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DIRECCIÓN DE NUEVAS CREACIONES

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ASUNTO

Radicación 10 – 159479
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Actuación 519
Oficio **11 - 20115**
Folios

Patente de Invención ☒ Patente de Modelo de Utilidad
Vía Nacional
Vía PCT (Fase Nacional) ☒ Capítulo I ☒ Capítulo II

No. Solicitud Internacional: PCT/US2009050934
Fecha de Presentación Internacional: Julio 17 de 2009

Como resultado del Examen de Fondo realizado, con fundamento en el Artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se comunica:

1. Documentos estudiados

Descripción:	Folios 152 a 258	Diciembre 20 de 2010
Reivindicaciones	Folios 259 a 282	Diciembre 20 de 2010
	Folios 289 a 316	Enero 25 de 2011
Prioridad:	US 61083,563	Julio 25 de 2008
	US 61160,804	Marzo 17 de 2009

2. Análisis de la Prioridad

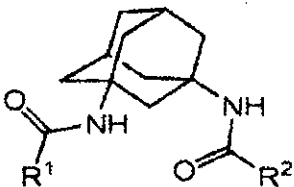
Se acepta la reivindicación de Prioridad porque esta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486) y su contenido técnico corresponde con el de la prioridad reivindicada.

3. Objeto de la invención

Título de la solicitud: "Derivados adamantil diamida y usos de los mismos"

El problema planteado en esta solicitud consiste en la obtención de compuestos alternativos para el tratamiento de patologías del SNC.

Para resolver este problema técnico, la solicitud en estudio plantea la obtención de compuestos derivados de adamantil diamida con actividad moduladora de receptores de glutamina, para el tratamiento de patologías del SNC



El objeto de la presente Solicitud se relaciona con la Clasificación Internacional de Patentes (CIP): A61K31/4412; A61K31/444; A61P25/00; C07C233/00; C07C233/79; C07D213/81; C07D215/48; C07D231/14; C07D241/44; C07D333/38; C07D401/12; C07D401/14; C07D403/12; C07D405/12; C07D405/14.

4. De la Solicitud de la Patente

Titulo

El titulo de la solicitud presentada en Colombia no corresponde al título de la presentación internacional, porque en Colombia la solicitud se titula “Derivados adamantil diamina y usos de los mismos”, mientras que en la solicitud internacional se titula “Derivados adamantil diamida y usos de los mismos”. Se solicita realizar la corrección.

Reivindicaciones (Art 30 D 486, Art 22 PCT)

La reivindicación 1 no es concisa porque se emplean expresiones muy generales tales como “alquilo”, “cicloalquilo”, “cetocicloalquilo”, “heterociclo”, “arilo”, “heteroarilo”, “frifluoroalquilo”, “alquilamino”, “dialquilamino”, “alcoxi”, “acilo”, entre otras, debido a que dentro de cada uno de los grupos se incluyen una cantidad indeterminada de sustituyentes y no se mencionan de manera especifica que sustituyentes son los preferentes (por ejemplo, al mencionar alquilo no se sabe si es metil, etil, propil; al mencionar arilo no se sabe si es benceno, naftaleno, antraceno, fenantreno; al mencionar heteroarilo no se sabe si es piridina, imidazol, furano, tiofeno, pirrol u otro heterociclo aromático; al mencionar cicloalquilo no se sabe si es ciclopropil, ciclobutil, ciclopentil, ciclohexil), que a su vez generan muchísimas posibilidades de sustitución generando alta complejidad y de esta manera no se puede definir un alcance certero de lo que se desea proteger en esta solicitud. Se sugiere limitar la solicitud a una generalización más razonable, de tal manera que en esta solicitud de invención se protejan los compuestos de real interés para el inventor. Se sugiere realizar dichas limitaciones para todos los sustituyentes de acuerdo a los compuestos soportados dentro del capítulo descriptivo, como se muestra en la siguiente tabla:

