

Preparation of Poly(amide-imide)s Derived from Biphenyltetracarboxylic Dianhydrides

AKINORI SHIOTANI,¹ MASAFUMI KOHDA¹

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

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ABSTRACT: Four new diimide-dicarboxylic acids (I–IV) were prepared by condensation of *s*- or *a*-BPDA with *para*- or *meta*-aminobenzoic acid. A series of aromatic poly(amide-imide)s containing these diimide-dicarboxylic units was prepared by three methods: (1) acid chloride method, (2) triphenylphosphite method, and (3) one-pot method. A typical polymer of the series is readily soluble in polar aprotic solvents such as *N*-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), and pyridine (py) and could be cast into tough and flexible films. These were characterized by inherent viscosity, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) measurements. The glass transition temperatures of these polymers were in the range of 220–290°C, and the 5% weight loss temperatures were 450–500°C. Films prepared by casting from polymer solutions exhibited good tensile properties. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 865–873, 1997

Key words: poly(amide-imide)s; 3,3',4,4'-biphenyltetracarboxylic dianhydride; 2,3,3',4'-biphenyltetracarboxylic dianhydride; *p*-aminobenzoic acid; *m*-aminobenzoic acid; polycondensation

INTRODUCTION

Aromatic polyimides (PIs) are well known as high-temperature, resistant materials and have been widely used in aerospace and microelectronics industries.^{1,2} Kapton® (poly(4,4'-oxydiphenylene pyromellitimide)) has been commercialized by DuPont Co. in the 1960s. We have developed a method of production for biphenyltetracarboxylic dianhydride (BPDA)^{3,4} and put a new polyimide Upilex®⁵ on the market in 1982. Wholly aromatic polyimides are absolutely infusible; thus, the two-step process is generally utilized for the production of polyimides. Aromatic poly(amide-imide) (PAIs) are more readily processed by the injection molding or extrusion technique. PAIs are important engineering plastics due to their excellent mechanical properties, high thermal stability, and improved processability, in particular, as

compared with PIs. A number of PAIs have been previously described: (1) PAI from trimellitic anhydride with diamines,⁶ (2) PAI from monoimide-dicarboxylic acids with diamines,^{7–9} (3) PAI from diimide-dicarboxylic acids with diamines,^{10–27} (4) PAI from diimide-diamines with dicarboxylic acids,²⁸ and (5) PAI by the Pd-catalyzed carbon-ylation of aromatic dihalides containing an imide-skeleton with diamines.^{29,30}

In this contribution, we wish to report the preparation of new diimide-dicarboxylic acids derived from BPDA and a number of PAIs therefrom.

EXPERIMENTAL

Materials

3,3',4,4'-biphenyltetracarboxylic dianhydride (*s*-BPDA) and 2,3,3',4'-biphenyltetracarboxylic dianhydride (*a*-BPDA) are products of UBE Industries Ltd. Other chemicals were commercially available. Aromatic diamines used were

Correspondence to: A. Shiotani

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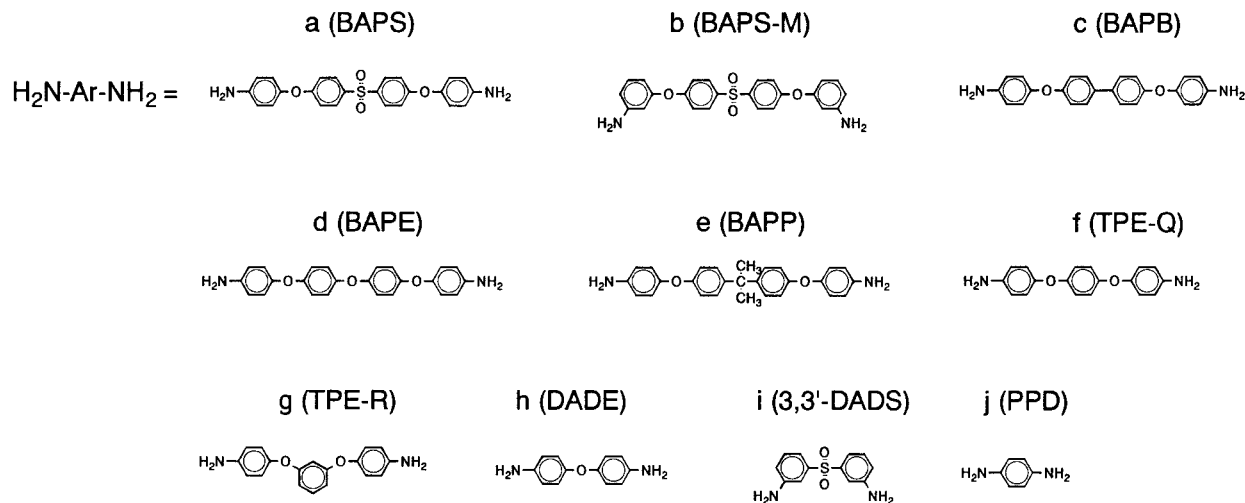


