×            |                   |                 |                    |
| XVIII          | 50     | 50     | BAPB    | ○                       | ○    | △    | ×  | ×            | Tough             | <sup>e</sup>    | 455                |
| VI             | 100    | 0      | BAPS    | ○                       | ○    | ○    | △  | ○            | Tough             | 251             | 447                |
| XIX            | 50     | 50     | BAPS    | ○                       | ○    | ○    | ○  | ○            | Tough             | <sup>e</sup>    | 451                |

<sup>a-d</sup> See footnotes a–d to Table II.

<sup>e</sup> Not clearly defined.

<sup>f</sup> A small amount of particles remained undissolved; therefore, film casting was not attempted.

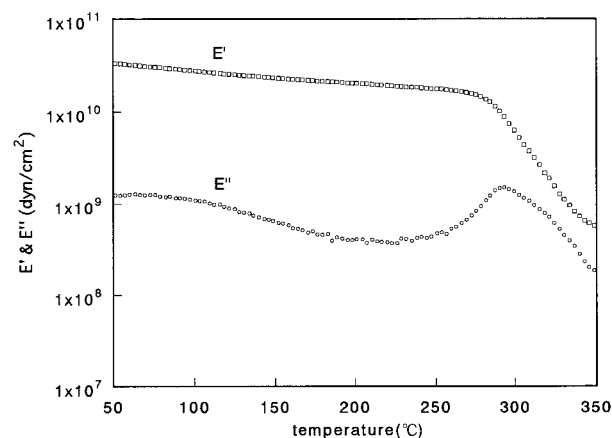
of the polymers ranged from 0.7 to 4.0 dL/g. The values of the inherent viscosities in 5% LiCl-containing DMAc are slightly higher than those in DMAc without LiCl. The low viscosities of polymers X, XI, and XII can be explained by the lower reactivity of the corresponding diamines. A similar result was reported in the poly(amide–imide) system.<sup>28</sup> The molecular weights of the polymers except XII were high enough to give tough and flexible films by the casting of polymer solutions. The 5% weight loss temperatures ( $T_d^{5s}$ ) of the new polymers were found in the range 430–470°C, indicating good thermal stabilities at elevated temperatures, and the glass transition temperatures ( $T_g$ 's) were in the range 200–300°C (Table II).

The PAs (VI–XII) containing flexible diamines showed good solubilities in polar aprotic solvents. However, the polymers (I–V) with diamines containing rigid structures exhibited low solubilities. In an attempt to prepare the polyamide of biphenyl-4,4'-dicarboxylic acid and DADE under similar conditions by the direct polycondensation method, the desired product could not be obtained, because the polymer was instantly precipitated from the reaction media. This result indicated that an incorporation of methyl groups into the biphenyl moiety would enhance the solubility of the polyamide. Indeed, the solubilities of copolyamides using Q-DMBA were remarkably improved (Table III). When the quantity of Q-DMBA in the acid components was increased to more than 50% in the polymer systems with DADE, copolymers were readily soluble even in *m*-cresol. In the case of BAPB, the copolymer

showed good solubility, while the homopolymer was less soluble. The enhancement of solubilities is ascribed to the bent units of Q-DMBA, as is usually observed with bent structures.<sup>20</sup>

The 5% weight loss temperatures ( $T_d^{5s}$ ) of the copolyamides were almost identical to those of the homopolymers; however, the glass transition temperatures ( $T_g$ 's) were not clearly observed for copolyamides in the DSC charts (Table III). We have included the DMS measurements for the copolymer systems with DADE.