Sustituyente	Soportado en la descripción
R ¹ y R ²	Piridina, pirazol, pirimidina, fenil, indazol, quinolina, isoquinolina, quinoxalina, tiazol, tiofeno, pirazina, piridazina, oxazol, isoxazol, naftiridina, benzofurano, benzotiazol, tiofen [3,4-b] dioxano, ciclopropil, ciclobutil, ciclopentil, ciclohexil, piridin [1,2-a] imidazol, benzoxazol, benzoisoxazol, indol,
R ³	Metil, etil, metoxi, etoxi, Cl, F, Br, 2-hidroxietyl, (2-hidroxi-2-metil)etil, trifluorometil, ciano, pirrolidina, furano, tiofeno, morfolina, cianometil, ciclopropil, clorometil, dimetilamino, difluorometoxi, piperazina, piperidina, hidroxipropilamino, fenil, imidazol

De igual manera, la reivindicación 14 no es concisa porque al mencionar las expresiones “heteroarilo” o “heterociclilo”, se incluye una cantidad muy amplia de posibles sustituyentes. Se sugiere limitar estos términos a lo descrito en la tabla anterior.

La reivindicación 17 no es concisa porque se enuncian muchísimos compuestos especificos. Se sugiere limitar la cantidad de compuestos a aquellos que han sido probados, que posean mejor actividad y que representen de mejor manera la solución al problema técnico planteado dentro de esta solicitud.

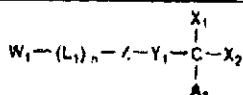
5. Determinación del Estado de la Técnica

El Estado de la Técnica se determinó con base en la fecha de solicitud de prioridad: Julio 25 de 2008 y se encontraron los siguientes documentos que anticipen el objeto de esta solicitud:

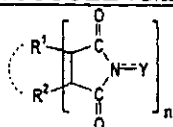
Item	Documento	Título	Fecha de Publicación
D1	JP2003050441	Thermally developable photographic sensitive material and image forming method	Febrero 21 de 2003
D2	EP0897747	Nitration or carboxylation catalysts	Febrero 24 de 1999
D4	<i>Journal of Polymer Science, Part A: Polymer Chemistry.</i> 1999: 37 (18): 3584-3590*	Synthesis of Aliphatic Polyimides Containing Adamantyl Units	Septiembre 15 de 1999

* Seino, H. Mochizuki, A. Ueda, M. Synthesis of Aliphatic Polyimides Containing Adamantyl Units. *Journal of Polymer Science, Part A: Polymer Chemistry.*1999: 37 (18):3584-3590

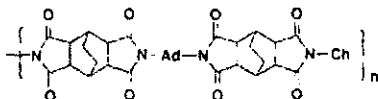
D1: Divulga la obtención de compuestos útiles para el desarrollo de fotografías con buena sensibilidad
http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=JP&NR=2003050441A&KC=A&FT=D&ND=3&date=20030221&DB=EPODOC&locale=es_LP



D2: Divulga un proceso catalítico para nitración o carboxilación de compuestos
http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=EP&NR=0897747A1&KC=A1&FT=D&ND=3&date=19990224&DB=EPODOC&locale=es_LP



D3: Divulga la obtención de polímeros de poliimidas alifáticas que contienen unidades de adamantina.



6. Examen de Patentabilidad (Art 14 D486)

Novedad (Art 16 D 486)

La reivindicación 1 divulga un compuesto de fórmula I, donde... (Folio 298)

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Solicitud	D1
Compuesto de la Fórmula I 	Compuesto 2t
R ¹ y R ² son alquilo mono, di o tri sustituidos por halógeno (puede ser metil trisustituido por Br)	Adamantan - 1, 3 - carboxamida sustituido por un átomo de carbono, que a su vez es trisustituido por Br

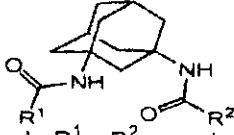
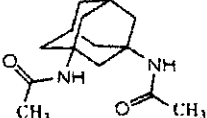
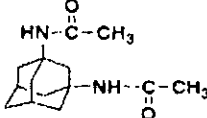
Las características técnicas esenciales de los compuestos de la reivindicación 1, han sido divulgadas previamente en D1 como Estado de la Técnica mas cercano (D1: Página 13, compuesto 2t), donde se divulgan compuestos utiles para el desarrollo de fotografías

En consecuencia, la reivindicación 1 de acuerdo a lo divulgado en D1, carece de Novedad.

La reivindicación 18, dependiente de la reivindicación 1, no divulga características adicionales que le otorguen novedad a los compuestos de la reivindicación 1. Por lo tanto, esta reivindicación también carece de Novedad.

