Soluble Polyimides Based on Alkyloxydiaminobenzene

Yusuke TSUDA, Kenichi KANEGAE,* and Satoshi YASUKOUCHI*

Department of Biochemistry and Applied Chemistry,
Kurume National College of Technology,
1-1-1 Komorino, Kurume, Fukuoka 830-8555, Japan

*Advanced Engineering School, Kurume National College of Technology,
1-1-1 Komorino, Kurume, Fukuoka 830-8555, Japan

(Received May 10, 2000; Accepted August 8, 2000)

ABSTRACT: The synthesis and characterization of a novel series of soluble polyimides, which are based on alkyloxydiaminobenzene (AODB) and have long-chain linear alkyl groups with 10–14 carbon atoms, are described. Polyimides obtained from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and AODB-10–14 were soluble in polar solvents such as *N*-methyl-2-pyrrolidone (NMP) and the effect of long-chain linear alkyl groups for the enhancement of solubility was confirmed. Soluble copolyimides based on AODB and the conventional aromatic diamine diaminodiphenylether (DDE) may also be obtained. The incorporation of DDE resulted in an increase of the molecular weight and improved the thermal stability. These polyimides and copolyimides based on AODB were soluble in various polar solvents and exhibited high thermal stability in air and nitrogen. The copolymerization experiments and the solubility tests demonstrated that the most effective alkyl chain length for improving the solubility is twelve.

KEY WORDS Polyimide / Soluble Polyimide / Alkyloxydiaminobenzene / Copolymerization / Thermal Stability / Solubility /

Polyimides exhibit excellent thermal and mechanical properties, and have extensive engineering and microelectronics applications.¹ Aromatic polyimides such as pyromellitic polyimides are prepared from aromatic diamines and aromatic tetracarboxylic dianhydrides *via* poly(amic acid)s. Since conventional aromatic polyimides are insoluble, these polymers are usually processed as the corresponding soluble poly(amic acid) precursors, and then either thermally or chemically imidized. However, there are some problems owing to the instability of poly(amic acid)s and the liberation of water in the imidization process. Therefore, soluble polyimides that are processable without difficulty are desired. Several approaches to improve the solubility of polyimides have been investigated.^{2–32} The solubility of polyimides has been successfully improved by the incorporation of fluorine moieties,^{2–7} chlorine moieties,⁸ bulky side groups,^{9–11} pendant phenyl groups,^{12–16} pendant benzoxazole or benzothiazole groups,¹⁷ polydimethylsiloxane segments,^{18–19} polyalicyclic structures,^{20–27} naphthalene moieties,²⁸ spiro structures,²⁹ pyrazoline moieties³⁰ or benzhydrol units³¹ into the polymer backbone. Recently, the authors reported the synthesis and characterization of soluble polyimides and copolyimides based on alkyldiaminobenzophenone (ADBP) having long-chain linear alkyl groups with 9–14 carbon atoms and conventional tetracarboxylic dianhydrides such as 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA)³² (Scheme 1). It was concluded that ADBP with an even number of carbon atoms was effective in enhancing the solubility, while polymers based on ADBP with an odd number of carbon atoms remained insoluble.

This paper reports the synthesis and characterization of a novel series of soluble polyimides based on alkyloxydiaminobenzenes (AODB) having long-chain linear alkyl groups with 10–14 carbon atoms. The factors affecting the solubility of the final polymers, such as the alkyl chain length of AODB, and the copolymerization effects

using the conventional aromatic diamine 4,4'-diaminodiphenylether (DDE) are discussed and compared with the results based on ADBP. Although polyimides based on AODB having 12 or 18 carbon atoms have already been reported,³³ the synthesis and characterization of such polymers were not described in detail and only three copolyimides based on cyclobutane tetracarboxylic dianhydride (CBDA), AODB, and DDE or 1,4-phenylenediamine (PDA) with fixed *co*-monomer ratios, *e.g.*, AODB-12/DDE (20/80), were reported using the conventional two-step method *via* poly(amic acid) precursors. These polyimides were designed for the use as alignment layers for LCDs, and are not soluble. This paper focuses on more fundamental research concerning the effects of long-chain linear alkyl groups on the polymer properties. The thermal stability of the polyimides and copolyimides is characterized with thermogravimetric analysis (TGA) and the solubility is determined in various common solvents. The Attaching of alkyl side chains to polyimides has recently been used to increase pretilt angles generated by the polymers in alignment layer applications of liquid crystal displays (LCDs) and,

BTDA/ADBP-9; Insoluble
BTDA/ADBP-10; Soluble
BTDA/ADBP-11; Insoluble
BTDA/ADBP-12; Soluble
BTDA/ADBP-13; Insoluble
BTDA/ADBP-14; Soluble
(NMP)

Scheme 1. Solubility of polyimides based on alkyldiaminobenzophenone (ADBP).

thus, these studies are of great practical importance.³³⁻³⁵

EXPERIMENTAL

Materials

2,4-Dinitrophenol and *n*-alkylbromides were purchased from Tokyo Chemical Industry Co., Ltd. and used as received, as were potassium carbonate and 10% Pd/C, which were purchased from Wako Pure Chemical Industries, Ltd. Hydrogen gas (Kyushu Fuel Co., Ltd.), 3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA) and 4,4'-diaminodiphenylether (DDE) (Wakayama Seika Kogyo Co., Ltd.) were also used as received. *N*-methyl-2-pyrrolidone (NMP) (Mitsubishi Chemicals) was distilled under reduced pressure. Reagent grade *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), 1,3-dimethyl-2-imidazolidinone (DMI), *m*-cresol, tetrahydrofuran (THF), dichloromethane, sulfuric acid, acetic anhydride and pyridine were purchased from Wako Pure Chemical Industries, Ltd. and used as received. Dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) and other conventional reagents were also used as received.