Figure 1 Diamines used in the polycondensation.

bis[4-(4-aminophenoxy)phenyl]sulfone (BAPS), bis[4-(3-aminophenoxy)phenyl]sulfone (BAPS-M), 4,4'-bis(4-aminophenoxy)biphenyl (BAPB), 4,4'-bis(4-aminophenoxy)biphenylether (BAPE), 2,2-bis(4-aminophenoxyphenyl)propane (BAPP), 1,4-bis(4-aminophenoxy)benzene (TPE-Q), 1,3-bis(4-aminophenoxy)benzene (TPE-R), 4,4'-diaminodiphenylether (DADE), 3,3'-diaminodiphenylsulfone (3,3'-DADS), and *p*-phenylenediamine (PPD). These diamines, as shown by their formulae in Figure 1, were used without further purification. *N*-Methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure. Pyridine (py), thionyl chloride, and toluene were distilled prior to use.

Diimide-dicarboxylic acids (DIDAs) were prepared by condensation of *s*- or *a*-BPDA with *para* or *meta*-aminobenzoic acid under nitrogen. The synthesis of *N,N'*-bis(4-carboxyphenyl)-biphenyl-3,3',4,4'-tetracarboxydiimide (I) serves to illustrate the method. The reaction vessel was a 500 mL three-necked round flask equipped with a mechanical stirrer, a water separating trap topped by a condenser, and a nitrogen inlet. In a typical experiment, *p*-amino-benzoic acid (27.43 g, 0.20M) in 300 mL of NMP was combined with *s*-BPDA (29.42 g, 0.10M) at room temperature. The mixture was heated to 100°C to afford a homogeneous solution within 0.5 h. 50 mL of toluene was added, and the reaction was completed under reflux for 4 h, removing the water azeotropically. After the first 40 minutes, a light yellow product began to precipitate from the reaction mixture. On standing overnight at room temperature, the product was filtered, washed with 500 mL of acetone, and dried in vacuum at 120°C for 3 h. The

yield of I was 50.61 g (95%); mp = 444°C (by DSC). IR (KBr disc.) was 1778 (imide C=O), 1732 (imide C=O), 1373 (imide ring C—N), and 754 (imide ring deformation). FD-MS: m/z = 532 (M^+). Anal. calcd: for $C_{30}H_{16}N_2O_8$ was as follows: C, 67.67; H, 3.03; N, 5.26. Found was as follows: C, 67.9; H, 3.3; N, 5.3. *N,N'*-bis(3-carboxyphenyl)-biphenyl-3,3',4,4'-tetracarboxydiimide (II), *N,N'*-bis(4-carboxyphenyl)-biphenyl-2,3,3',4'-tetracarboxydiimide (III), and *N,N'*-bis(3-carboxyphenyl)-biphenyl-2,3,3',4'-tetracarboxydiimide (IV) were prepared accordingly.

II: yield was 91%; mp = 426°C (by DSC). IR (KBr disc.) was 1776 (imide C=O), 1730 and 1722 (imide C=O), 1379 (imide ring C—N), and 758 (imide ring deformation). FD-MS: m/z = 532 (M^+). Anal. found: C, 67.9; H, 3.3; N, 5.3.

III: yield was 88%; mp = 414°C (by DSC). IR (KBr disc.): 1776 (imide C=O), 1720 (imide C=O), 1375 (imide ring C—N), and 762 (imide ring deformation). FD-MS: m/z = 532 (M^+). Anal. found: C, 67.2; H, 2.8; N, 5.2.