La reivindicación 1 divulga un compuesto de fórmula I, donde... (Folio 298)

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Solicitud	D2	D3
Compuesto de la Fórmula I  Donde R ¹ y R ² son alquilo (en este caso metil)	Se divulga la obtención de 1,3 - bis (acetilamino) adamantan como intermediario de reacción 	Se divulga la obtención de 1,3 - bis (acetilamino) adamantan como intermediario de reacción 

Las características técnicas esenciales de los compuestos de la reivindicación 1, han sido divulgadas previamente en D1 y D2 como estados de la técnica más cercanos (D2: Página 31, ejemplo 83, líneas 49 y 50; D3: Página 3587, esquema 2, compuesto DAAA), donde se divulga el 1,3 - bis (acetilamino) adamantan como intermediario de procesos sintéticos. En el caso de D2, este compuesto es intermediario en el proceso de nitración de adamantina, mientras que en D3, este compuesto es intermediario para la obtención de polímeros de imina que contienen adamantina.

En consecuencia, la reivindicación 1 de acuerdo a lo divulgado en D2 y D3, carece de Novedad.

La reivindicación 18, dependiente de la reivindicación 1, no divulga características adicionales que le otorguen novedad a los compuestos de la reivindicación 1. Por lo tanto, esta reivindicación también carece de Novedad

7. Conclusión

Los requisitos de Patentabilidad de la presente Solicitud están afectados así:

Item	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	JP2003050441	1 y 18	Novedad
D2	EP0897747	1 y 18	Novedad
D3	<i>Journal of Polymer Science, Part A: Polymer Chemistry</i> , 1999: 37 (18): 3584-3590*	1 y 18	Novedad

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta (60) días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única No. 10 de 2001.


JOSE LUIS SALAZAR LOPEZ
Director de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha
06 NOV. 2012

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Synthesis of Aliphatic Polyimides Containing Adamantyl Units

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ABSTRACT: Aliphatic polyimides containing adamantyl units (**APIs**) were prepared by the poly(addition/condensation) of a dianhydride bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic 2,3 : 5,6-dianhydride with a rigid diamine, 1,3-diaminoadamantane or 3,3'-diamino-1,1'-biadamantyl, and a flexible diamine, 4,4'-methylenebis(cyclohexylamine) or 1,4-cyclohexanediamine. One-step polymerizations were conducted at 80–200°C in *m*-cresol, producing **APIs** with inherent viscosities up to 0.53 dL g⁻¹. These **APIs** are soluble in haloalkanes, *m*-cresol, and sulfuric acid and show high thermal stability and excellent transparency. © 1999 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 37: 3584–3590, 1999

Keywords: fully aliphatic polyimide; alicyclic monomer; adamantyl unit; high thermal stability; high transparency

INTRODUCTION

Recently, in the microelectric industry, much attention has been paid to polyimides (PIs) with high dimensional stability and low dielectric constant to minimize the stresses between films and substrates and to increase circuit speeds.¹ High transparency also expands the applications of PIs; for example, to optoelectric materials.² It is well known that the rigid-rod structure reduces the coefficient of thermal expansion (CTE) of PIs.³ Numata et al. found that the CTE of PI film is well correlated with the rigidity of the PI structure.⁴ Rigid-rod or ladder structure and strong in-plane orientation of polymer lead to high dimensional stability. Many aromatic rigid-rod PIs with high dimensional stability were developed in the last decade, because aromatic compounds are

easily modified by rigid moieties.^{1,5} However, aromatic PIs have high dielectric constants and are light or dark yellow. The color of PIs films arises from both the intramolecular and intermolecular charge transfer (CT) interactions between the five-membered ring of the imide group and the aromatic ring.⁶ Efforts to suppress the CT interaction have included the use of aliphatic,⁷ siloxane,⁸ sulfonyl,⁹ and fluorinated¹⁰ moieties. Among these, aliphatic structures display a lower dielectric constant because of a low molecular density and polarity. However, aliphatic PIs have the disadvantages of low thermal and dimensional stability, caused by the high flexibility and low bonding strength of aliphatic compounds as compared to aromatic compounds. Chung et al. recently reported the synthesis of relatively thermally stable polyimides with inherent viscosities of 0.14–0.38 dL g⁻¹ from aromatic dianhydrides and 1,3-diaminoadamantane.¹¹ However, to the best of our knowledge, no report has ever been published on the synthesis of fully alicyclic polyimides containing adamantyl units (**APIs**) in the

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main chains. Therefore, it is of interest to prepare and characterize fully alicyclic polyimides in which adamantane units are incorporated. In this article we describe the successful synthesis of full APIs by poly(addition/condensation) of alicyclic dianhydride with diamines containing adamantyl units and alicyclic diamines.

