

Soluble Polyimides Based on Long-chain Alkyl Groups
via Amide LinkagesBy Yusuke TSUDA,^{1,*} Manami KOJIMA,² Takaaki MATSUDA,¹ and Jae Min OH³

The synthesis and characterization of a novel series of soluble polyimides bearing long-chain alkyl groups on their side chains using aromatic diamine monomers such as *N*-alkyl-3,5-diaminobenzamide (ADBA-X, X = carbon numbers of alkyl chain, 9~14) and *N*-(3,5-diaminophenyl)-3,4,5-tris(alkoxy)benzamide (DPABA-X, X = 6,12) are described. Polyimides obtained from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and ADBA-9~14 were insoluble, however, copolyimides based on BTDA, ADBA-9~14, and 4,4'-diaminodiphenylether (DDE) were soluble. The solubility of these copolyimides may be improved by the entropy effect of long-chain linear alkyl groups as well as the randomizing effect based on copolymerization. The effect of ADBA for the enhancement of solubility was compared with a series of functional diamines bearing long-chain alkyl groups *via* various linkage groups reported from our laboratory such as alkoxydiaminobenzene (AODB, ether linkage), alkyldiaminobenzophenone (ADBP, benzoyl linkage) and diaminobenzoic acid alkylester (DBAE, ester linkage), and it is concluded that the effect of functional diamines are increased as AODB (ether linkage) > ADBP (benzoyl linkage) > ADBA (amide linkage) > DBAE (ester linkage). The polyimides and copolyimides based on BTDA, DPABA-6 or DPABA-12, and DDE containing 50 mol % or more DPABA were soluble, showing that the effect of DPABA for the enhancement of solubility was larger than ADBA. It is speculated that the three long-chain alkyl groups in DPABA enhance the solubility of polyimides. Above polyimides and copolyimides were soluble in various polar solvents and exhibited good heat-resistance.

KEY WORDS: Polyimide / Soluble Polyimide / Amide Linkage / Long Chain Alkyl Group / 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, owing to the instability of poly(amic acid)s and the liberation of water in the imidization process, problems can arise. Extensive research has been recently carried out to improve the solubility of polyimides and successful examples involve the incorporation of fluorine moieties,^{2–17} bulky side groups,^{18–24} alicyclic structure,²⁵ spiro structure,²⁶ cardo groups,^{27,28} pyridine moiety,^{29,30} porphyrin moiety,³¹ acridine moiety,³² and sulfonated structure,^{33–36} and the applications include the functional materials such as low-*k* material,^{3,14,15,25} colorless or light-colored polyimides,^{9,10,12} gas transport membranes,^{16,17,24} electrochromism materials,²² pervaporation membranes,⁷ materials for organic light-emitting diode (OLED),^{27,32} and membranes for polymer electrolyte fuel cell (PEFC).^{19,33–36} Soluble polyimides bearing long-chain alkyl groups have been also reported,^{37–43} and their applications mainly involve the polyimide alignment film for liquid crystal displays (LCDs).

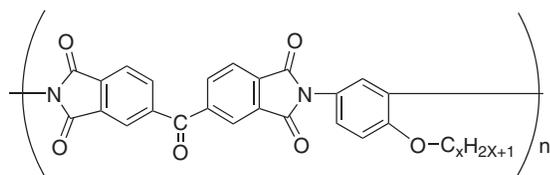
We have systematically investigated the synthesis and characterization of soluble polyimides based on alicyclic dianhydride such as 2,3,5-tricarboxycyclopentyl acetic dianhydride (TCA-AH),^{44,45} 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (cyclohexene-DA),⁴⁶ and 4-(2,5-dioxotetrahydrofuran-3-yl)-tetralin-1,2-dicarboxylic anhydride (tetralin-DA),⁴⁶ and the polyimides based on aromatic diamine having long-chain alkyl groups such as alkyldiaminobenzophenone (ADBP),⁴⁷ alkoxydiaminobenzene (AODB),⁴⁸ and diaminobenzoic acid alkylester (DBAE).⁴⁹ As far as the soluble polyimides based on long-chain alkyl groups are concerned, the following interesting results have been obtained in our laboratory (Scheme 1); (1) ADBP with an even number of carbon atoms were effective in enhancing the solubility, while polymers based on ADBP with an odd number of carbon atoms remained insoluble. It can be assumed that the conformation around C-C bonds of the long-chain alkyl groups and alignment of benzene ring attached with these alkyl groups and carbonyl group affect this odd-even effect.⁴⁷ (2) AODB bearing alkyl groups *via* an ether linkage were more effective for the enhancement of solubility in comparison with ADBP. (3) Copolymerization using the conventional aromatic diamine, 4,4'-diaminodiphenylether (DDE) resulted in the improvement of both the molecular weight and the thermal stability. (4) The copolymerization study based on AODB-10~14 and DDE

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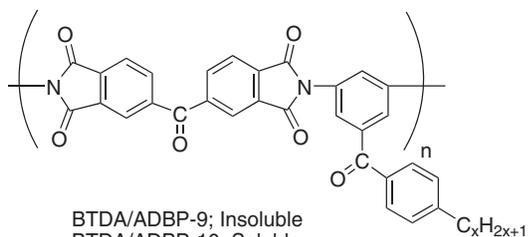
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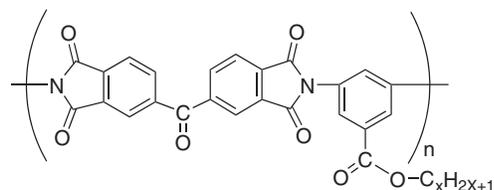
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BTDA/AODB-10; Soluble
BTDA/AODB-11; Soluble
BTDA/AODB-12; Soluble
BTDA/AODB-13; Soluble
BTDA/AODB-14; Soluble
(NMP)



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)



BTDA/DBAE-8; Insoluble
BTDA/DBAE-9; Insoluble
BTDA/DBAE-10; Insoluble
BTDA/DBAE-11; Insoluble
BTDA/DBAE-12; Insoluble
BTDA/DBAE-13; Insoluble
BTDA/DBAE-14; Insoluble
(NMP)

Scheme 1. Soluble polyimides based on alkyldiaminobenzophenone (ADBP), alkoxydiaminobenzene (AODB), and diaminobenzoic acid alkylester (DBAE).

demonstrated that AODB-12 having 12 methylene units was the most effective in enhancing the solubility. (5) DBAE was the least effective for the enhancement of solubility. However, it was found that two methods improve the solubility. One is the use of branched alkyl groups such as nonan-5-yl and 2,6-dimethylheptane-4-yl, and the other is the use of relatively flexible diamine co-monomer, 4,4'-diaminodiphenylmethane (DDM). The recent our paper has described the soluble polyimides having dendritic moieties on their side chain,⁵⁰ and the synthesis of soluble polyimides in ionic liquids was also investigated.⁵¹

In this paper, the synthesis and characterization of a novel series of soluble polyimides, that are based on *N*-alkyl-3,5-diaminobenzamide (ADBA-X, X = carbon numbers of alkyl

chain) having long-chain alkyl groups with 9–14 carbon atoms, and the polyimides based on *N*-(3,5-diaminophenyl)-3,4,5-tris(alkoxy)benzamide (DPABA-X, X = carbon numbers of alkyl chain) are described. Although polyimides based on ADBA having 4,6,8,10,12,14,16 carbon atom have already been reported,^{37,41} the structure-properties relationships of polymers were not investigated thoroughly. The effect of ADBA bearing long-chain alkyl groups *via* amide linkage for the enhancement of solubility was compared with a series of functional diamines having long-chain alkyl groups reported from our laboratory such as AODB, ADBP and DBAE. As it was clarified the effect of branched alkyl groups for the enhancement of solubility in comparison with linear alkyl groups in the study of DBAE polyimides,⁴⁹ the fan-shape three long-chain alkyl groups were introduced to the polyimide backbone *via* benzamide linkage by the copolymerization of DPABA-6,12, and the results were compared with those of soluble polyimides bearing long-chain alkyl groups reported from our laboratory. The attaching of alkyl side chains to polyimides has recently been used to increase the pretilt angles, the angle that the optical axis of a nematic liquid crystalline molecule make at a boundary surface of the cell, in alignment layer applications of liquid crystal displays (LCDs) and, thus, these studies are of great practical importance.^{38–43}