IV: yield was 80%; mp = 423°C (by DSC). IR (KBr disc.): 1768 (imide C=O), 1716 (imide C=O), 1375 (imide ring C—N), and 754 (imide ring deformation). FD-MS: m/z = 532 (M^+). Anal. found: C, 67.2; H, 2.8; N, 5.1. Diimide-dicarboxylic acid dichlorides (DIDA-Cl) were synthesized by the chlorination of DIDA with excess thionyl chloride. As a typical procedure, the synthesis of *N,N'*-bis(4-chlorocarbonylphenyl)-biphenyl-3,3',4,4'-tetracarboxydiimide (I-Cl) is given as follows: In a 300 mL round flask, a mixture of I (5.00 g), thionyl chloride (150 mL), and three drops of dimethylformamide as a catalyst was heated under reflux for 6 h. On standing overnight, thionyl chloride

was distilled off; and the product was washed two times with 30 mL of dry toluene, filtered, and dried in vacuum at 80°C for 6 h. Yield was 5.23 g (98%). Anal. calcd. for C₃₀H₁₄N₂O₆Cl₂: C, 63.29; H, 2.45; N, 4.92; Cl, 12.45. Found: C, 63.4; H, 2.5; N, 4.9; Cl, 12.6. N,N'-bis(3-chlorocarbonylphenyl)-biphenyl-3,3',4,4'-tetracarboxydiimide (II-Cl), N,N'-bis(4-chlorocarbonylphenyl)-biphenyl-2,3,3',4'-tetracarboxydiimide (III-Cl), and N,N'-bis(3-chlorocarbonylphenyl)-biphenyl-2,3,3',4'-tetracarboxydiimide (IV-Cl) were prepared accordingly.

II-Cl: yield was 99%. Anal. found: C, 63.3; H, 2.5; N, 4.9; Cl, 12.5. III-Cl: yield was 99%, Anal. found: C, 63.5; H, 2.6; N, 4.8; Cl, 12.6. IV-Cl: yield was 98%, Anal. found: C, 62.3; H, 2.6; N, 5.0; Cl, 12.6.

Polycondensation

Acid Chloride Method

As a typical experiment, the polycondensation of II-Cl with BAPS under nitrogen was conducted as follows. In a 100 mL four-necked round flask equipped with a mechanical stirrer, a condenser, a dropping funnel, and a nitrogen inlet were combined II-Cl (1.423 g, 2.5mM), NMP (15 mL), and pyridine (0.5 mL). A solution containing BAPS (1.081 g, 2.5mM) and NMP (5 mL) was added through a funnel into the reaction mixture at 60°C within 15 min. The funnel was washed with an additional 3 mL of NMP. After several minutes, a polymerization started, and the reaction temperature was maintained at 60°C for 100 min in an oil bath. The resulting viscous solution was poured into 1 L of water under rapid stirring, and the product precipitated 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 was 2.219 g (96%).

Triphenyl Phosphite Method

As a typical procedure, the polycondensation of IV with TPE-Q is described. Using the identical equipment IV (1.331 g, 2.5mM), TPE-Q (0.731 g, 2.5mM), CaCl₂ (1.2 g), NMP (20 mL), pyridine (4 mL), and P(OPh)₃ (1.5 mL) were combined. The reaction mixture was heated to 150°C to afford a clear solution within 5 min. The reaction temperature was maintained at 150°C for 3 h. The resulting viscous solution was treated as aforementioned. Yield was 1.873 g (95%).

One-Pot Method

As a typical example, the polycondensation of s-BPDA and m-ABA with DADE is given. In a 100

mL three-necked round flask, *m*-aminobenzoic acid (0.686 g, 5.0mM) in 7 mL of anhydrous NMP under nitrogen was combined with s-BPDA (0.736 g, 2.5mM) at room temperature. The mixture was heated to 100°C to afford a homogeneous solution within 0.5 h. Addition of 6 mL of toluene after 20 min induced precipitation of a light yellow product. To remove water azeotropically, the reaction mixture was kept under reflux for 4 h. After cooling to room temperature and removing the water separating trap, DADE (0.511 g, 2.55 mM), CaCl₂ (1.2 g), NMP (14 mL), pyridine (4 mL), and P(OPh)₃ (1.5 mL) were added to the mixture, which was heated to 150°C to afford a clear solution within 5 min. After 3 h, at 150°C, a viscous solution resulted, which was treated as aforementioned. Yield was 1.707 g (98%).

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 30 min, 80–170°C for 30 min, 200°C for 30 min, 200–300°C for 15 min, and 300°C for 30 min.