EXPERIMENTAL

Materials

m-Cresol was purified by vacuum distillation. Other reagents and solvents were obtained commercially and used as received.

Bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic 2,3:5,6-dianhydride (BODA) was prepared according to the reported procedure.¹² m.p. 272°C (decomposition). IR (KBr): ν (cm⁻¹) = 1860, 1770 (C=O), 1230, 1100 (C-O-C). ¹H-NMR (CDCl₃): δ (ppm) = 1.38 (4H, m, H-7,8), 2.50–2.51 (2H, m, H-1,4), 3.52–3.61 (16H, m, H-2,3,5,6,7,8), 3.68 (12H, s, CH₃).

1,3-Dibromoadamantane (DBA) was prepared following a procedure outlined in the literature.¹³ m.p. 106–108°C (literature¹³ 110°C). IR (KBr): ν (cm⁻¹) = 695 (C-Br), 2855, 2930 (CH₂, CH). ¹H-NMR (CDCl₃): δ (ppm) = 1.70 (2H, m, H-6); 2.26 (2H, m, H-5,7); 2.30 (10H, m, H-4,8,9,10); 2.87 (2H, s, H-2). ¹³C-NMR (CDCl₃): δ : 33.9 (C-6); 35.3 (C-5,7); 47.4 (C-4,8,9,10); 59.3 (C-2); 62.5 (C-1,3).

ANAL. calcd for C₁₀H₁₄Br₂: C, 40.85; H, 4.80. Found: C, 40.89; H, 4.97.

1,3-Diacetamidoadamantane (DAAA)

To a solution of DBA (15.6 g, 53 mmol) in acetonitrile (180 mL) was added sulfuric acid (30 mL) dropwise with stirring. This solution was refluxed for 24 h, then poured into ice-water (500 mL). The precipitate was filtered off, and the filtrate was neutralized with an aqueous sodium hydrogen carbonate solution and extracted by ethyl acetate (500 mL). The organic layer was concentrated under reduced pressure. The residue was recrystallized from ethyl acetate to give white plates: Yield: 8.0 g (61%), m.p. 231°C. IR (KBr): ν (cm⁻¹) = 1540, 3315 (NH), 1650 (C=O). ¹H-NMR (DMSO-*d*₆): δ (ppm) = 1.50 (2H, m, H-6); 1.74 (6H, s, CH₃); 1.81–1.83 (8H, m, H-4,8,9,10); 2.08 (2H, m, H-5,7); 2.14 (2H, s, H-2); 7.39 (NH). ¹³C-NMR (DMSO-*d*₆): δ (ppm) = 23.6 (CH₃); 29.1 (C-

5,7); 35.0 (C-6); 40.0 (C-4,8,9,10); 44.5 (C-2); 51.8 (C-1,3); 168.6 (C=O).

ANAL. calcd for C₁₄H₂₂N₂O₂: C, 67.17; H, 8.86; N, 11.19. Found: C, 67.46; H, 9.26; N, 11.21.

1,3-Diaminoadamantane Dihydrochloride (DAA · 2HCl)

A solution of DAAA (3.0 g, 12 mmol) in 2*N*-HCl solution (108 mL) was stirred at 100°C for 60 h, then the solvent was removed under reduced pressure. Yield: 2.76 g (96%), m.p. decomposition at 213°C. IR (KBr): ν (cm⁻¹) = 3425 (—NH₃⁺). ¹H-NMR (D₂O): δ (ppm) = 1.66 (2H, m, H-6); 1.89 (8H, m, H-4,8,9,10); 2.07 (2H, s, H-2); 2.43 (2H, m, H-5,7); 7.90 (3H, broad, —H₃⁺). ¹³C-NMR (D₂O): δ (ppm) = 29.8 (C-5,7); 33.7 (C-6); 39.0 (C-4,8,9,10); 43.4 (C-2); 53.8 (C-1,3).

ANAL. calcd for C₁₀H₂₀Cl₂N₂: C, 50.22; H, 8.43; N, 11.71. Found: C, 50.01; H, 8.89; N, 11.55.