EXPERIMENTAL

Materials

3,5-Dinitrobenzoyl chloride and aliphatic amines having long-chain alkyl groups were purchased from Tokyo Chemical Industry Co., Ltd. (TCI) and used as received, as were triethylamine and 10% Pd/C, which were purchased from Wako Pure Chemical Industries, Ltd (Wako). 3,3',4,4'-Benzo-phenonetetracarboxylic dianhydride (BTDA) and 4,4'-diaminodiphenylether (DDE) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI) and purified by following method; BTDA, mp 228.3 °C, recrystallized from acetic anhydride; DDE, mp 193.6 °C, recrystallized from ethanol. DPABA-6 and DPABA-12 synthesized by the method previously reported,⁵² were provided from Cheil. Ind. Inc. Spectra data of new compound, DPABA-6 is listed below. *N*-Methyl-2-pyrrolidone (NMP) (Mitsubishi Chemicals) was distilled under reduced pressure from 4 Å molecular sieves. Reagent grade *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), dimethyl sulfoxide-*d*₆ (DMSO-*d*₆), 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. Other conventional reagents were purchased from TCI or Wako and used as received.

N-(3,5-Diaminophenyl)-3,4,5-tris(hexoxy)benzamide (DPABA-6)

Mp. 149.6 °C; ¹H NMR (CDCl₃): δ 0.91 (t, 9H, -(CH₃)₃, J = 6.99 Hz), 1.35 (m, 18H, -(CH₂)₃-CH₃)₃, 1.48 (m, 6H,

(-O-CH₂-CH₂-)₃, 4.02 (m, 6H, (-O-CH₂-)₃), 5.85 (s, 1H, 4-ArH), 6.46 (d, 2H, 2,6-ArH of dinitro aniline, *J* = 2.0 Hz), 7.00 (s, 2H, 2,6-ArH of gallic acid methyl), 7.45 (s, 1H, -NH-); IR (KBr): 1230 (-O-), 1620 (C=O), 3300 (NH), 3450 (NH₂) cm⁻¹.

Measurements

¹H NMR spectra were measured on a JEOL JNM-AL400 FT NMR in CDCl₃ or dimethyl sulfoxide-d₆ with tetramethylsilane (TMS) as an internal reference. IR spectra were measured on a JASCO IR Report-100 spectrophotometer. The inherent viscosities of all polymers were measured using Cannon Fenske viscometers at a concentration of 0.5 g/dL in NMP at 30 °C. Size exclusion chromatography (SEC) measurements were performed in NMP containing 10 mM LiBr at 40 °C with a TOSOH HLC-8020 equipped with a TSK-GEL ALPHA-M. Number average molecular weight (*M_n*), weight average molecular weight (*M_w*) and polydispersity (*M_w*/*M_n*) were determined by TOSOH Multi Station GPC-8020 calibrated with a series of polystyrenes as a standard. The polyimide film samples for the measurement of differential scanning calorimeter (DSC) and thermomechanical analysis (TMA) were prepared by the following casting method. Five wt % polyimide solution in NMP were cast on aluminum cup and the solution were slowly evaporated by heating at approximately 100–120 °C until the films were dried, then the films were dried in a vacuum oven at 100 °C for 12 h. Differential scanning calorimeter (DSC) traces were measured on a Shimadzu DSC-60 under nitrogen (flow rate 30 mL/min) at a heating rate of 20 °C/min using 30 mg of the film samples and glass transition temperatures (*T_g*) were read at the midpoint of the heat capacity jump from the second heating scan after cooling from 250 °C. Thermomechanical analysis (TMA) was performed on a Shimadzu TMA-50 under nitrogen (30 mL/min) at a heating rate of 10 °C/min with a 10 g load in the penetration mode using the film samples approximately 300 μm in thickness. Softening temperatures were taken as the onset temperature of the probe displacement on the second TMA scan after cooling from 220 °C. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50 in air or under nitrogen (50 mL/min) at a heating rate of 10 °C/min using 5 mg of a dry powder sample, and initial decomposition temperatures (*T_{d0}*), 5% weight loss temperatures (*T_{d5}*), and 10% weight loss temperatures (*T_{d10}*) were calculated from the second heating scan after cooling from 250 °C.

Synthesis of 3,5-Dinitro-*N*-undecylbenzamide

1-Aminoundecane (7.0 g, 41 mmol) and triethylamine (5.4 g, 53 mmol) were dissolved in 35 mL of THF. After 3,5-dinitrobenzoyl chloride (9.4 g, 41 mmol) in 35 mL of THF was added dropwise, the reaction mixture was stirred at r. t for 3 h. The reaction mixture was then poured onto a large amount 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 recrystallized from

ethanol to give 11.8 g (33 mmol, 79% yield) of white crystals. Mp 101.1 °C; ¹H NMR (CDCl₃): δ 0.88 (t, 3H, -CH₃, *J* = 6.80 Hz), 1.27 (m, 16H, -(CH₂)₈-CH₃), 1.68 (m, 2H, -NH-CH₂-CH₂-), 3.53 (m, 2H, -NH-CH₂-), 6.30 (s, 1H, -NH), 8.94 (d, 2H, 2,6-ArH, *J* = 2.0 Hz), 9.17 (t, 1H, 4-ArH, *J* = 1.8 Hz); IR (KBr): 3300 (NH), 1640 (C=O), 1560 and 1350 (NO₂) cm⁻¹. *Anal.* Calcd for C₁₈H₂₇N₃O₅: C, 59.16%; H, 7.45%; N, 11.50%. Found: C, 59.10%; H, 7.41%; N, 11.44%.

Other alkyl 3,5-dinitrobenzoates were synthesized according to the procedure described above (60–80% yield). Melting points (mp), ¹H NMR, IR and elemental analyses are as follows. In case of known compounds, only melting points are listed.

3,5-Dinitro-*N*-nonylbenzamide

Mp 97.6 °C; ¹H NMR (DMSO-d₆): δ 0.85 (t, 3H, CH₃, *J* = 5.90 Hz), 1.24 (m, 12H, -(CH₂)₆-CH₃), 1.56 (m, 2H, -NH-CH₂-CH₂-), 3.27 (m, 2H, -NH-CH₂-), 8.95 (t, 1H, 4-ArH, *J* = 2.0 Hz), 9.05 (d, 2H, 2,6-ArH, *J* = 2.0 Hz), 9.17 (m, 1H, NH); IR (KBr): 3300 (NH), 1640 (C=O), 1535 and 1340 (NO₂) cm⁻¹. *Anal.* Calcd for C₁₆H₂₃N₃O₅: C, 56.96%; H, 6.87%; N, 12.46%. Found: C, 56.84%; H, 6.83%; N, 12.42%.

3,5-Dinitro-*N*-decylbenzamide

Mp 87.0 °C (lit.,⁴¹ not reported)

3,5-Dinitro-*N*-dodecylbenzamide

Mp 97.5 °C (lit.,⁴¹ not reported)

3,5-Dinitro-*N*-tridecylbenzamide

Mp 87.0 °C; ¹H NMR (CDCl₃): δ 0.88 (t, 3H, -CH₃, *J* = 6.80 Hz), 1.27 (m, 20H, -(CH₂)₁₀-CH₃), 1.68 (m, 2H, -NH-CH₂-CH₂-), 3.53 (m, 2H, -NH-CH₂-), 6.30 (s, 1H, -NH), 8.94 (d, 2H, 2,6-ArH, *J* = 2.0 Hz), 9.17 (t, 1H, 4-ArH, *J* = 1.8 Hz); IR (KBr): 3290 (NH), 1650 (C=O), 1560 and 1340 (NO₂) cm⁻¹. *Anal.* Calcd for C₂₀H₃₁N₃O₅: C, 61.05%; H, 7.94%; N, 10.68%. Found: C, 61.23%; H, 7.89%; N, 10.54%.