Differential scanning calorimetry (DSC) measurements were conducted on a Seiko-Denshi DS2000 instrument in aluminium pans at a heating rate of 20°C/min under nitrogen. Glass transition temperatures (T_{gs}) were determined from the DSC curves. T_{gs} of polymers VII (Table IV) could not be unambiguously determined from the DSC measurements. Thermogravimetric measurements (TGA) were conducted at a heating rate of 10°C/min under nitrogen. The 5% weight loss temperatures (T_{d5}) were determined from the TGA curve. Inherent viscosities were measured with a Cannon Fenske viscosimeter in NMP solution (0.5 g/dL, 30°C). Infrared spectra were recorded on a Nihondenshi JIR-5500 Fourier transform infrared (FTIR) spectrometer. Test pieces (6 cm long, 0.4 mm wide, and 0.02 mm thick) for mechanical measurements were prepared by a casting method, as described above, and the tensile data were obtained according to the ASTM D882 standard.

RESULTS AND DISCUSSION

Monomer Synthesis

Four novel diimide-dicarboxylic acids (I–IV) have been prepared by condensation of *s*- or *a*-

Table I Conditions for the Acid Chloride Method and Inherent Viscosities of PAIs^a

| Polymer | DIDA | Diamine | Polycondensation | | Yield (%) | η_{inh}^b (dL/g) |
|---------|------|---------|------------------|------------|-----------|-----------------------|
| | | | Temp. (°C) | Time (min) | | |
| Va | I | a | 70 | 95 | 97 | 1.34 |
| Vb | | b | 70 | 105 | 93 | 1.35 |
| Ve | | e | 70 | 180 | 95 | 1.64 |
| Vi | | i | 70 | 60 | 90 | 1.17 |
| VIa | II | a | 60 | 100 | 91 | 0.83 |
| VIc | | c | 60 | 65 | 82 | 0.84 |
| VIId | | d | 60 | 65 | 84 | 0.73 |
| VIe | | e | 60 | 180 | 92 | 0.50 |
| VIIf | | f | 60 | 65 | 86 | 1.04 |
| VIg | | g | 60 | 180 | 94 | 0.81 |
| VIh | | h | 80 | 180 | 94 | 0.89 |
| VIIi | III | i | 60 | 80 | 89 | 0.36 |
| VIIa | | a | 65 | 90 | 84 | 1.17 |
| VIIb | | b | 60 | 100 | 90 | 0.99 |
| VIIc | | c | 60 | 120 | 85 | 1.01 |
| VIIIf | | f | 65 | 30 | 87 | 1.47 |
| VIIh | | h | 60 | 25 | 77 | 1.35 |
| VIIi | | i | 60 | 180 | 78 | 0.52 |

^a Reaction condition: 2.5 mmol of each monomer; 0.5 mL of pyridine; monomer concentration = ca. 10 wt % in NMP.

^b Inherent viscosity in NMP of 0.5 g/L at 30°C.

Table II Conditions for the Triphenyl Phosphite Method and Inherent Viscosities of PAIs^a

| Polymer | DIDA | Diamine | Molar Ratio | Yield (%) | η_{inh}^b (dL/g) |
|---------|------|---------|------------------|-------------|-----------------------|
| | | | (DIDA : diamine) | | |
| VIIIa | IV | a | 1 : 1 | 98 | 0.57 |
| VIIIc | | c | 1 : 1 | 96 | 1.16 |
| VIIIId | | d | 1 : 1 | 91 | 0.54 |
| VIIIe | | e | 1 : 1 | 94 | 0.80 |
| VIIIf | | f | 1 : 1 | 95 | 0.92 |
| VIIIg | | g | 1 : 1 | 95 | 0.88 |
| VIIIh | | h | 1 : 1 | 97 | 0.84 |
| VIIIi | | i | 1 : 1 | 94 | 0.39 |
| VIIIj | | j | 1 : 1 | 95 | 0.76 |
| VIc | | II | c | 1.00 : 1.02 | 97 |
| VIId | d | | 1.00 : 1.02 | 97 | 0.57 |
| VIIf | f | | 1.00 : 1.02 | 98 | 0.72 |
| VIg | g | | 1.00 : 1.02 | 96 | 0.69 |
| VIi | i | | 1.00 : 1.02 | 98 | 0.37 |
| VIj | j | | 1.00 : 1.02 | 96 | 0.76 |
| VIIa | III | a | 1.00 : 1.02 | 95 | 0.58 |
| VIIc | | c | 1.00 : 1.02 | 93 | 0.60 |
| VIIIf | | f | 1.00 : 1.02 | 95 | 0.51 |
| VIIh | | h | 1.00 : 1.02 | 97 | 0.65 |

^a Reaction condition: 2.5 mmol of DIDA and 2.5 (or 2.55) mmol of diamine, 1.5 mL of triphenyl phosphite, 1.2 g of calcium chloride, 4 mL of pyridine in 20 mL of NMP, at 150°C for 3 h.