In Figure 3 is depicted the temperature dependence of the dynamic storage modulus ( $E'$ ) and the loss modulus ( $E''$ ) for polymer XIV (P-DMBA/Q-DMBA(50/50)–DADE). The quantity  $E''$  displays a maximum value at 291°C. The transition temperatures at the  $E''$  maximum value were



**Figure 3** Temperature dependence of moduli  $E'$  and  $E''$  for copolymer XIV.

**Table IV** Tensile Properties of PA Films

| Polymer | $\eta_{inh}^a$<br>(dL/g) | Strength<br>at Break<br>(kgf/cm <sup>2</sup> ) | Initial<br>Modulus<br>(kgf/cm <sup>2</sup> ) | Elongation<br>at Break<br>(%) |
|---------|--------------------------|--|--|-------------------------------|
| I       | 3.79                     | 1650   | 42,800                                       | 8                             |
| I       | 1.34                     | 1500   | 39,000                                       | 7                             |
| II      | 3.48 <sup>b</sup>        | 1600   | 42,100                                       | 29                            |
| III     | 3.25 <sup>b</sup>        | 1400   | 43,800                                       | 27                            |
| IV      | 2.67 <sup>b</sup>        | 1320   | 34,800                                       | 21                            |
| VI      | 1.81                     | 920  | 25,600                                       | 14                            |
| VII     | 1.12                     | 950  | 27,700                                       | 9                             |
| VIII    | 1.97                     | 920  | 24,800                                       | 11                            |
| IX      | 0.88                     | 1390   | 35,200                                       | 10                            |
| XI      | 0.98 <sup>b</sup>        | 1240   | 31,300                                       | 14                            |
| XIII    | 3.12                     | 1680   | 40,100                                       | 10                            |
| XIV     | 2.44                     | 1260   | 30,700                                       | 8                             |
| XV      | 1.94                     | 1240   | 28,500                                       | 11                            |
| XVI     | 1.59                     | 1190   | 26,900                                       | 11                            |
| XVII    | 0.79                     | 1200   | 25,600                                       | 10                            |

Films were prepared by casting of polymer solutions.

<sup>a</sup> Inherent viscosity in neat DMAc of 0.5 g/dL, at 30°C.

<sup>b</sup> Inherent viscosity in DMAc containing 5% LiCl of 0.5 g/dL, at 30°C.

practically constant, when the composition of the acid components was varied: 295°C (polymer I), 289°C (polymer XIII), 289°C (polymer XV), and 291°C (polymer XVI). Such relaxation was reported to correlate with a glass transition and  $E''_{(max)}$  corresponds to the  $T_g$ .<sup>29-31</sup> However, as the transition temperatures from  $E''_{(max)}$  for copolymers prepared were much higher than the expected  $T_g$ 's, we assume that these transition temperatures around 290°C are likely to be the softening temperatures of polymers. One can assume that the softening temperatures are not varied in the whole range of compositions P-DMBA/Q-DMBA. We have reported that P-DMBA and Q-DMBA have almost the same influence on the depression of melting temperatures of aromatic copolyesters.<sup>32</sup>

The tensile properties of typical PAs are given in Table IV. Films prepared by casting from polymer solutions exhibited good tensile properties. Tensile strengths at break of ca. 900–1,700 kgf/cm<sup>2</sup>, elongation at break of 5–30%, and initial moduli of ca. 25,000–44,000 kgf/cm<sup>2</sup> were typically found. When the difference of inherent viscosity for polymer I was compared, the tensile properties were already saturated at  $\eta_{inh} = 1.34$ . The homopolymer of Q-DMBA with DADE and the copolymer containing P-DMBA/Q-DMBA showed poorer tensile properties than those of homopolymer of P-DMBA with DADE, indicating

that the Q-DMBA monomer brings about disruption of the polymer chain packing and changes the intermolecular interactions.

## CONCLUSIONS

A series of wholly aromatic polyamides containing 3,3'-dimethylbiphenyl-4,4'-dicarboxylic acid (P-DMBA) and 3,4'-dimethylbiphenyl-4,3'-dicarboxylic acid (Q-DMBA) could be conveniently prepared by the direct polycondensation method using triphenylphosphite and pyridine. Most of the polymers are readily soluble in polar aprotic solvents and could be cast into tough and flexible films. The solubilities of copolyamides containing P-DMBA and Q-DMBA as acid components were remarkably improved.

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