3,5-Dinitro-*N*-tetrabenzamide

Mp 87.2 °C (litalature,⁴¹ not reported)

Synthesis of 3,5-Diamino-*N*-dodecylbenzamide (ADBA-11)

A mixture of 3,5-dinitro-*N*-undecylbenzamide (7.0 g, 19.2 mmol) and 10% palladium on carbon (Pd/C, 1.368 g, 50 mg to the 1 mmol of dinitro-compounds) in a mixture of ethanol (25 mL) and THF (180 mL) was stirred at 80 °C for 24 h under 0.2–0.3 MPa of a hydrogen gas using a medium pressure hydrogenator (Ishii Laboratory Works Co., Ltd.). The solution was filtered and the solvents were evaporated. The crude diamine was recrystallized from an ethanol to give 4.7 g (80% yield) of a pale brown powder. Mp 115.4 °C; ¹H NMR (CDCl₃): δ 0.88 (t, 3H, -CH₃, *J* = 7.20 Hz), 1.26 (m, 16H, -(CH₂)₉-CH₃), 1.57 (m, 2H, -NH-CH₂-CH₂-), 3.39 (m, 2H, -NH-CH₂-), 3.5–3.7 (broad s, 4H, -NH₂), 5.98 (s, 1H, -NH), 6.12 (t, 1H, 4-ArH, *J* = 2.0 Hz), 6.45 (d, 2H, 2,6-ArH, *J* = 2.4 Hz); IR (KBr): 3350 and 3400 (NH and NH₂), 1630 and

1590 (C=O) cm^{-1} . *Anal.* Calcd for $\text{C}_{18}\text{H}_{31}\text{N}_3\text{O}$: C, 70.78%; H, 10.23%; N, 13.76%. Found: C, 70.59%; H, 10.18%; N, 13.60%. Other 3,5-diamino-*N*-alkylbenzamide were synthesized according to the procedure described above (60–80% yield). Melting points (mp), ^1H NMR, IR and elemental analyses are as follows. In case of known compounds, only melting points are listed.

3,5-Diamino-*N*-nonylbenzamide (ADBA-9)

Mp 114.2 °C; ^1H NMR (DMSO- d_6): δ 0.88 (t, 3H, CH_3 , $J = 6.8$ Hz), 1.25 (m, 12H, $-(\text{CH}_2)_6\text{-CH}_3$), 1.56 (m, 2H, $-\text{NH-CH}_2\text{-CH}_2\text{-}$), 3.39 (m, 2H, $-\text{NH-CH}_2\text{-}$), 3.5–3.7 (broad s, 4H, $-\text{NH}_2$), 5.99 (s, 1H, $-\text{NH}$), 6.13 (t, 1H, 4-*ArH*, $J = 2.0$ Hz), 6.45 (d, 2H, 2,6-*ArH*, $J = 2.0$ Hz); IR (KBr): 3350 and 3400 (NH and NH_2), 1630 and 1590 (C=O) cm^{-1} . *Anal.* Calcd for $\text{C}_{16}\text{H}_{27}\text{N}_3\text{O}$: C, 69.27%; H, 9.81%; N, 15.15%. Found: C, 69.14%; H, 9.92%; N, 15.05%.

3,5-Diamino-*N*-decylbenzamide (ADBA-10)

Mp 115.1 °C (lit.,⁴¹ mp 95.1 °C)

3,5-Diamino-*N*-dodecylbenzamide (ADBA-12)

Mp 116.2 °C (lit.,⁴¹ mp 94.7 °C)

3,5-Diamino-*N*-tridecylbenzamide (ADBA-13)

Mp 114.5 °C; ^1H NMR (DMSO- d_6): δ 0.88 (t, 3H, CH_3 , $J = 6.8$ Hz), 1.25 (m, 20H, $-(\text{CH}_2)_{10}\text{-CH}_3$), 1.56 (m, 2H, $-\text{NH-CH}_2\text{-CH}_2\text{-}$), 3.39 (m, 2H, $-\text{NH-CH}_2\text{-}$), 3.5–3.7 (broad s, 4H, $-\text{NH}_2$), 6.03 (s, 1H, $-\text{NH}$), 6.10 (t, 1H, 4-*ArH*, $J = 2.0$ Hz), 6.44 (d, 2H, 2,6-*ArH*, $J = 2.0$ Hz); IR (KBr): 3350 and 3400 (NH and NH_2), 1630 and 1590 (C=O) cm^{-1} . *Anal.* Calcd for $\text{C}_{20}\text{H}_{35}\text{N}_3\text{O}$: C, 72.03%; H, 10.58%; N, 12.60%. Found: C, 72.24%; H, 10.68%; N, 12.18%.

3,5-Diamino-*N*-tetradecylbenzamide (ADBA-14)

Mp 115.1 °C (lit.,⁴¹ mp 98.0 °C)

Preparation of Poly(amic acid)s and Polyimides

The preparation of poly(amic acid)s and polyimides was carried out by the method previously reported.^{44–50} The imidization reaction of the poly(amic acid)s was monitored by ^1H NMR technique and the conversion from poly(amic acid)s to polyimides were found to be 100%. Copoly(amic acid)s and copolyimides using DDE as a 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. Diamine compositions of obtained copolyimides were confirmed by ^1H NMR and detailed descriptions are given in the next section. ^1H NMR spectra, IR Spectra and results of elemental analysis of representative poly(amic acid)s and polyimides are as follows.

Poly(amic acid) Based on BTDA/ADBA-12/DDE (100/50/50 mol %)

^1H NMR (DMSO- d_6): δ 0.83 (m, CH_3), 1.23 (m, $-(\text{CH}_2)_9\text{-}$

CH_3), 1.50 (m, $-\text{NH-CH}_2\text{-CH}_2\text{-}$), 3.3 (m, $-\text{NH-CH}_2\text{-}$), 7.02, 7.15, 7.47–8.32 (m, *ArH*), 8.41 (m, $\text{NH-CH}_2\text{-CH}_2\text{-}$), 10.50–10.70 (m, NH-COOH); IR (KBr): 3310 (NH and OH), 1725 and 1660 (C=O), 1240 (C-O) cm^{-1} . *Anal.* Calcd for $\text{C}_{67}\text{H}_{62}\text{N}_5\text{O}_{16}$ [$\text{C}_{38}\text{H}_{44}\text{N}_3\text{O}_8$ (BTDA/ADBA-12 unit) + $\text{C}_{29}\text{H}_{18}\text{N}_2\text{O}_8$ (BTDA/DDE unit)]: C, 67.44%; H, 5.24%; N, 5.87%. Found: C, 66.51%; H, 5.36%; N, 5.93%. The carbon analysis value was found lower than the calculated value and a trace amount of residue was observed after elemental analysis, probably due to the formation of char characteristic of heat resistant polymers.^{44,45,48,53}

Polyimide Based on BTDA/ADBA-12/DDE (100/50/50 mol %)

^1H NMR (DMSO- d_6): δ 0.83 (m, CH_3), 1.23 (m, $-(\text{CH}_2)_9\text{-CH}_3$), 1.53 (m, $-\text{NH-CH}_2\text{-CH}_2\text{-}$), 3.3 (m, $-\text{NH-CH}_2\text{-}$), 7.26 (d, *ArH* in DDE, $J = 7.6$ Hz), 7.54 (d, *ArH* in DDE, $J = 8.0$ Hz), 7.82 (m, *ArH*), 8.17–8.30 (m, *ArH*), 8.54 (m, *NH*); IR (KBr): 3300 (NH), 1770 and 1715 (C=O), 1370 (C-N) cm^{-1} . *Anal.* Calcd for $\text{C}_{67}\text{H}_{50}\text{N}_5\text{O}_{12}$ [$\text{C}_{38}\text{H}_{36}\text{N}_3\text{O}_6$ (BTDA/ADBA-12 unit) + $\text{C}_{29}\text{H}_{14}\text{N}_2\text{O}_6$ (BTDA/DDE unit)]: C, 71.42%; H, 4.61%; N, 6.41%. Found: C, 70.28%; H, 5.23%; N, 6.60%. The carbon analysis value was found lower than the calculated value for the same reason described above.