Measurements

The inherent viscosities of all polymers were measured using Cannon Fenske viscometers at a concentration of 0.5 g dL⁻¹ in NMP at 30°C. Thermogravimetric analysis (TGA) was performed on a Shimadzu thermogravimetric analyzer (Model TGA-50) under air or nitrogen at a heating rate of 10°C min⁻¹. ¹H NMR spectra were measured on a JEOL JNM-EX 270 FT NMR in dimethyl sulfoxide-*d*₆ with tetramethylsilane (TMS) as an internal reference. IR spectra were measured on a JASCO IR Report-100 spectrophotometer.

Synthesis of 1-Dodecyloxy-2,4-dinitrobenzene

2,4-Dinitrophenol (3.00 g, 16.0 mmol) and 1-bromodecane (4.06 g, 16.0 mmol) were dissolved in 30 mL of DMAc. After potassium carbonate (4.50 g, 32.6 mmol) was added, the reaction mixture was stirred at 120°C for 24 h. The reaction mixture was then poured onto 100 mL of ice water. Toluene was added to dissolve the precipitate and the organic layer was separated and washed sequentially with H₂O, 10% aqueous NaOH, and H₂O. Subsequently, it was dried over anhydrous sodium sulfate, filtered and the toluene was evaporated. The obtained solid was decolorized with charcoal and recrystallized from hexane to give 4.72 g (13.4 mmol, 88% yield) of white crystals. Mp 45°C; ¹H NMR (DMSO-*d*₆): δ 0.85 (t, 3H, -O-CH₂-CH₂-(CH₂)₉-CH₃, *J*=6.43 Hz), 1.2–1.5 (m, 18H, -O-CH₂-CH₂-(CH₂)₉-CH₃), 1.6–1.8 (m, 2H, -O-CH₂-CH₂-(CH₂)₉-CH₃), 4.31 (t, 2H, -O-CH₂-CH₂-(CH₂)₉-CH₃, *J*=6.27 Hz), 7.59 (d, 1H, 6-H, *J*=9.57 Hz), 8.48 (dd, 1H, 5-H, *J*₁=2.64 Hz, *J*₂=9.57 Hz), 8.74 (d, 1H, 3-H, *J*=2.64 Hz); IR (KBr): 1520, 1340 (NO₂), 1270 (-O-) cm⁻¹. *Anal.* Calcd for C₁₈H₂₈N₂O₅: C, 61.34%; H, 8.01%; N, 7.95%. Found: C, 61.68%; H, 8.10%; N, 7.80%.

Other 1-alkyloxy-2,4-dinitrobenzenes were synthesized according to the procedure described above (60–70% yield). Melting points (mp), ¹H NMR, IR and elemental analyses are as follows.

1-Decyloxy-2,4-dinitrobenzene

Mp 30.9°C; ¹H NMR (DMSO-*d*₆): δ 0.85 (t, 3H, -O-CH₂-CH₂-(CH₂)₇-CH₃, *J*=6.60 Hz), 1.2–1.5 (m, 14H, -O-CH₂-CH₂-(CH₂)₇-CH₃), 1.6–1.8 (m, 2H, -O-CH₂-CH₂-(CH₂)₇-CH₃), 4.31 (t, 2H, -O-CH₂-CH₂-(CH₂)₇-CH₃, *J*=6.35 Hz), 7.59 (d, 1H, 6-H, *J*=9.28 Hz), 8.48 (dd, 1H, 5-H, *J*₁=2.69 Hz, *J*₂=9.28 Hz), 8.74 (d, 1H, 3-H, *J*=2.64 Hz); IR (KBr): 1520, 1340 (NO₂), 1280 (-O-) cm⁻¹. *Anal.* Calcd for C₁₆H₂₄N₂O₅: C, 59.24%; H, 7.46%; N, 8.64%. Found: C, 59.41%; H, 7.48%; N, 8.58%.

1-Undecyloxy-2,4-dinitrobenzene

Mp 43.2°C; ¹H NMR (DMSO-*d*₆): δ 0.85 (t, 3H, -O-CH₂-CH₂-(CH₂)₈-CH₃, *J*=6.27 Hz), 1.2–1.5 (m, 16H, -O-CH₂-CH₂-(CH₂)₈-CH₃), 1.6–1.8 (m, 2H, -O-CH₂-CH₂-(CH₂)₈-CH₃), 4.31 (t, 2H, -O-CH₂-CH₂-(CH₂)₈-CH₃, *J*=6.11 Hz), 7.59 (d, 1H, 6-H, *J*=9.24 Hz), 8.48 (dd, 1H, 5-H, *J*₁=2.48 Hz, *J*₂=9.21 Hz), 8.74 (d, 1H, 3-H, *J*=2.97 Hz); IR (KBr): 1530, 1340 (NO₂), 1280 (-O-) cm⁻¹. *Anal.* Calcd for C₁₇H₂₆N₂O₅: C, 60.34%; H, 7.74%; N, 8.28%. Found: C, 60.59%; H, 7.78%; N, 8.22%.