3,3'-Dibromo-1,1'-biadamantyl (DBBA)

To a solution of 1-bromoadamantane (25.0 g, 116 mmol) in xylene (50 mL) was added a total of 2.7 g of small pieces of sodium over a period of 4 h with refluxing and stirring. This solution was refluxed for 12 h and then diluted with 150 mL of toluene. The sodium bromide was filtered off in the hot state, and the filtrate was concentrated under reduced pressure. The crude biadamantyl (BA) was treated with bromine to generate DBBA following a procedure outlined in the literature.¹⁴ Yield: 82%, m.p. 234–236°C (literature¹⁴ 236°C). IR (KBr): ν (cm⁻¹) = 685 (C-Br), 2910, 2940 (CH₂, CH). ¹H-NMR (CDCl₃): δ (ppm) = 1.59 (4H, m, H-8,9); 1.64 (2H, m, H-6); 2.19 (4H, m, H-4,10); 2.25 (2H, m, H-5,7); 2.29 (2H, s, H-2). ¹³C-NMR (CDCl₃): δ (ppm) = 32.8 (C-5,7), 33.9 (C-8,9), 35.5 (C-6), 42.9 (C-1), 47.9 (C-2), 49.2 (C-4,10), 68.3 (C-3).

ANAL. calcd for C₂₀H₂₈Br₂: C, 56.09; H, 6.59. Found: C, 56.17; H, 6.95.

3,3'-Diamino-1,1'-biadamantyl (DABA)

To a solution of DBBA (10.0 g, 23.4 mmol) in acetonitrile (160 mL) was added sulfuric acid (4.8 mL) dropwise with stirring. The solution was refluxed for 24 h and then poured into ice-water (300 mL). The precipitate was filtered off, washed with water, and dried. The obtained solid (1.90 g,

5.0 mmol) and sodium hydroxide (8.25 g, 80 mmol) was dissolved in ethylene glycol (30 mL). This solution was stirred at 180°C for 24 h and then poured into cold water (20 mL). The precipitate was filtered off and dried. The obtained solid was purified by sublimation to give DABA. Yield: 0.75 g (50%), m.p. 178–182°C. IR (KBr): ν (cm⁻¹) = 3425 (NH₂). ¹H-NMR (DMSO-*d*₆): δ (ppm) = 1.28 (4H, m, H-5,7), 1.33–1.46 (24H, m, H-2,4,6,8,9,10), 2.04 (4H, s, NH₂). ¹³C-NMR (DMSO-*d*₆): δ (ppm) = 29.2 (C-5,7), 33.7 (C-8,9), 35.5 (C-6), 38.0 (C-1), 44.1 (C-2), 45.3 (C-4,10), 47.2 (C-3).

ANAL. calcd for C₂₀H₃₂N₂: C, 79.94; H, 10.73; N, 9.32. Found: C, 79.70; H, 10.82; N, 9.18.

Polymer Synthesis

A typical example of the polymer synthesis procedure is as follows. A solution of 3,3'-diamino-1,1'-biadamantyl (0.301 g, 1.0 mmol) and bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic 2,3 : 5,6-dianhydride (0.250 g, 1.0 mmol) in *m*-cresol (2.2 mL) was heated in the following steps: 100°C for 12 h, 150°C for 4 h, and 200°C for 48 h. The solution was then cooled to ambient temperature, diluted with *m*-cresol (2.5 mL), and poured into methanol (100 mL). The polymer was filtered off and dried *in vacuo* at 60°C. The yield was 0.51 g (99%). The inherent viscosity of the polymer in H₂SO₄ was 0.24 dL g⁻¹ at a concentration of 0.5 g dL⁻¹ at 30°C. IR (KBr): ν (cm⁻¹) = 1760, 1695 (C=O).

Anal. calcd for (C₃₂H₃₈N₂O₄ · 7H₂O)_n: C, 72.89; H, 7.53; N, 5.31. Found: C, 73.04; H, 7.70; N, 4.82.

The resulting polyimide was a white powder. The solution of the polyimide (1 g) in DMF (4 mL) was cast on a glass plate and then heated on the hot plate in the following steps: 100°C for 2 h, 150°C for 2 h, 200°C for 0.5 h, 250°C for 0.5 h, and 300°C for 2 h.