RESULTS AND DISCUSSION

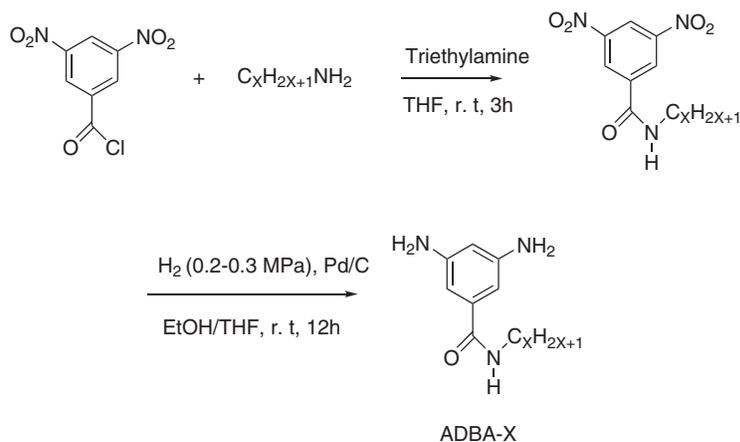
Monomer Synthesis

The functional diamines containing long-chain alkyl groups, *N*-alkyl-3,5-diaminobenzamide (ADBA-X, X = carbon numbers of alkyl chain), were prepared in two steps using 3,5-dinitrobenzoyl chloride as a starting material. The synthetic route is illustrated in Scheme 2. The condensation reaction using 3,5-dinitrobenzoyl chloride and aliphatic amines having long-chain alkyl groups catalyzed by triethyl amine in THF gave *N*-alkyl-3,5-dinitrobenzamide in satisfactory yields (60–80%). The reduction of *N*-alkyl-3,5-dinitrobenzamide was performed by catalytic hydrogenation using Pd/C and a hydrogen gas at 0.2–0.3 MPa in a medium pressure hydrogenator in satisfactory yields (60–80%).

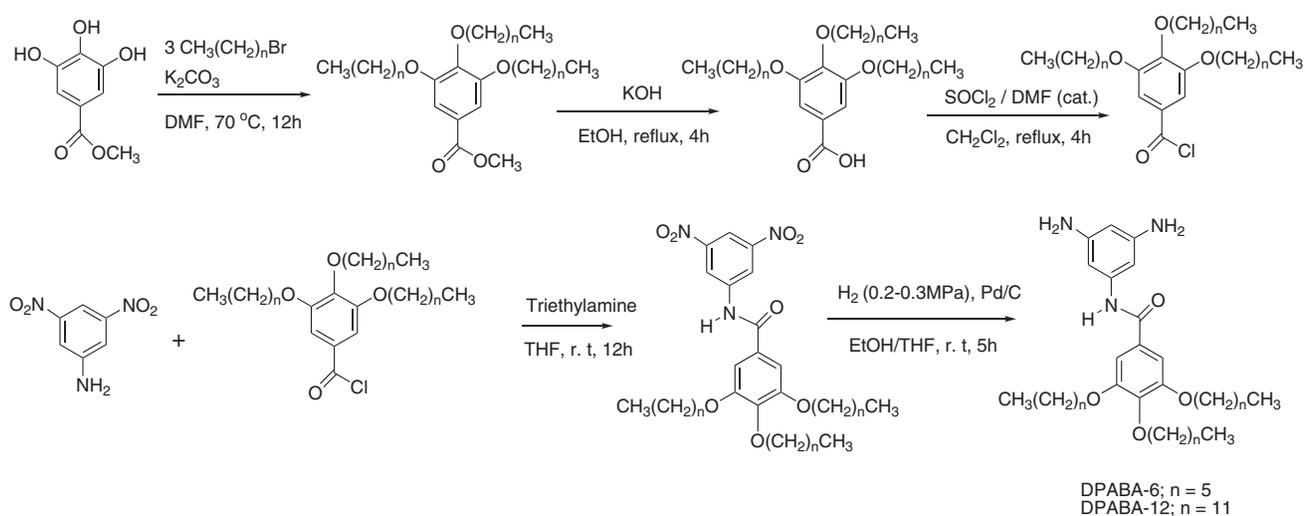
The synthesis of DPABA-6, 12 is illustrated in Scheme 3. 3,4,5-Trialkoxybenzoyl chloride, known as the building blocks for Percec-type dendrons,⁵⁴ was synthesized from 3,4,5-trihydroxybenzoic acid methyl ester (gallic acid methyl ester) followed by Williamson-etherification with alkylbromide catalyzed by potassium carbonate, hydrolysis of ester groups by potassium hydroxide, then acid chlorination using thionyl chloride. The condensation reaction using above acid chlorides and 3,5-dinitroaniline catalyzed by triethyl amine gave the dinitro-precursors of DPABA, these were finally hydrogenated to DPABA.

Polymer Synthesis

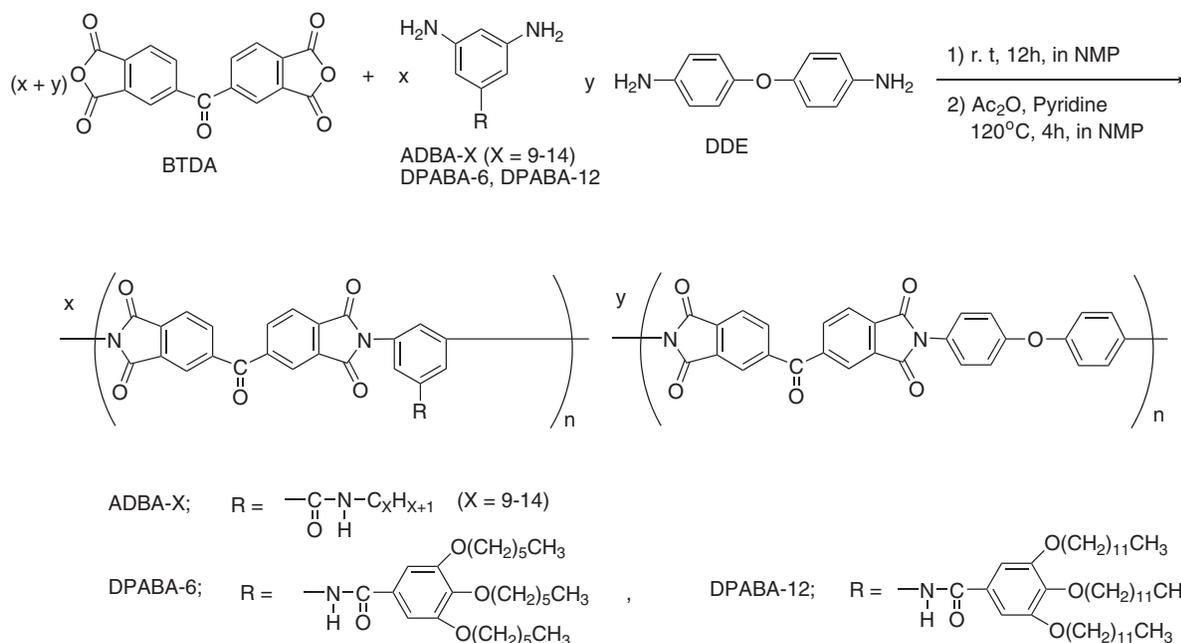
The synthetic route of the polyimides and copolyimides based on BTDA, ADBA-9~14 or DPABA-6, 12 is illustrated in Scheme 4. Two step polymerization systems including



Scheme 2. Synthesis of alkyldiaminobenzamide (ADBA).



Scheme 3. Synthesis of diaminophenylalkoxybenzamide (DPABA).



Scheme 4. Synthesis of polyimides and copolyimides based on alkyldiaminobenzamide (ADBA) and diaminophenylalkoxybenzamide (DPABA).

poly(amic acid)s synthesis and chemical imidization were performed. The poly(amic acid)s were obtained by reacting the mixture of diamines with an equimolar amount of BTDA at room temperature for 12 h under a nitrogen atmosphere. The polyimides were obtained by chemical imidization at 120 °C in the presence of pyridine as a base catalyst and acetic anhydride as a dehydrating reagent. These are the optimized synthetic conditions previously developed for the synthesis of soluble polyimides in our laboratory.^{44–50} If the polyimides were insoluble in the polymerization solvent, NMP, gelation or precipitation happened in the course of imidization process. The conversion of the poly(amic acid)s to the polyimides were confirmed by the disappearance of NH proton signals (10.5–10.7 ppm) of the poly(amic acid)s in ¹H NMR measurement. BTDA that is high reactive and common aromatic tetracarboxylic dianhydride was used as a dianhydride monomer, and DDE that is high reactive and common aromatic diamine was used as a diamine co-monomer. Although 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA), 3-cyclohexene-1,2-dicarboxylic anhydride (cyclohexene-DA), and 2,2-bis(3,4-anhydrodicarboxyphenyl)hexafluoropropane (6FDA), etc. are known as the representative tetracarboxylic dianhydride monomers suitable for soluble polyimides, BTDA was chosen as the tetracarboxylic dianhydride monomer in this study. Since the solubility of BTDA based polyimides are relatively easy to be affected by the structure of diamines, BTDA have been used as the standard tetracarboxylic dianhydride for the estimation of the effect of diamine structure for the enhancement of solubility in our laboratory.