^b Inherent viscosity in NMP of 0.5 g/L, at 30°C.

Table III Conditions for the One-pot Method and Inherent Viscosities of PAIs^a

| Polymer | BPDA | ABA | Diamine | Yield (%) | η_{inh}^b (dL/g) |
|---------|------|-----|---------|-----------|-----------------------|
| VIa | s- | m- | a | 91 | 0.51 |
| VIh | s- | m- | h | 98 | 0.68 |
| VIIc | a- | p- | c | 90 | 0.56 |
| VIIIh | a- | m- | h | 88 | 0.50 |

^a Reaction condition: a mixture of 2.5 mmol of *s*- or *a*-BPDA and 5.0 mmol of *p*- or *m*-ABA and 7 mL of NMP was refluxed for 4 h, then 2.55 mmol of diamine (molar ratio of DIDA : diamine = 1.00 : 1.02), 1.5 mL of triphenyl phosphite, 1.2 g of calcium chloride, and 4 mL of pyridine were added to the reaction mixture. The polymerization was carried out at 150°C for 3 h.

^b Inherent viscosity in NMP of 0.5 g/L at 30°C.

BPDA with para- or meta-aminobenzoic acid (*p*- or *m*-ABA). For instance, *s*-BPDA was reacted with two mole equivalents of *m*-ABA to form an amic acid in homogeneous solution. In a subsequent cyclodehydration reaction, II was formed, which precipitated from the reaction mixture

(Scheme I). The proposed molecular structure and polymer structure are based on a sequence of simple and well-known reactions. They are also confirmed by characteristic absorptions in the FTIR spectra, which for DIDA-II and its polycondensation product PAI-VIh are shown in

Table IV Properties of PAIs

| PAI | Solubility ^a | | | Film ^b | T_g^c (°C) | T_d^{5d} (°C) |
|--------|-------------------------|------|----|-------------------|--------------|-----------------|
| | NMP | DMSO | py | | | |
| Va | ○ | △ | × | tough | 258 | 485 |
| Vb | ○ | △ | × | tough | 262 | 467 |
| Vi | ○ | △ | × | tough | 256 | 456 |
| VIa | ○ | ○ | △ | tough | 258 | 472 |
| VIc | ○ | △ | △ | tough | 270 | 470 |
| VIId | ○ | ○ | ○ | tough | 244 | 462 |
| VIe | ○ | ○ | ○ | tough | 257 | 480 |
| VIf | ○ | ○ | ○ | tough | 244 | 456 |
| VIg | ○ | ○ | ○ | tough | 253 | 478 |
| VIh | ○ | ○ | ○ | tough | 253 | 474 |
| VIIi | ○ | ○ | ○ | tough | 247 | 472 |
| VIIa | ○ | ○ | ○ | tough | 287 | 478 |
| VIIb | ○ | ○ | ○ | tough | 241 | 492 |
| VIIc | ○ | ○ | × | tough | ^e | 496 |
| VIIIf | ○ | △ | × | tough | ^e | 491 |
| VIIh | ○ | ○ | × | tough | ^e | 487 |
| VIIi | ○ | ○ | ○ | tough | ^e | 455 |
| VIIIa | ○ | ○ | ○ | tough | 263 | 485 |
| VIIIc | ○ | ○ | ○ | tough | 275 | 507 |
| VIIIId | ○ | ○ | ○ | tough | 260 | 491 |
| VIIIe | ○ | ○ | ○ | tough | 261 | 483 |
| VIIIIf | ○ | ○ | ○ | tough | 268 | 483 |
| VIIIg | ○ | ○ | ○ | tough | 253 | 491 |
| VIIIh | ○ | ○ | ○ | tough | 291 | 488 |
| VIIIi | ○ | ○ | ○ | tough | 261 | 480 |
| VIIIj | ○ | ○ | ○ | tough | 328 | 474 |