Measurements

FTIR spectra were recorded on a Horiba FT-210 FTIR spectrophotometer under the following conditions: spectral width 4000–400 cm⁻¹, 10 accumulations, resolution 4 cm⁻¹, and signal processed by H-G apodization. Samples were recorded as a potassium bromide pellet. NMR spectra were recorded on a JEOL EX270 (270 MHz) spectrometer in DMSO-*d*₆, CDCl₃, or D₂O solution at ambient temperature. TGA measure-

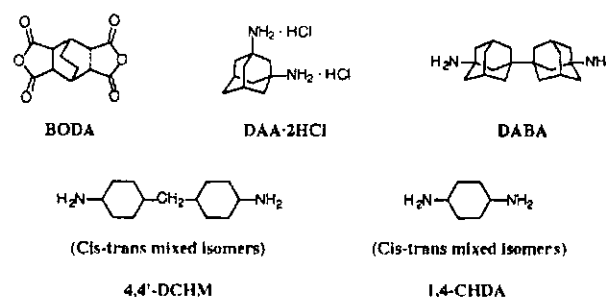
ments were performed on a Seiko SSS 5000-TG/DTA 200 instrument at a heating rate of 10°C min⁻¹. Viscosity measurements were done on an Ostwald viscometer at 30°C. Ultraviolet-visible (UV-vis) spectra were recorded on a JASCO V-560 UV/VIS spectrophotometer under the following conditions: spectral width 200–600 nm, 1 accumulation, resolution 0.5 nm, and scanning rate 200 nm min⁻¹. Polymer films were used as the samples.

RESULTS AND DISCUSSION

Selection of Monomers

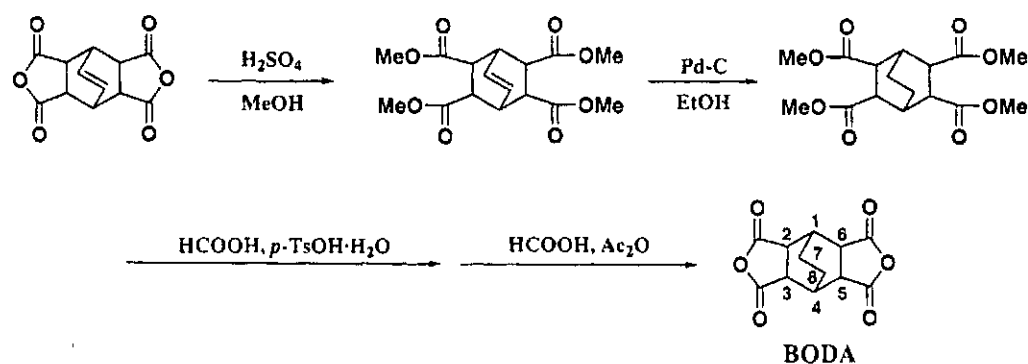
The introduction of adamantyl units would be expected to improve the dielectric constant and dimensional stability of aliphatic PIs due to their low molecular polarization and rigidity. As diamines containing adamantyl units, DAA · 2HCl and DABA were selected because of their synthetic facility. On the other hand, BODA was used as a rigid polycyclic dianhydride.

As mentioned earlier, aliphatic polycyclic PIs would be expected to have low dielectric constancy and high thermal and dimensional stability. However, matching the coefficient thermal expansion (CTE) of polymer with substrates is difficult. Effective approaches, such as combining rigid monomers and flexible monomers, have been reported.¹ Therefore, we decided to prepare copolyimides derived from rigid and flexible monomers. Thus, 4,4'-methylenebis(cyclohexylamine) (*cis-trans* mixed isomers) (4,4'-DCHM) or 1,4-cyclohexanediamine (*cis-trans* mixed isomers) (1,4-CHDA) were used as flexible alicyclic diamines.