Experimental results of homopolymerization and copolymerization based on BTDA/ADBA-9~14/DDE are summarized in Table I. Although all poly(amic acid)s were soluble in NMP that is a polymerization solvent, however, all homopolyimides based on BTDA and ADBA-9~14 were insoluble in NMP. As it was previously reported that the copolymerization using conventional diamines such as DDE improve the solubility by the randomizing effect,^{47–49} the incorporation of the second diamine monomer, DDE was examined. Consequently, all copolyimides based on BTDA/ADBA-9~14/DDE containing 50 or 75 mol % of DDE were soluble in NMP. The solubility of these copolyimides may be improved by the entropy effect of long-chain linear alkyl groups as well as the randomizing effect based on copolymerization. Since all copolyimides BTDA/DBAE-8~14/DDE were insoluble in NMP,⁴⁹ ADBA is more effective for the enhancement of solubility in comparison with DBAE. Scheme 5 summarizes the effect of functional diamines bearing long-chain alkyl groups for the enhancement of solubility investigated in our laboratory, these are AODB-X, ADBP-X, ADBA-X and DBAE-X. From the results shown in Scheme 1, it is concluded that AODB-X bearing long-chain alkyl groups *via* flexible ether linkage is the most effective and ADBP-X bearing the long-chain alkyl groups *via* benzoyl linkage is the second effective. It is speculated that relatively rigid benzoyl linkage of ADBP-X reduce the polymer solubility even though the entropy effect of long-chain alkyl groups exist in the system.

The polyimides based on ADBP-X is the only system that show the odd-even dependence of solubility (Scheme 1 and lit. 47). It is speculated that the polyimides bearing long-chain alkyl groups *via* quasi-rigid benzoyl linkage are easy to receive the effect of the alkyl chain length. In the cases of ADBA-X bearing long-chain alkyl groups *via* rigid amide linkages and DBAE-X bearing long-chain alkyl groups *via* rigid ester linkages, the effects are low in comparison with AODB-X and ADBP-X. The ranking of ADBA-X and DBAE-X can be judged from the copolymerization experiments using DDE as a co-monomer, and it is concluded that ADBA-X is more effective than DBAE-X as described above. However, it seems that the ranking of ADBA-X and DBAE-X is reverse, because it is generally known that amide linkage is more rigid than ester linkage. It can be assumed that amide linkage is more compatible for the amide solvent, NMP and this phenomena compensate the reduction of solubility due to rigid amide linkage.

Experimental results of homopolymerization and copolymerization based on DPABA that is the functional diamine bearing three long-chain alkyl groups *via* benzamide linkage are also summarized in Table I. The homopolyimides based on BTDA/DPABA-6,12 and copolyimides containing more than 50% of DPABA-6,12 were soluble in NMP. It is speculated that radially extended long-chain alkyl groups behave as a branched alkyl chain and eventually enhance the solubility as a similar manner as DBAE having branched alkyl chains enhance the solubility.⁴⁹

Structures of polyimides were confirmed by ¹H NMR in case these polyimides are soluble in common deuterium solvents such as DMSO-d₆. For example, Figure 1 shows the ¹H NMR spectrum of the copolyimide based on ADBA-12/DDE (50/50) that is soluble in DMSO-d₆ and all peaks support this polymer structure. The intensity ratio of CH₃ protons of long-chain alkyl groups and the aromatic proton H_A or H_B are approximately 3/4, meaning that copolymer composition correspond the monomer initial ratios. In the case of copolyimide based on DPABA-6/DDE (50/50), the copolymer composition was not calculated by ¹H NMR because aromatic protons are overlapped, however, it was confirmed that the long-chain alkyl groups were certainly introduced to the polymer backbone (Figure 2).

Inherent viscosities (η inh) of obtained polyimides, which are connected to the molecular weights of polymers, were in the range of 0.32–0.68 dLg⁻¹. The weight average molecular weights determined by SEC measurements were in the range of 55300 to 133900. These values indicated that the molecular weights of these polyimides are considered medium or rather lower values for polyimides, however, all polyimides show the good film formation ability. In all cases, the molecular weights were increased with the percentage of DDE, that is high reactive diamine. The representative SEC traces are shown in Figure 3, indicating that the both ADBA polyimides and DPABA polyimides have typical monomodal molecular weights distribution and polydispersity were in the range of 1.9–2.9, these are the typical values for polycondensation polymers.

Table I. Polyimides and copolyimides based on BTDA/ADBA-X, DPABA-X/DDE

Diamine ^a		poly(amic acid)s		Polyimide			
ADBA-X	DDE	η_{inh}^b	Solubility in NMP	η_{inh}^b	Molecular Weight ^c		
mol%		dLg ⁻¹		dLg ⁻¹	M_n	M_w	M_w/M_n
ADBA-9							
0	100	1.15	insoluble				
25	75	0.63	insoluble				
50	50	0.55	soluble	0.51	40900	100000	2.4
75	25	0.48	soluble	0.39	32700	95800	2.9
100	0	0.38	insoluble				
ADBA-10							
0	100	1.15	insoluble				
25	75	0.64	insoluble				
50	50	0.63	soluble	0.63	52800	133900	2.5
75	25	0.47	soluble	0.46	45600	105900	2.3
100	0	0.38	insoluble				
ADBA-11							
0	100	1.15	insoluble				
25	75	0.78	insoluble				
50	50	0.73	soluble	0.68	49500	118800	2.4
75	25	0.59	soluble	0.35	30700	67900	2.2
100	0	0.33	insoluble				
ADBA-12							
0	100	1.15	insoluble				
25	75	0.95	insoluble				
50	50	0.66	soluble	0.57	43700	97000	2.2
75	25	0.59	soluble	0.36	27900	54200	1.9
100	0	0.45	insoluble				
ADBA-13							
0	100	1.15	insoluble				
25	75	0.67	insoluble				
50	50	0.48	soluble	0.58	29200	63090	2.2
75	25	0.46	soluble	0.34	32700	88400	2.7
100	0	0.37	insoluble				
ADBA-14							
0	100	1.15	insoluble				
25	75	0.82	insoluble				
50	50	0.61	soluble	0.67	50700	94700	1.9
75	25	0.59	soluble	0.44	37200	90800	2.4
100	0	0.46	insoluble				
DPABA-6							
0	100	1.15	insoluble				
25	75	0.69	insoluble				
50	50	0.44	soluble	0.41	37300	94800	2.5
75	25	0.44	soluble	0.39	37000	108000	2.9
100	0	0.35	soluble	0.32	35200	84900	2.4
DPABA-12							
0	100	1.15	insoluble				
25	75	0.96	insoluble				
50	50	0.83	soluble	0.65	45300	119100	2.6
75	25	0.60	soluble	0.39	31500	77200	2.5
100	0	0.53	soluble	0.37	25600	55300	2.2

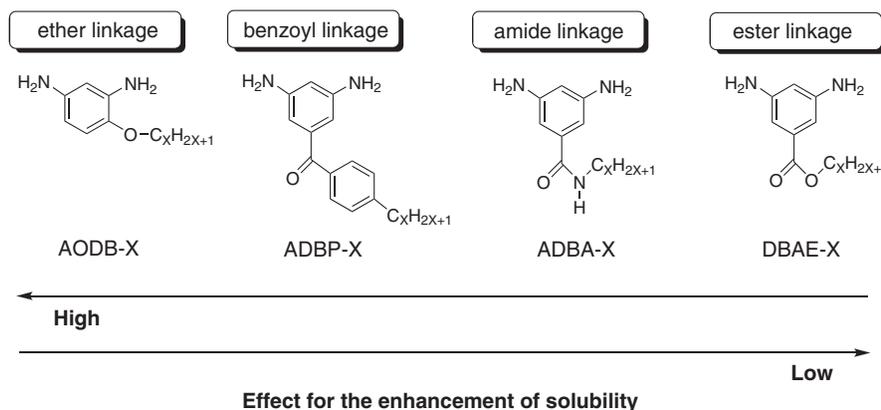
^aEquimolar amount of BTDA was used to the total amount of diamine. ^bMeasured at 0.5 g dL⁻¹ in NMP at 30 °C. ^cDetermined by SEC in NMP containing 10 mM LiBr calibrated with a series of polystyrenes as a standard.