1-Tridecyloxy-2,4-dinitrobenzene

Mp 53.8°C; ¹H NMR (DMSO-*d*₆): δ 0.85 (t, 3H, -O-CH₂-CH₂-(CH₂)₁₀-CH₃, *J*=6.27 Hz), 1.2–1.5 (m, 20H, -O-CH₂-CH₂-(CH₂)₁₀-CH₃), 1.6–1.8 (m, 2H, -O-CH₂-CH₂-(CH₂)₁₀-CH₃), 4.31 (t, 2H, -O-CH₂-CH₂-(CH₂)₁₀-CH₃, *J*=6.27 Hz), 7.59 (d, 1H, 6-H, *J*=9.57 Hz), 8.48 (dd, 1H, 5-H, *J*₁=2.64 Hz, *J*₂=9.57 Hz), 8.74 (d, 1H, 3-H, *J*=2.97 Hz); IR (KBr): 1520, 1340 (NO₂), 1280 (-O-) cm⁻¹. *Anal.* Calcd for C₁₉H₃₀N₂O₅: C, 62.27%; H, 8.25%; N, 7.67%. Found: C, 62.40%; H, 8.25%; N, 7.61%.

1-Tetradecyloxy-2,4-dinitrobenzene

Mp 51.0°C; ¹H NMR (DMSO-*d*₆): δ 0.85 (t, 3H, -O-CH₂-CH₂-(CH₂)₁₁-CH₃, *J*=6.60 Hz), 1.22 (m, 22H, -O-CH₂-CH₂-(CH₂)₁₁-CH₃), 1.75 (m, 2H, -O-CH₂-CH₂-(CH₂)₁₁-CH₃), 4.30 (t, 2H, -O-CH₂-CH₂-(CH₂)₁₁-CH₃, *J*=6.27 Hz), 7.59 (d, 1H, 6-H, *J*=9.24 Hz), 8.48 (dd, 1H, 5-H, *J*₁=2.97 Hz, *J*₂=9.24 Hz), 8.73 (d, 1H, 3-H, *J*=2.97 Hz); IR (KBr): 1530, 1340 (NO₂), 1280 (-O-) cm⁻¹. *Anal.* Calcd for C₂₀H₃₂N₂O₅: C, 63.13%; H, 8.48%; N, 7.36%. Found: C, 63.61%; H, 8.61%; N, 7.18%.

Synthesis of 1-Dodecyloxy-2,4-diaminobenzene (AODB-12)

A mixture of 2 g (5.6 mmol) of 1-dodecyloxy-2,4-dinitrobenzene and 0.582 g of 10% palladium on carbon (Pd/C) in 30 mL of DMF was stirred at 80°C for 24 h under 2.0–2.5 atm of hydrogen gas using a medium pressure hydrogenator (Ishii Laboratory Works Co., Ltd.). The solution was filtered and the DMF was evaporated. The crude diamine was recrystallized from an ethanol/water mixture with charcoal to give 1.39 g (84% yield) of a pale brown powder. Mp 58.4°C; ¹H NMR (DMSO-*d*₆): δ 0.85 (t, 3H, -Ar-O-CH₂-CH₂-(CH₂)₉-CH₃, *J*=6.43 Hz), 1.2–1.4 (m, 18H, -Ar-O-CH₂-CH₂-(CH₂)₉-CH₃), 1.6–1.7 (m, 2H, -Ar-O-CH₂-CH₂-(CH₂)₉-CH₃), 3.74 (t, 2H, -Ar-O-CH₂-CH₂-(CH₂)₉-CH₃, *J*=6.43 Hz), 4.2–4.4 (m, 4H, NH₂), 5.74 (dd, 1H, 5-H, *J*₁=2.64 Hz, *J*₂=8.24 Hz), 5.95 (d, 1H, 3-H, *J*=2.64 Hz), 6.45 (d, 1H, 6-H, *J*=8.24 Hz). IR (KBr): 3300, 3400 (NH₂), 1230 (-O-) cm⁻¹. *Anal.*

Scheme 2. Synthesis of alkyloxydiaminobenzenes (AODB).

Calcd for $C_{18}H_{32}N_2O$: C, 73.92%; H, 11.03%; N, 9.58%. Found: C, 73.92%; H, 10.94%; N, 9.47%. Other 1-alkyloxy-2,4-diaminobenzenes (AODB-10, 11, 13, 14) were synthesized according to the procedure described above (54–77% yield). Melting points (mp), 1H NMR, IR and elemental analyses are as follows.

1-Decyloxy-2,4-diaminobenzene (AODB-10)

Mp 50.5°C; 1H NMR (DMSO- d_6): δ 0.85 (t, 3H, -Ar-O-CH₂-CH₂-(CH₂)₇-CH₃, J =6.60 Hz), 1.2–1.4 (m, 14H, -Ar-O-CH₂-CH₂-(CH₂)₇-CH₃), 1.6–1.7 (m, 2H, -Ar-O-CH₂-CH₂-(CH₂)₇-CH₃), 3.74 (t, 2H, -Ar-O-CH₂-CH₂-(CH₂)₇-CH₃, J =6.60 Hz), 4.2–4.4 (m, 4H, NH₂), 5.74 (dd, 1H, 5-H, J_1 =2.64 Hz, J_2 =8.30 Hz), 5.95 (d, 1H, 3-H, J =2.64 Hz), 6.45 (d, 1H, 6-H, J =8.30 Hz). IR (KBr): 3300, 3400 (NH₂), 1230 (-O-) cm^{-1} . Anal. Calcd for $C_{16}H_{28}N_2O$: C, 72.68%; H, 10.67%; N, 10.59%. Found: C, 72.28%; H, 10.45%; N, 10.49%.