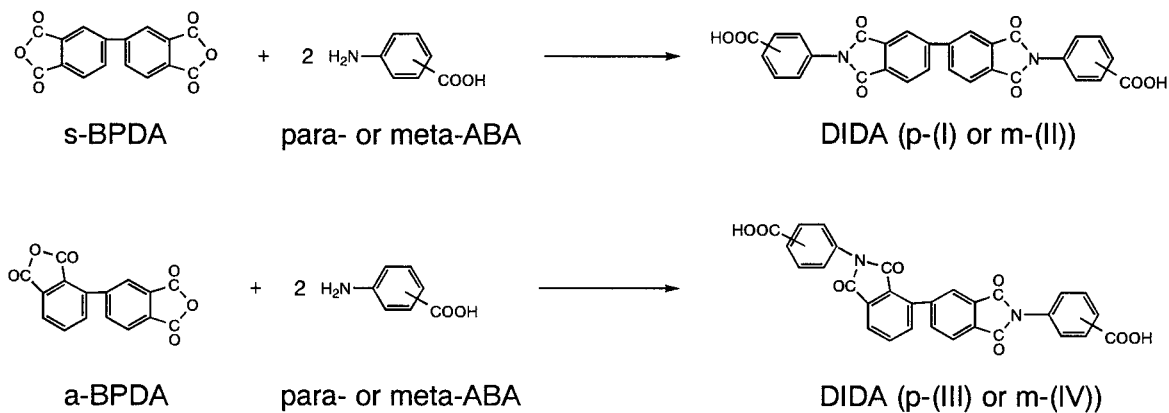
^a NMP: *N*-methyl-2-pyrrolidone. DMSO: dimethylsulfoxide. py: pyridine. ○: soluble at room temp. △: partially soluble. ×: insoluble.

^b Polymer film cast on a glass plate and cured at 300°C.

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

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

^e Not clearly defined.



Scheme I Preparation of DIDA monomers.

Figure 2. Elemental analyses and FD-MS spectra are as expected. All DIDAs described here were prepared in good yields by a convenient method. From these materials, diimide-dicarboxylic acid dichlorides were obtained by the reaction with excess thionyl chloride at reflux temperature using dimethylformamide as a catalyst.

Polymer Synthesis

A series of new PAIs was prepared by three methods, as shown in Scheme II.

Acid Chloride Method

Polycondensation of equimolar amounts of diamines and diimide-dicarboxylic acid dichlorides