Polymer Properties

The glass transition temperatures (T_g) of these polyimides were determined by DSC measurements and TMA measurements, and the thermal stabilities were evaluated by initial decomposition temperature (T_{d0}), 5% weight-loss temperatures (T_{d5}), and 10% weight-loss temperatures (T_{d10}) in TGA measurements. All data are summarized in Table II, and representative DSC trace, TMA trace, and TGA traces are

shown in Figures 4–8, respectively.

T_g of all ADBA polyimides and the most of DPABA polyimides were not recognized by DSC measurements, probably due to the rigid amide linkages or benzamide linkages connecting the long-chain alkyl groups to the polymer backbones. The few exceptions are the polyimides based on BTDA/DPABA-6/DDE (100/50/50) and BTDA/DPABA-12/DDE (100/50/50), that are relatively flexible polyimides due to



Scheme 5. Effect of diamines bearing long-chain alkyl groups for the enhancement of polyimide solubility.

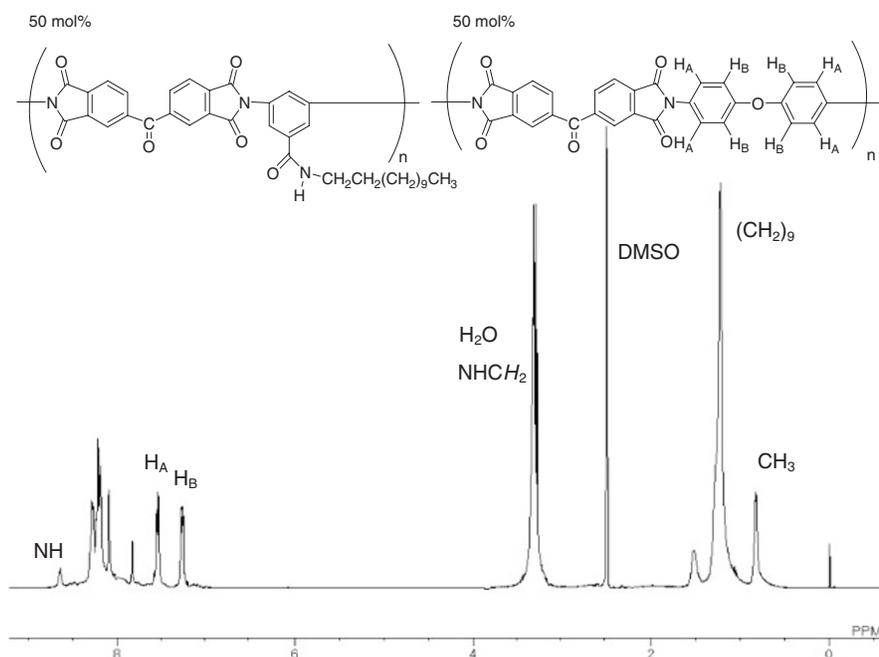


Figure 1. 1H NMR spectrum of a copolyimide based on BTDA/ADDBA-12/DDE (100/50/50). 1H NMR (DMSO- d_6): δ 0.83 (m, CH_3), 1.23 (m, $-(CH_2)_9-CH_3$), 1.53 (m, $-NH-CH_2-CH_2-$), 3.3 (m, $-NH-CH_2-$), 7.23 (d, ArH in DDE, $J = 8.0$ Hz), 7.54 (d, ArH in DDE, $J = 8.4$ Hz), 7.83 (m, ArH), 8.17–8.30 (m, ArH), 8.63 (m, NH).

three long-chain alkyl groups and the randomizing effect of copolymerization, and T_g were in the range of 253–262 °C, the similar values that were observed in a series of polyimides bearing long-chain alkyl groups studied in our laboratory. TMA measurements were performed to determine T_g of all polyimides in detail. Many literatures described that the softening temperature (T_s) obtained from TMA measurements correspond the apparent T_g of polymers.⁵⁵ As can be seen from Table II, T_s values obtained by TMA were in the ranged from 240–268 °C are comparable to the T_g values obtained by DSC. T_s values of DPABA based polyimides (240–247 °C) were slightly lower than T_s values of ADDBA based polyimides (243–268 °C), probably due to the relatively flexible nature of DPABA polyimides. In the case of ADDBA copolyimides, T_s values of the polyimides based on BTDA/ADDBA-X/DDE

(100/50/50) were lower than the values based on BTDA/ADDBA-X/DDE (100/75/25). The authors reported that the effect of copolymerization for the enhancement of flexibility in polyimides bearing long-chain alkyl groups reach to the maximum at the middle composition such as BTDA/DBAE-8-13/DDM (100/50/50).⁴⁹ It can be assumed that the flexibility of the copolyimides based on ADDBA-X also reached to the maximum at the middle composition, thus lower the T_s values. Above T_g (T_s) values of obtained polyimides are 100–150 °C lower than the conventional fully aromatic polyimides, however, 100–150 °C higher than the commodity thermoplastics. Consequently, these soluble polyimides based on ADDBA and DPABA can be ranked as heat resistant polymers.

The thermal stabilities of obtained soluble polyimides were evaluated in air and under nitrogen atmospheres using Td_{10} ,

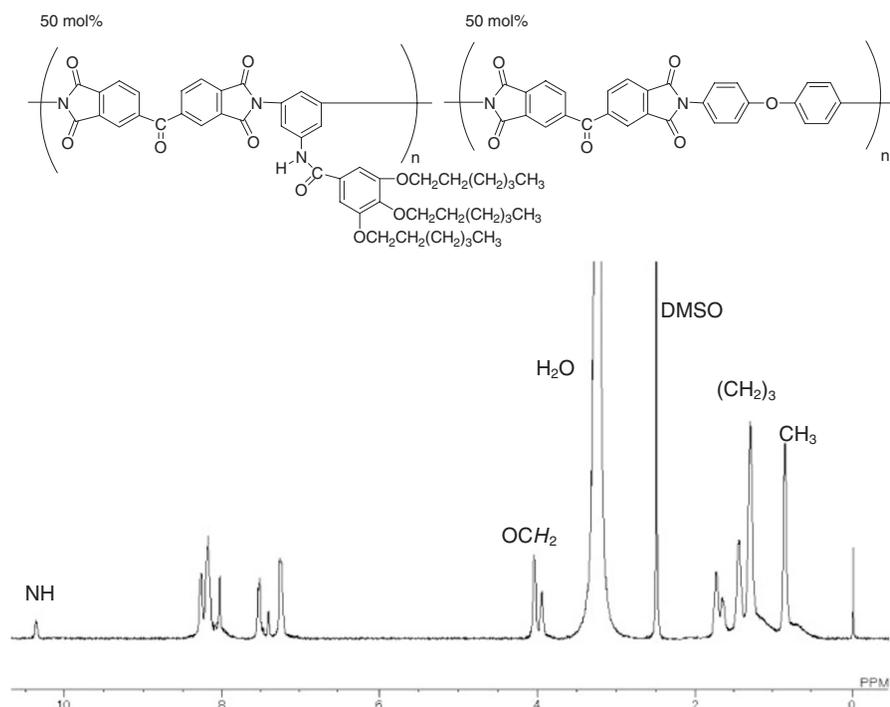


Figure 2. ^1H NMR spectrum of a copolyimide based on BTDA/DPABA-6/DDE (100/50/50 mol). ^1H NMR (DMSO-d_6): δ 0.87 (m, CH_3), 1.30–1.45 (m, $-(\text{CH}_2)_3-\text{CH}_3$), 1.66–1.74 (m, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 3.95–4.04 (m, $-\text{O}-\text{CH}_2-$), 7.26–7.52 (m, ArH), 8.02–8.26 (m, ArH), 10.36 (m, NH).