1-Undecyloxy-2,4-diaminobenzene (AODB-11)

Mp 61.9°C; 1H NMR (DMSO- d_6): δ 0.86 (t, 3H, -Ar-O-CH₂-CH₂-(CH₂)₈-CH₃, J =6.60 Hz), 1.2–1.4 (m, 16H, -Ar-O-CH₂-CH₂-(CH₂)₈-CH₃), 1.6–1.7 (m, 2H, -Ar-O-CH₂-CH₂-(CH₂)₈-CH₃), 3.74 (t, 2H, -Ar-O-CH₂-CH₂-(CH₂)₈-CH₃, J =6.43 Hz), 4.2–4.4 (m, 4H, NH₂), 5.74 (dd, 1H, 5-H, J_1 =2.64 Hz, J_2 =8.25 Hz), 5.95 (d, 1H, 3-H, J =2.64 Hz), 6.45 (d, 1H, 6-H, J =8.25 Hz). IR (KBr): 3300, 3400 (NH₂), 1230 (-O-) cm^{-1} . Anal. Calcd for $C_{17}H_{30}N_2O$: C, 73.33%; H, 10.86%; N, 10.06%. Found: C, 72.83%; H, 10.67%; N, 9.95%.

1-Tridecyloxy-2,4-diaminobenzene (AODB-13)

Mp 66.5°C; 1H NMR (DMSO- d_6): δ 0.85 (t, 3H, -Ar-O-CH₂-CH₂-(CH₂)₁₀-CH₃, J =6.60 Hz), 1.2–1.4 (m, 20H, -Ar-O-CH₂-CH₂-(CH₂)₁₀-CH₃), 1.6–1.7 (m, 2H, -Ar-O-CH₂-CH₂-(CH₂)₁₀-CH₃), 3.74 (t, 2H, -Ar-O-CH₂-CH₂-(CH₂)₁₀-CH₃, J =6.43 Hz), 4.2–4.4 (m, 4H, NH₂), 5.74 (dd, 1H, 5-H, J_1 =2.64 Hz, J_2 =8.58 Hz), 5.95 (d, 1H, 3-H, J =2.64 Hz), 6.45 (d, 1H, 6-H, J =8.58 Hz). IR (KBr): 3400, 3500 (NH₂), 1220 (-O-) cm^{-1} . Anal. Calcd for $C_{19}H_{34}N_2O$: C, 74.46%; H, 11.18%; N, 9.14%. Found: C, 74.10%; H, 10.95%; N, 8.75%.

1-Tetradecyl-2,4-diaminobenzene (AODB-14)

Mp 66.0°C; 1H NMR (DMSO- d_6): δ 0.85 (t, 3H, -Ar-O-CH₂-CH₂-(CH₂)₁₁-CH₃, J =6.43 Hz), 1.2–1.4 (m, 22H, -Ar-O-CH₂-CH₂-(CH₂)₁₁-CH₃), 1.6–1.7 (m, 2H, -Ar-O-CH₂-CH₂-(CH₂)₁₁-CH₃), 3.73 (t, 2H, -Ar-O-CH₂-CH₂-(CH₂)₁₁-CH₃, J =6.43 Hz), 4.2–4.4 (m, 4H, NH₂), 5.74 (dd, 1H, 5-H, J_1 =2.64 Hz, J_2 =8.24 Hz), 5.94 (d, 1H, 3-H, J =2.64 Hz), 6.45 (d, 1H, 6-H, J =8.25 Hz). IR (KBr): 3400, 3500 (NH₂), 1230 (-O-) cm^{-1} . Anal. Calcd for $C_{20}H_{36}N_2O$: C, 74.95%; H, 11.32%; N, 8.74%. Found: C, 74.66%; H, 11.18%; N, 8.55%.

Preparation of Poly(amic acid)s

In a typical example, 0.786 g (2.44 mmol) of BTDA and 0.714 g (2.44 mmol) of AODB-12 were placed in a 30 mL flask. The system was purged with nitrogen and NMP was added. The monomer concentration was kept at 20 wt% and the mixture stirred at 60°C under nitrogen for 12 h to allow the viscosity to increase. The BTDA/AODB-12 poly(amic acid) solution was diluted with NMP, keeping the polymer concentration at 10 wt%. A one-third portion of the mixture was poured into a large amount of water or methanol. The precipitated poly(amic acid) was filtered, washed with excess methanol and dried at room temperature for 2 days. The residual two-thirds of the poly(amic acid) solution were used for the subsequent polyimide preparation. 1H NMR (DMSO- d_6): δ 0.81 (m, 3 H, -Ar-O-CH₂-CH₂-(CH₂)₉-CH₃), 1.1–1.4 (m, 18H, -Ar-O-CH₂-CH₂-(CH₂)₉-CH₃), 1.6–1.7 (m, 2H, -Ar-O-CH₂-CH₂-(CH₂)₉-CH₃), 3.95 (t, 2H, -Ar-O-CH₂-CH₂-(CH₂)₉-CH₃), 7.0–8.3 (m, 9H, arom.), 9.3–9.6 (m, 2H, -NH-) ppm. IR (KBr): 3500 (O-H and N-H), 1780, 1710, 1660 (C=O) cm^{-1} . Anal. Calcd for $C_{35}H_{39}N_2O_8$: C, 68.28%; H, 6.38%; N, 4.55%. Found: C, 67.42%; H, 6.61%; N, 5.01%.