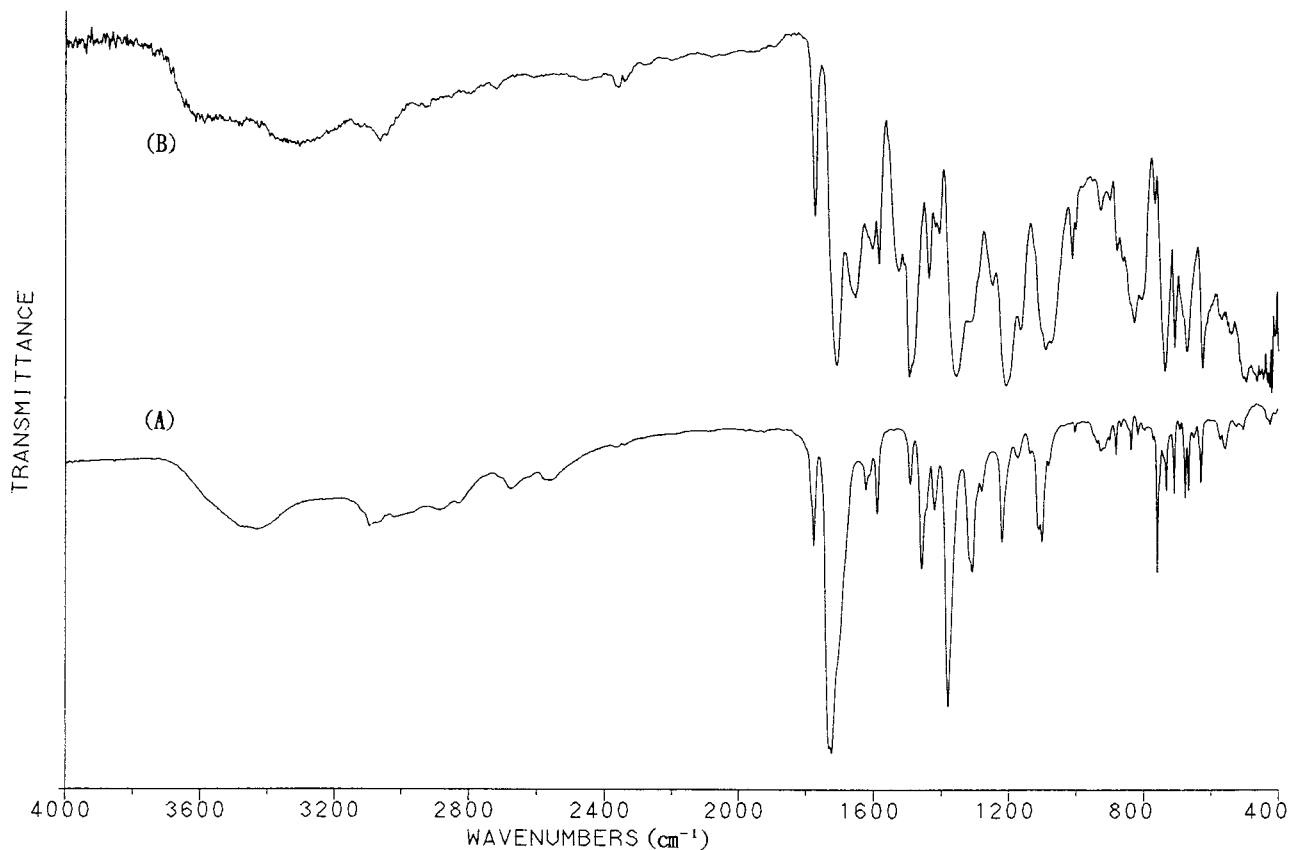
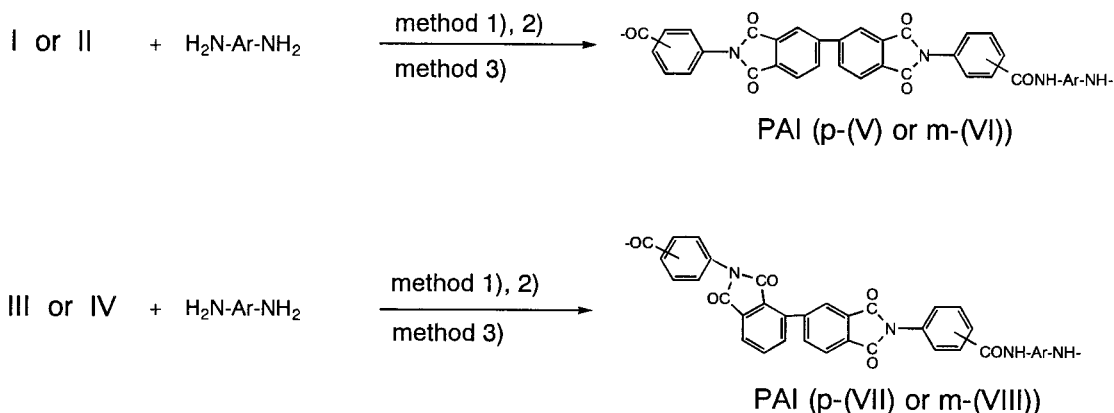


Figure 2 FTIR spectra of (a) DIDA-II (KBr) and (b) PAI-VIh (film).



Scheme II Polycondensation of PAIs: Method 1, from an acid chloride and an diamine; method 2, from an acid and an diamine using triphenyl phosphite and pyridine as a catalyst; method 3, from BPDA and ABA to give DIDA, and successively with an diamine using method 2.

in NMP at 60°C readily afforded a viscous polymer solution. In the case of I-Cl, most of PAIs precipitated from the reaction mixture. This property was expected because a linear structure of the product usually reduces the solubility. Therefore, the desired products could not be obtained by combining I-Cl with BAPB, BAPE, TPE-Q, and TPE-R, although a similar constituent structure has been recently reported to arise from *s*-BPDA and *N,N'*-*p*-phenylene bis(*p*-aminobenzamide) in a conventional polyamic acid method.³¹ We have successfully prepared PAIs in the series starting from II-Cl and III-Cl with all diamines investigated. However, IV-Cl afforded solutions of low viscosity, and the polymerization did not proceed as expected. This appeared to be due to the fact that IV-Cl is unstable even at room temperature.

Triphenyl Phosphite Method

Direct polycondensation of DIDAs with diamines using triphenyl phosphite and pyridine readily gives polymers in almost quantitative yields. This synthesis was also successfully applied to IV and diamines and afforded the desired products, which were not obtained by the acid chloride method. We met with no problems performing polycondensations of II and III. However, the inherent viscosities have been adjusted in the range of 0.5–0.7 using a molar ratio of DIDA : diamine (1.00 : 1.02) for an easy casting of polymers from solution. In view of the properties with a linear backbone as obtained by method 1, we did not try to prepare materials containing I as a component by method 2.