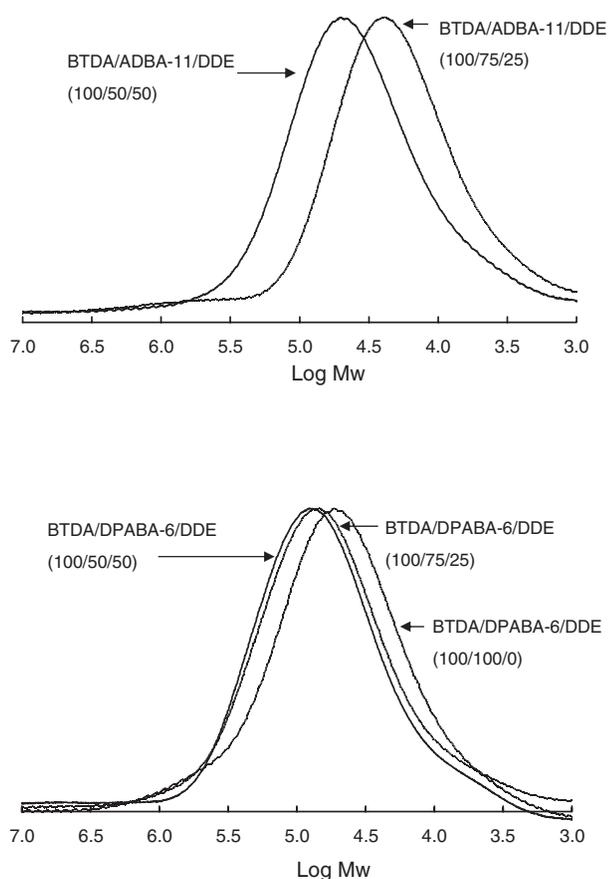


Figure 3. Representative SEC traces of polyimides based on ADBA and DPABA.

T_{d_5} , and $T_{d_{10}}$ for comparison. T_{d_0} of copolyimides based on ADBA-9~14 and DPABA-6,12 were in the range of 291–331 °C in air and 313–387 °C under nitrogen, T_{d_5} of these were in the range of 337–460 °C in air and 405–467 °C under nitrogen, and $T_{d_{10}}$ of these were in the range of 352–505 °C in air and 429–490 °C under nitrogen (Table II). As the incorporation of DDE resulted in a reduction of aliphatic components of the polyimides, T_{d_0} , T_{d_5} , and $T_{d_{10}}$ of these polyimides tended to increase by the increment of the DDE component in the polyimides containing the same monomer components. In most cases, T_d values in air were lower than T_d values under nitrogen following the general fact that oxidative degradation proceed rapidly in air. However, in the cases of copolyimides based on ADBA, $T_{d_{10}}$ in air were higher than $T_{d_{10}}$ under nitrogen, in spite that the degradation of polymers finally preceded more rapidly in air than under nitrogen (Figure 6). 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.^{56–58} On the other hand, TGA traces of polyimides based on DPABA-6, 12 showed steep weight loss at the initial stage of degradation, probably due to the degradation of three long-chain alkyl groups (Figure 7, 8). Accordingly, $T_{d_{10}}$ of DPABA polyimides were in the range of 352–450 °C in air and 429–457 °C under nitrogen, showing lower values than the $T_{d_{10}}$ of ADBA polyimides. Consequently, above degradation temperatures are 100–200 °C lower than the conventional fully aromatic polyimides, however, obtained polyimides

Table II. Thermal properties of polyimides and copolyimides based on BTDA/ADBA-X, DPABA-X/DDE

Diamine ^a		Thermal properties							
ADBA-X	DDE	T_g^b °C	T_s^c °C	Td_0^d		Td_5^e		Td_{10}^f	
mol%				Air	N ₂	Air	N ₂	Air	N ₂
		°C	°C	°C	°C	°C	°C	°C	°C
ADBA-9									
50	50	g	250	302	344	410	451	498	486
75	25		268	299	357	369	432	411	457
ADBA-10									
50	50	g	250	322	365	421	452	499	480
75	25	g	244	313	355	367	426	413	450
ADBA-11									
50	50	g	243	305	387	460	467	505	490
75	25	g	257	305	313	397	412	469	460
ADBA-12									
50	50	g	247	303	369	413	442	474	468
75	25	g	260	300	345	375	405	452	435
ADBA-13									
50	50	g	244	311	375	423	448	489	476
75	25	g	248	305	341	382	410	450	440
ADBA-14									
50	50	g	253	291	368	402	421	472	454
75	25	g	262	295	333	386	433	467	451
DPABA-6									
50	50	262	245	331	369	397	441	450	457
75	25	g	240	308	358	379	438	419	453
100	0	g	240	321	366	379	433	410	447
DPABA-12									
50	50	253	241	306	362	371	431	429	446
75	25	g	235	314	332	364	426	400	441
100	0	g	247	298	325	337	410	352	429

^aEquimolar amount of BTDA was used to the total amount of diamine. ^bGlass transition temperature, measured by DSC at a heating rate of 20 °C/min in N₂ on second heating. ^cSoftening temperature, measured by TMA at a heating rate of 10 °C/min in N₂ on second heating. ^dInitial decomposition temperature, measured by TGA at a heating rate of 10 °C/min. ^e5% Weight loss temperature, measured by TGA at a heating rate of 10 °C/min. ^f10% Weight loss temperature, measured by TGA at a heating rate of 10 °C/min. ^gNo discernible transition was observed.

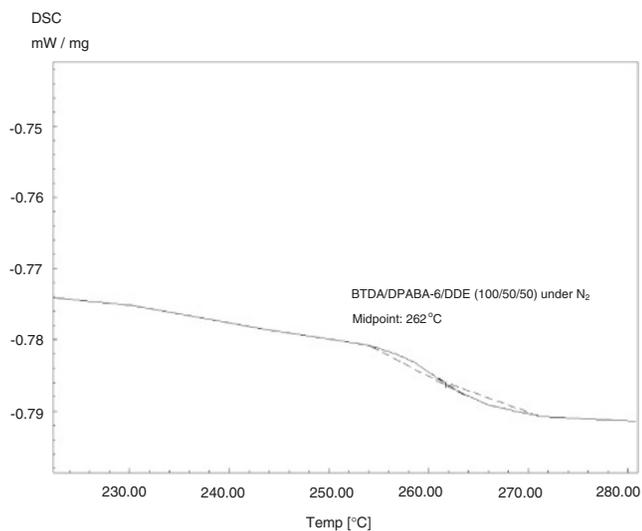


Figure 4. Representative DSC trace of polyimides based on DPABA.

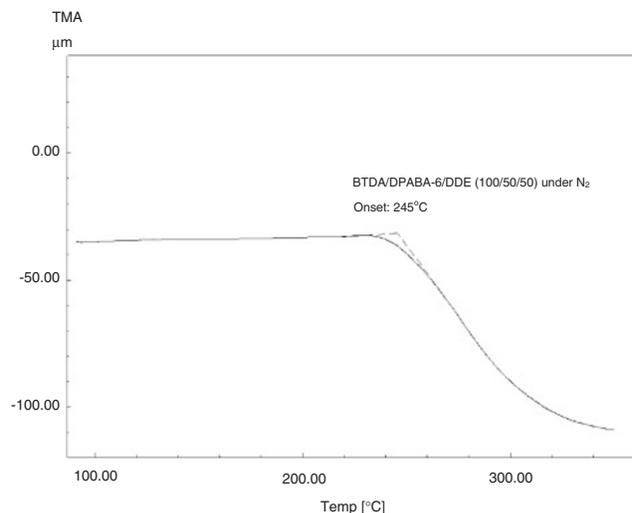


Figure 5. Representative TMA trace of polyimides based on DPABA.

bearing long-chain alkyl groups still can be ranked as heat resistant polymers.