Preparation of Polyimides

In a typical example, to 10 g of the above 10 wt% BTDA/AODB-12 poly(amic acid) solution were added 0.643 g (8.13 mmol) of pyridine and 0.664 g (6.60 mmol) of acetic anhydride. The system was purged with nitrogen and was stirred at 120°C under nitrogen for 5 h. The polyimide was obtained as a powder by precipitation in a large amount of methanol, filtering, washing with a large amount of methanol, and drying at 100°C for 1 day. 1H NMR (DMSO- d_6): δ 0.81 (broad s, 3H, -Ar-O-CH₂-CH₂-(CH₂)₉-CH₃), 1.1–1.4 (m, 18H, -Ar-O-CH₂-CH₂-(CH₂)₉-CH₃), 1.5–1.7 (m, 2H, -Ar-O-CH₂-CH₂-(CH₂)₉-CH₃), 4.05 (m, 2H, -Ar-O-CH₂-CH₂-(CH₂)₉-CH₃), 7.3–8.3 (m, 9H, arom.) ppm. IR (KBr): 1780, 1740 (C=O), 1360 (C-N) cm^{-1} . Anal. Calcd for $C_{35}H_{35}N_2O_6$: C, 72.52%; H, 6.09%; N, 4.83%. Found: C, 70.04%; H, 5.84%; N, 4.99%.

Copoly(amic acid)s and copolyimides using DDE as diamine co-monomer were carried out in the same manner. An equimolar amount of BTDA was used with respect to the total amount of diamines and all monomers were added at the beginning of reaction.

RESULTS AND DISCUSSION

Monomer Synthesis

The diamines, alkyloxydiaminobenzene (AODB), were prepared in two steps using 2,4-dinitrophenol as a starting material. The synthetic route is illustrated in Scheme 2. The Williamson reaction using 2,4-dinitrophenol and 1-bromoalkanes catalyzed by potassium car-

Scheme 3. Synthesis of homopoly(amic acid)s and homopolyimides based on alkyoxydiaminobenzene (AODB).

bonate in DMAc gave 1-alkyloxy-2,4-dinitro-benzenes in satisfactory yields (60–88%). The reduction of 1-alkyloxy-2,4-dinitro-benzenes were performed by catalytic hydrogenation using Pd/C and hydrogen gas at 2–2.5 atm. Although the hydrazine hydrate/ethanol system or relatively mild hydrogenation using a laboratory balloon filled with hydrogen gas can be used for the reduction of nitrocompounds, the medium pressure system is preferable due to the yields and purity of the products. Thus, AODB-10–14 were obtained in satisfactory yields (54–84%) and well characterized by ¹H NMR, IR and elemental analyses.

Polymer Synthesis

The synthetic route to the soluble polyimides based on AODB and BTDA, which is a representative aromatic tetracarboxylic dianhydride, is illustrated in Scheme 3. It consists of a poly(amic acid) synthesis followed by chemical imidization. The poly(amic acid) units based on BTDA can theoretically exist as three isomers due to the unsymmetrical structure.^{30,37} The poly(amic acid)s were obtained by reacting AODB with an equimolar amount of BTDA at 60°C for 12 h under a nitrogen atmosphere. The polyimides were obtained by chemical imidization at 120°C in the presence of pyridine as base catalyst and acetic anhydride as dehydrating agent. These are the optimized synthetic conditions previously developed for the synthesis of soluble polyimides in our laboratory.^{26,27,32} All results for the copolymerization experiments using the conventional aromatic diamine DDE with AODB in various compositions are summarized in Table I. All polymers were well characterized by ¹H NMR and IR. Carbon analysis values were found to be lower than the calculated ones and a trace amount of residue was observed after elemental analysis, probably due to the formation of char, which is characteristic for heat-resistant polymers.³⁶

The polyimides based on BTDA and AODB-10–14 were soluble in NMP. As BTDA did not give NMP-soluble polyimides in combination with conventional aromatic diamines such as PDA, 4,4'-diaminodiphenylmethane (DDM) and DDE,³⁰ the effect of AODB in en-

hancing the solubility was confirmed. In the case of ADBP, it was reported that only ADBP having an even number of carbon atoms gave soluble polyimides in combination with BTDA.³² Therefore, it can be speculated that AODB bearing long-chain linear alkyl groups *via* a flexible ether linkage would be more effective in increasing the solubility in comparison with ADBP, where these groups are attached by less flexible benzoyl groups.

Inherent viscosities (η_{inh}), which are connected to the molecular weights of polymers, were low and in the range of 0.15–0.17 dL g⁻¹ for the polyimides based on AODB. This is probably due to the lower reactivity of AODB compared to conventional aromatic diamines such as DDE. Because AODB is a meta-substituted diamine and sterically hindered due to the bulky long-chain alkyl groups.