One-Pot Method

In a most convenient procedure, the preparation of DIDA and their subsequent polycondensation may be conducted in the same reaction vessel. This method presents considerable advantages in a large-scale production of PAI because it is not necessary to isolate DIDA. Thus, BPDA reacted with two mole equivalents of ABA in an aprotic solvent to form a DIDA. This was successively polycondensated with a diamine by the triphenyl phosphite method, affording a viscous solution. However, formation of a gelatinous product was observed when mixtures of *s*-BPDA, *m*-ABA, and DADE were heated in the presence of the condensing reagents.

The FTIR spectrum of polymer VIIh showed the characteristic bathochromic shifts of absorption bands (track B in Fig. 2): from 1776 to 1772 cm^{-1} for the symmetric and from 1730 and 1722 to 1709 cm^{-1} for the asymmetric imide C=O stretching mode. A new band at 1653 cm^{-1} (amide C=O stretching), and shifts from 1379 to 1356 cm^{-1} for the imide ring C—N, and from 758 to 737 cm^{-1} for the imide ring deformation mode were observed in accord with our expectations.³²

Properties of Polymers

All polymers except PAIs-V exhibit good solubilities in polar aprotic solvents such as NMP, DMSO, and py. The solubilities of PAIs correlate with the polymer structures. Polymer V, containing a straight chain structure, showed the lowest solubility. On the other hand, the en-

Table V Tensile Properties of PAI Films^a

| Polymer | η_{inh} (dL/g) | Strength at Break kgf/cm ² | Initial Modulus kgf/cm ² | Elongation at Break (%) |
|---------|------------------------|--|--|----------------------------|
| VIa | 0.51 | 1000 | 29,700 | 28 |
| VIb | 0.50 | 1020 | 32,000 | 7 |
| VIc | 0.71 | 1000 | 30,200 | 23 |
| VIId | 0.57 | 1120 | 31,300 | 50 |
| VIe | 0.70 | 980 | 27,700 | 41 |
| VIIf | 0.72 | 1100 | 32,200 | 30 |
| VIg | 0.69 | 1060 | 30,800 | 9 |
| VIh | 0.68 | 1220 | 32,000 | 38 |
| VIi | 0.37 | 1320 | 38,800 | 8 |
| VIIb | 0.99 | 1100 | 30,000 | 5 |
| VIIIj | 0.76 | 1240 | 35,300 | 10 |

^a Films were prepared by casting of polymer solutions.

hanced solubilities of PAIs-VIII are likely to result from the bent units of the a-BPDA components. The difference in solubilities is probably due to the fact that the bent structure provides few interchain interactions and prevents efficient packing of polymer chains.¹⁴ Inherent viscosities ranged at ca. 0.5–1.5 dL/g for most polymers. Although the reaction conditions were not optimized, the molecular weights of the polymers were high enough to give tough and flexible films when cast on a glass plate, followed by curing up to 300°C. The low viscosities of VI, VII, and VIII can be explained by the lower reactivity of 3,3'-DADS, which is due to the presence of the electron attracting sulfonyl groups. Even polymer VII showing the lowest viscosity (0.37 dL/g) gave a tough and flexible film (Table V). The 5% weight loss temperatures (T_d^5 s) and the glass transition temperatures (T_g s) are summarized in Table IV. The T_d^5 s of new polymers were found in the range 450–500°C, indicating good thermal stabilities at elevated temperatures. The glass transition temperatures (T_g s) were in the range of 220–290°C. There is no significant difference in T_g s between the polymers V–VIII and the polymers containing monoimide-dicarboxylic acids.⁸ Polymers VIII with a-BPDA skeleton have somewhat higher T_g s than polymers VI containing s-BPDA units. A similar tendency was found in polyimides (PI derived from s-BPDA and TPE-R: 220°C.³³ PI derived from a-BPDA and TPE-R: 250°C.* Tensile properties of typical PAIs are given in Table V. Tensile strengths at break of ca. 1000–1300 kgf/cm², elongation at break of 5–50%, and initial

moduli of ca. 30,000–39,000 kgf/cm² were typically found. Films prepared by casting from polymer solutions exhibited good tensile properties.

CONCLUSION

Four new diimide-dicarboxylic acids (DIDAs I–IV) were prepared by condensation of s- or a-BPDA with para- or meta-aminobenzoic acid. A series of new aromatic poly(amide-imide)s was prepared from these DIDAs using aromatic diamines. Most of polymers described here were readily soluble in polar aprotic solvents and could be cast into tough and flexible films.

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