The solubility of the obtained polyimides was determined in 9 common solvents at 5 wt % concentration (Table III). These

polyimides were soluble in various polar solvents in addition to NMP, however, the solubility depended on the structure of polyimides. Among copolyimides based on ADBA-9~14, ADBA-12 and ADBA-9 copolyimides are more soluble in

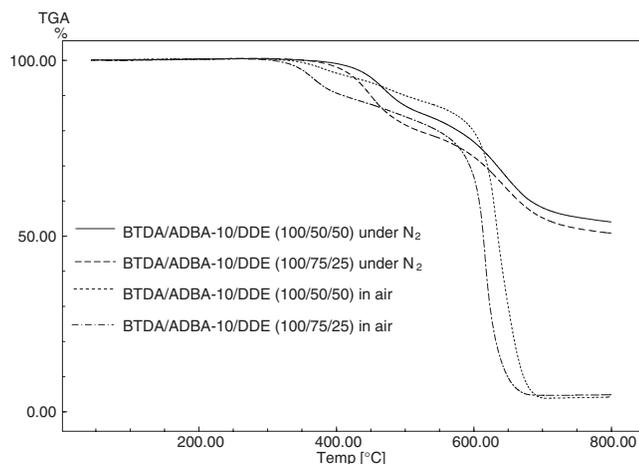


Figure 6. TGA traces of soluble copolyimides based on ADDBA-10 (BTDA/ADDBA-10/DDE).

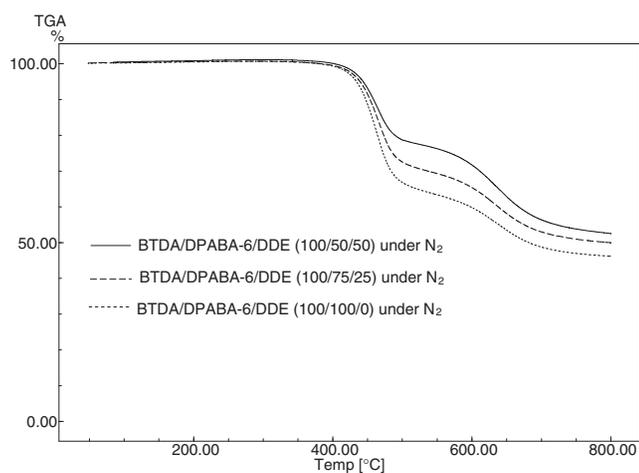


Figure 7. TGA traces under nitrogen of soluble polyimides and copolyimides based on DPABA-6 (BTDA/DPABA-6/DDE).

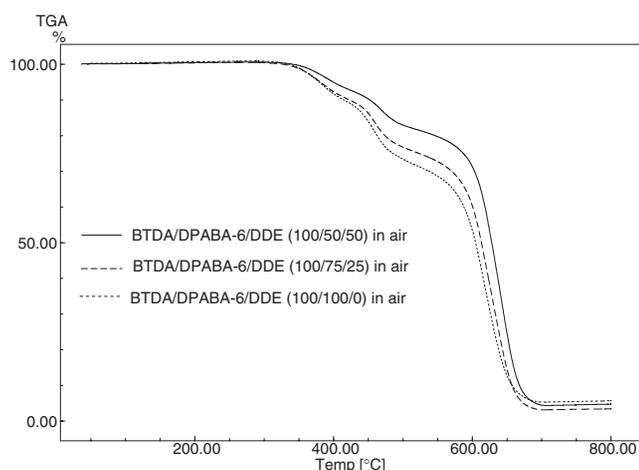


Figure 8. TGA traces in air of soluble polyimides and copolyimides based on DPABA-6 (BTDA/DPABA-6/DDE).

various solvents than other ADDBA based copolyimides. According to the literature concerning on AODB polyimides previously reported from our laboratory,⁴⁸ it was recognized that the most effective alkyl chain length for the enhancement of entropy effect was twelve, and it was presumed that the entropy effect of long-chain linear alkyl groups increased 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. This speculation may support the fact that polyimides based on ADDBA-12 are more soluble. In the cases of copolyimide based on ADDBA-9, it can be presumed that the enthalpy effects may contribute the enhancement of solubility. Since the concentration of amide linkage groups in polymer backbones increase in the polyimides bearing relatively shorter long-chain alkyl groups, it can be speculated that the interaction such as H-bonding between amide groups and polar solvents increase. The solubility of homopolyimides and copolyimides of DPABA-6,12 seem to be better than those of ADDBA polyimides, and some of those are soluble even in non polar solvent such as CH₂Cl₂. It can be imagined that three long-chain alkyl groups contribute the enhancement of solubility.

CONCLUSION

The synthesis and characterization of a novel series of soluble polyimides, that are based on aromatic diamine bearing long-chain alkyl groups *via* amide linkages such as ADDBA-9~14 and DPABA-6,12 are described. The homopolyimides obtained from BTDA and ADDBA-9~14 were insoluble, however, the copolyimides obtained from BTDA, ADDBA-9~14, and DDE were soluble. The solubility of these copolyimides may be improved by the entropy effect of long-chain linear alkyl groups as well as the randomizing effect based on copolymerization. The effect of ADDBA for the enhancement of solubility was compared with a series of functional diamines bearing long-chain alkyl groups *via* different linkage groups reported from our laboratory such as AODB (ether linkage), ADBP (benzoyl linkage), and DBAE (ester linkage), and it is concluded that the effect of functional diamines are increased in the order of AODB > ADBP > ADDBA > DBAE. Although this tendency seems to follow the rigidity of linkage groups, the ranking between ADDBA and DBAE seem to be reverse because amide linkage is generally more rigid than ester linkage. Some interaction between amide linkage of ADDBA and the amide solvent such as NMP likely compensate the reduction of solubility due to rigid amide linkage. DPABA-6,12 showed the better ability for the enhancement of the solubility of polyimides in comparison with ADDBA-9~14. It is speculated that the three long chain alkyl groups in DPABA enhance the solubility of polyimides. The obtained polyimides are soluble in various polar solvents and their chemical heat-resistance such as T_d and mechanical heat-resistance such as T_g and T_s are relatively lower than the heat-resistance of fully aromatic polyimides, however, still sufficient for heat resistant polymers.

Table III. Solubility behavior of polyimides and copolyimides based on BTDA/ADBA-X or DPABA-6, 12/DDE in various solvents

Diamines		Solubility ^a								
mol%		NMP	DMF	DMAc	DMSO	DMI	<i>m</i> -Cresol	THF	CH ₂ Cl ₂	H ₂ SO ₄
ADBA-9	DDE									
50	50	S	S	S	S	S	S	I	I	S
75	25	S	PS(h)	PS(h)	PS(h)	S	S	I	I	S
ADBA-10	DDE									
50	50	S	I	I	I	S(h)	S	I	I	S
75	25	S	I	S(h)	S(h)	S	S	I	I	S
ADBA-11	DDE									
50	50	S	I	I	I	S(h)	S	I	I	S
75	25	S	I	I	I	S	S	I	I	S
ADBA-12	DDE									
50	50	S	S	S	S	S	S	I	I	S
75	25	S	I	I	S	S	S	I	I	S
ADBA-13	DDE									
50	50	S	I	PS(h)	I	S	S	I	I	S
75	25	S	I	PS(h)	I	S	S	I	I	S
ADBA-14	DDE									
50	50	S	I	PS(h)	I	S	S	I	I	S
75	25	S	I	PS(h)	I	S	S	I	I	S
DPABA-6	DDE									
50	50	S	S(h)	S(h)	S(h)	S	S	I	I	S
75	25	S	S(h)	S(h)	S(h)	S	S	I	I	S
100	0	S	S(h)	S(h)	S(h)	S	S	PS	PS	S
DPABA-12	DDE									
50	50	S	S(h)	I	PS(h)	S	S	I	I	S
75	25	S	S(h)	S(h)	PS(h)	S(h)	S	PS	PS(h)	S
100	0	S	S(h)	S(h)	PS(h)	S	S	S	PS	S

^aThe qualitative solubility was determined in the 5 mL of the solvent at 5 wt % concentration. S, soluble after standing at room temperature for 12 h; S(h), soluble after heating at 70 °C for 12 h; PS, partially soluble after standing at room temperature for 12 h; PS(h), partially soluble after heating at 70 °C for 12 h; I, insoluble even after heating at 70 °C for 12 h.

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