In order to reduce the amount of special monomer, AODB, and improve the molecular weight of the polymers, copolymerization experiments using DDE as diamine *co*-monomer have been examined (Scheme 4, Table II). In the case of copolyimides, the sequential addition of monomers has sometimes been carried out in order to compensate the difference in monomer reactivity.^{38,39} The authors have investigated random copolyimides, and added all the monomers at the beginning of the reaction in accordance with literature procedures.^{27,32,33,40} As polymer yields were nearly 100% for all copolyimides, solubilities and thermal stabilities of these copolyimides are considered simply based on the initial molar ratios of both diamine monomers. BTDA/AODB-10/DDE and BTDA/AODB-14/DDE copolyimides containing 75 mol% of AODB units were soluble in NMP, while those containing less than 75 mol% of AODB units were not soluble in NMP. BTDA/AODB-11/DDE and BTDA/AODB-13/DDE copolyimides containing 50 mol% or more of AODB units were soluble in NMP, while those containing less than 50 mol% of AODB units were not soluble in this solvent. AODB-12 was found to be the most effective AODB unit for preparing soluble polyimides, and BTDA/AODB-12/DDE copolyimides containing 25 mol% or more of AODB-12 units were also soluble in NMP. It is interesting to note that the effect of the chain length of AODB can be summarized as follows; AODB-12 > AODB-11, 13 > AODB-10, 14. It can be presumed that the entropy effect of long-chain linear alkyl groups increases up to a chain length of 12 methylene units, however, the crystallization of long-chain linear alkyl groups might become dominant in the case of those having more than 12 units, and eventually decrease the solubility of the polymers. The incorporation of the highly reactive aromatic diamine DDE results in the increment of the inherent viscosities, and the maximum values is 0.37 dL g⁻¹. In the case of soluble copolyimides, clear polymer solutions in NMP were eventually obtained. However, in the case of insoluble polyimides, gelation or precipitation occurred in the course of the imidization process. The inherent viscosities increased in proportion to the amounts of DDE used, and the copolyimides finally became insoluble (Table I). Therefore, it may be considered that the solubility of copolyimides results not only from the copolymer structures but also from the molecular weights. However, the authors presume that the copolymer structures, *i.e.*, diamine compositions and chain length of the

Table I. Polyimides and copolyimides based on BTDA/AODB/DDE

Diamine ^a		Polyamic acid	Polyimide			
AODB-X DDE		η_{inh}^b	Solubility in NMP	η_{inh}^b	10% Weight-loss temperature ^c	
mol%		dL g ⁻¹		dL g ⁻¹	in Air	in N ₂
					°C	°C
AODB-10						
0	100	0.68	Insoluble			
25	75	0.35	Insoluble			
50	50	0.25	Insoluble			
75	25	0.15	Soluble	0.17	444	452
100	0	0.14	Soluble	0.15	437	443
AODB-11						
0	100	0.68	Insoluble			
25	75	0.54	Insoluble			
50	50	0.35	Soluble	0.37	471	468
75	25	0.26	Soluble	0.26	448	454
100	0	0.18	Soluble	0.16	434	445
AODB-12						
0	100	0.68	Insoluble			
25	75	0.39	Soluble	0.29	460	456
50	50	0.21	Soluble	0.23	456	457
75	25	0.14	Soluble	0.19	447	452
100	0	0.14	Soluble	0.16	436	441
AODB-13						
0	100	0.68	Insoluble			
25	75	0.52	Insoluble			
50	50	0.33	Soluble	0.34	467	472
75	25	0.22	Soluble	0.24	451	454
100	0	0.15	Soluble	0.17	433	434
AODB-14						
0	100	0.68	Insoluble			
25	75	0.37	Insoluble			
50	50	0.19	Insoluble			
75	25	0.18	Soluble	0.22	447	441
100	0	0.14	Soluble	0.16	438	442

^a An equimolar amount of BTDA was used with respect to the total amount of diamine. ^b Measured at 0.5 g dL⁻¹ in NMP at 30 °C.

^c Measured at a heating rate of 10 °C min⁻¹.

lateral alkyl groups, are the dominant factors in the solubility of these copolyimides, as there are several examples of polyimides with low inherent viscosities being insoluble (AODB-14/DDE=50/50 in Table I, lit 26, 27, and 32).

High imidization ratios are required to obtain stable polyimides with excellent performance.⁴¹ In the case of soluble polyimides, NMR measurements are convenient, because solutions of the samples can be prepared and give quantitative imidization ratio data.^{26,27,32} The imidization ratios of these polyimides and copolyimides based on AODB were judged from the reduction of intensity of the NH proton signals in the poly(amic acid)s to the aromatic proton signals, and were found to be 100%.

Polymer Properties

The thermal stability of these polyimides were evaluated by 10% weight-loss temperatures in TGA measurements. The ten percent weight-loss temperatures of AODB polyimides were sufficiently high and in the range of 433–471 °C in air and 434–472 °C under nitrogen (Table I). As the incorporation of DDE resulted in a reduction of aliphatic components of the polyimides, 10% weight-loss temperatures of BTDA/AODB/DDE copolyimides tended to increase by the increment of the DDE component. Generally, 10% weight-loss temperatures of the polyimides under nitrogen were higher than those in air, with the exception of the BTDA/AODB polyimides,

which showed similar values both in air and under nitrogen. It is presumed that oxidation of the long-chain alkyl groups affects the thermal degradation in air, as several literature references have demonstrated that polymers with methyl and polymethylene groups show higher degradation temperatures in air than under nitrogen due to the oxidation of these groups and increase in weight.^{42–44}

The solubility of the obtained polyimides was determined in 9 common solvents at 5 wt% concentration (Table II). Homopolyimides containing AODB-10–14 were soluble in polar solvents such as NMP, DMF, DMAc, DMI, *m*-cresol, CH₂Cl₂, and H₂SO₄. It is interesting to note that the solubility in DMSO and THF again points to twelve as being the most effective alkyl chain length. The copolyimides based on BTDA/AODB-10–14/DDE were less soluble in comparison with the homopolyimides. All the copolyimides were soluble in NMP, *m*-cresol, and H₂SO₄, however, some of these copolyimides were insoluble in DMF, DMAc, DMSO, DMI, THF, and CH₂Cl₂. The solubility data of copolyimides in DMAc and DMSO suggests that the copolyimides containing AODB-12 are the most soluble, while the data for DMF, DMAc, DMSO, DMI, THF, and CH₂Cl₂ demonstrates that the solubility decreased with the increase of DDE.

Scheme 4. Synthesis of copoly(amic acid)s and copolyimides based on alkyoxydianaminobenzene (AODB).

Table II. Solubility behavior of polyimides and copolyimides based on AODB in various solvents

Monomer composition ^a	Solubility ^b								
Diamine/mol%	NMP	DMF	DMAc	DMSO	DMI	<i>m</i> -Cresol	THF	CH ₂ Cl ₂	H ₂ SO ₄
Polyimides									
AODB-10(100)	S	S	S	S	S	S	I	S	S
AODB-11(100)	S	S	S	S(h)	S	S	S(h)	S	S
AODB-12(100)	S	S	S	S	S	S	S	S	S
AODB-13(100)	S	S	S	S(h)	S	S	S(h)	S	S
AODB-14(100)	S	S	S	S(h)	S	S	I	S	S
Copolyimides									
AODB-11(75) DDE(25)	S	S	S	S(h)	S	S	S(h)	S	S
AODB-11(50) DDE(50)	S	I	I	I	I	S	I	I	S
AODB-12(75) DDE(25)	S	S	S	S	S	S	S(h)	S	S
AODB-12(50) DDE(50)	S	I	S	I	S	S	I	I	S
AODB-12(25) DDE(75)	S	I	S	I	S	S	I	I	S
AODB-13(75) DDE(25)	S	S	S	S(h)	S	S	S(h)	S	S
AODB-13(50) DDE(50)	S	I	I	I	S	S	I	I	S
AODB-14(75) DDE(25)	S	S	S	S(h)	S	S	S	S	S

^a An equimolar amount of BTDA was used with respect to the total amount of diamine. ^b S, soluble; S(h), soluble at heated temperature; I, insoluble.

CONCLUSION

Novel polyimides and copolyimides based on alkyoxydianaminobenzene (AODB), which have long-chain linear alkyl groups, and the conventional tetracarboxylic dianhydride BTDA were successfully synthesized and showed excellent solubility in various polar solvents and thermal stability. This solubility is assumed to result from the entropy effect of flexible alkyl groups. AODB bearing alkyl groups *via* an ether linkage are more effective in comparison with alkyldianaminobenzophenone (ADBP) where these groups are attached by benzoyl groups. Copolymerization using the conventional aromatic diamine DDE resulted in the improvement of both the molecular weight and the thermal stability, and demonstrated that AODB-12 was the most effective in enhancing the solubility of the AODB-10–14-based polyimides. It can be presumed that the entropy effect of long-chain linear alkyl groups increases up to 12 methylene units, however, the crystallization of these side groups having more than 12 methylene units might decrease the solubility of the polymers.

Acknowledgments. The authors thank Dr. Yoshiyuki Oishi of Iwate University, Drs. Shuntaro Mataka and

Atsushi Takahara of Kyushu University, and Drs. Virgil Percec and Catherine Mitchell of the University of Pennsylvania for valuable advice. Financial support from the Technopolis Foundation of Kurume-Tosu is gratefully acknowledged.

REFERENCES

1. a) K. L. Mittal, Ed., "Polyimides", Plenum Press, New York, N.Y., 1984; b) M. K. Ghosh and K. L. Mittal, Ed., "Polyimides", Marcel Dekker, New York, N.Y., 1996.
2. J. E. McGrath, M. E. Rogers, C. A. Arnold, Y. J. Kim, and J. C. Hedrick, *Macromol. Chem., Macromol. Symp.*, **51**, 103 (1991).
3. S. Z. D. Cheng, F. E. Arnold, Jr., A. Zhang, S. L. -C. Hsu, and F. W. Harris, *Macromolecules*, **24**, 5856 (1991).
4. F. E. Arnold, Jr., S. Z. D. Cheng, S. L. -C. Hsu, C. J. Lee, F. W. Harris, and S. -F. Lau, *Polymer*, **33**, 5179 (1992).
5. M. E. Rogers, M. H. Brink, J. E. McGrath, and A. Brennan, *Polymer*, **34**, 849 (1993).
6. J. W. Park, M. Lee, M. -H. Lee, J. W. Liu, S. D. Kim, J. Y. Chang, and S. B. Rhee, *Macromolecules*, **27**, 3459 (1994).
7. S. -H. Lin, F. Li, S. Z. D. Cheng, and F. W. Harris, *Macromolecules*, **31**, 2080 (1998).
8. P. A. Falcigno, S. Jasne, and M. King, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 1433 (1992).
9. C. -P. Yang and J. -H. Lin, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 423 (1994).
10. D. -J. Liaw and B. -Y. Liaw, *J. Polym. Sci., Polym. Chem. Ed.*,

- 35, 1527 (1997).
11. D. J. Liaw and B. Y. Liaw, *Polymer*, **40**, 3183 (1999).
12. Y. Oishi, M. Ishida, M. Kakimoto, Y. Imai, and T. Kurosaki, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 1027 (1992).
13. I. K. Spiliopoulos and J. A. Mikroyannidis, *Macromolecules*, **31**, 1236 (1998).
14. I. K. Spiliopoulos, J. A. Mikroyannidis, and G. M. Tsivgoulis, *Macromolecules*, **31**, 522 (1998).
15. X. Sun, Y. -K. Yang, and F. Lu, *Macromolecules*, **31**, 4291 (1998).
16. J. K. Kallitsis, K. G. Gravalos, A. Hilberer, and G. Hadzilioannou, *Macromolecules*, **30**, 2989 (1997).
17. J. A. Mikroyannidis, *Macromolecules*, **28**, 5177 (1995).
18. C. A. Arnold, J. D. Summers, Y. P. Chen, R. H. Bott, D. Chen, and J. E. McGrath, *Polymer*, **30**, 986 (1989).
19. N. Furukawa, Y. Yamada, M. Furukawa, M. Yuasa, and Y. Kimura, *J. Polym. Sci., Polym. Chem. Ed.*, **35**, 2239 (1997).
20. S. Itamura, M. Yamada, S. Tamura, T. Matsumoto, and T. Kurosaki, *Macromolecules*, **26**, 3940 (1993).
21. M. Yamada, M. Kusama, T. Matsumoto, and T. Kurosaki, *Macromolecules*, **26**, 4961 (1993).
22. M. Kusama, T. Matsumoto, and T. Kurosaki, *Macromolecules*, **27**, 1117 (1994).
23. Y. -T. Chern, *Macromolecules*, **31**, 1898 (1998).
24. D. J. Liaw and B. Y. Liaw, *Macromol. Chem. Phys.*, **200**, 1326 (1999).
25. D. J. Liaw, B. Y. Liaw, and C. Y. Chung, *J. Polym. Sci., Polym. Chem. Ed.*, **37**, 2815 (1999).
26. Y. Tsuda, Y. Tanaka, K. Kamata, N. Hiyoshi, S. Mataka, Y. Matsuki, M. Nishikawa, S. Kawamura, and N. Bessho, *Polym. J.*, **29**, 574 (1997).
27. Y. Tsuda, K. Etou, N. Hiyoshi, M. Nishikawa, Y. Matsuki, and N. Bessho, *Polym. J.*, **30**, 222 (1998).
28. D. Sek, A. Wanic, and E. Shab-Balcerzak, *J. Polym. Sci., Polym. Chem. Ed.*, **35**, 539 (1997).
29. S. -H. Hsiao, C. -P. Yang, and C. -Y. Yang, *J. Polym. Sci., Polym. Chem. Ed.*, **35**, 1487 (1997).
30. J. A. Mikroyannidis, *J. Polym. Sci., Polym. Chem. Ed.*, **35**, 1353 (1997).
31. D. J. Liaw, B. Y. Liaw, L. J. Li, B. Sillion, R. Mercier, R. Thiria, and H. Sekiguchi, *Chem. Mater.*, **10**, 734 (1998).
32. Y. Tsuda, T. Kawauchi, N. Hiyoshi, and S. Mataka, *Polym. J.*, **32**, 594 (2000).
33. K. -W. Lee, S. -H. Paek, A. Lien, C. Durning, and H. Fukuro, *Macromolecules*, **29**, 8894 (1996).
34. H. Wang, Z. Shen, M. Guo, S. Z. D. Cheng, and F. W. Harris, *Polym. Prep., Am. Chem. Soc., Div. Polym. Chem.*, **40**(2), 884 (1999).
35. Y. Tsuda, *Polym. Prep., Am. Chem. Soc., Div. Polym. Chem.*, **40**(2), 1215 (1999).
36. Y. Oishi, M. Ishida, H. Takado, M. Yoneyama, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 1763 (1990).
37. V. M. Denisov, V. M. Svetlichnyi, A. Gindin, V. A. Zubkov, A. I. Kol'tsov, M. M. Koton, and V. V. Kudryavtsev, *Polym. Sci. USSR*, **A21**, 1644 (1979).
38. C. A. Arnold, J. D. Summers, Y. P. Chen, T. H. Yoon, B. E. McGrath, D. Chen, and J. E. McGrath, in "Polyimides: Materials, Chemistry and Characterization," C. Feger, M. M. Khojasteh, and J. E. McGrath, Ed., Elsevier, New York, N.Y., 1989, pp 69–89.
39. T. V. John and V. B. Valenty, in "Polyimides: Materials, Chemistry and Characterization," C. Feger, M. M. Khojasteh, and J. E. McGrath, Ed., Elsevier, New York, N.Y., 1989, pp 91–101.
40. J. L. Hedrick, J. W. Labadie, T. D. Palmer, and T. P. Russell, in "Polyimides: Materials, Chemistry and Characterization," C. Feger, M. M. Khojasteh, and J. E. McGrath, Ed., Elsevier, New York, N.Y., 1989, pp 61–68.
41. M. Nishikawa, Y. Yokoyama, N. Bessho, D. -S. Seo, Y. Iimura, and S. Kobayashi, *Jpn. J. Appl. Phys.*, **33**, L810 (1994).
42. D. J. Liaw, B. Y. Liaw, J. R. Chene, and C. M. Yang, *Macromolecules*, **32**, 6860 (1999).
43. F. M. Rugg, J. J. Smith, and R. C. Bacon, *J. Polym. Sci.*, **13**, 535 (1954).
44. J. P. Luongo, *J. Polym. Sci.*, **42**, 139 (1960).