Monomer Synthesis

Alicyclic dianhydride, BODA was synthesized following a reported procedure from bicyclo[2.2.2]oct-



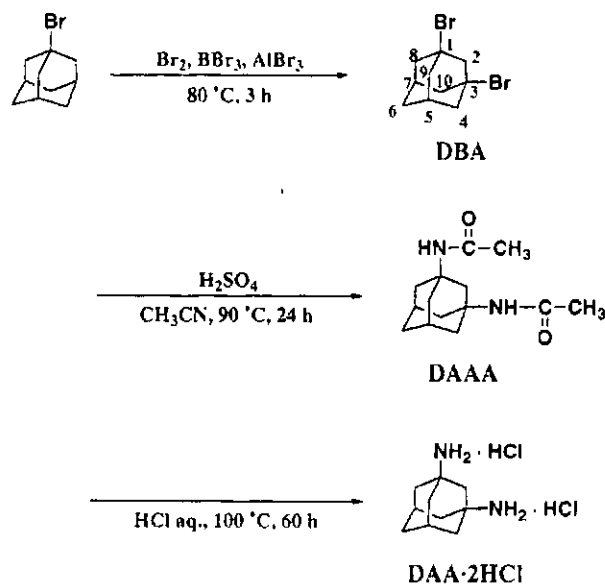
Scheme 1.

7-ene-2,3,5,6-tetracarboxylic dianhydride in four steps, as shown in Scheme 1. The BODA was composed of the *endo-endo* and *endo-exo* isomers. Two rigid polycyclic diamine, DAA·2HCl and DABA, were prepared starting from 1-bromoadamantane in three and four steps as shown in Schemes 2 and 3, respectively. The synthetic route of DAA·2HCl reported by Chern et al.¹¹ is rather complicated. Thus, a different synthetic route was used. DBA, obtained by bromination of 1-bromoadamantane in the presence of bromine, boron tribromide and aluminum bromide as catalysts, was converted to DAAA by treatment with sulfuric acid in acetonitrile. Then, hydrolysis of DAAA in 2*N*-HCl solution gave DAA·2HCl. On the other hand, DABA was prepared in four steps starting from 1-bromoadamantane. First, BA was obtained by the Wurtz reaction of 1-bromoadamantane in xylene. Then bromination of BA produced the corresponding DBBA, which was converted to 3,3'-diacetoamino-1,1'-biadamantyl (DAABA) by treating with sulfuric acid in acetonitrile. Finally, hydrolysis of DAABA with sodium hydroxide in diethylene glycol yielded DABA.

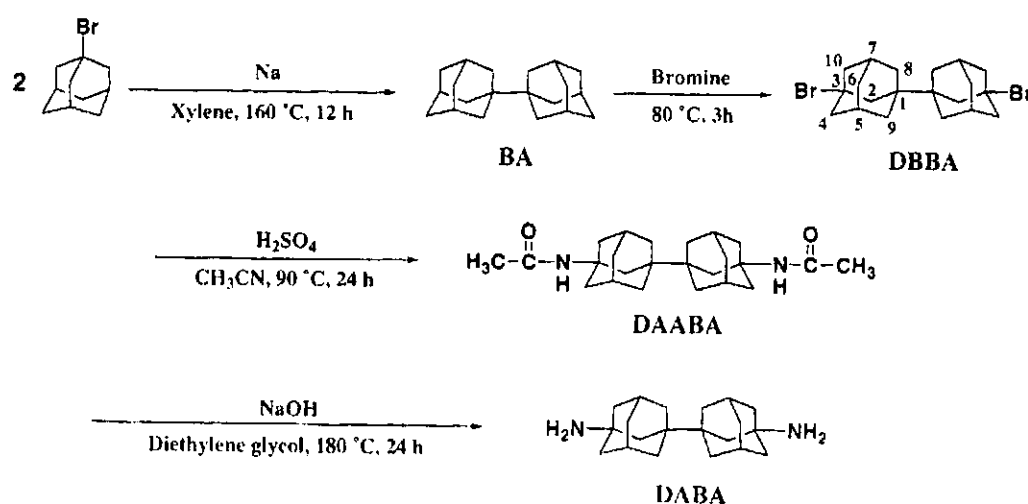
Polymerization

Generally, the reaction of anhydrides with highly basic diamines, such as aliphatic and alicyclic diamines, provides amic acids, and then free amines form carboxylic acid salts with carboxyl group of amic acids due to their high basicity.¹⁵ In the polymerization, salt formation prevents the attainment of high molecular weight poly(amic acid) (PAA). In fact, the polymerization, which was carried out in polar aprotic solvents, such as *N*-methyl-2-pyrrolidinone (NMP) and *N,N*-dimethylacetamide (DMAc), provided the low-molecular-weight PAAs whose inherent viscosities

were 0.07–0.08 dL g⁻¹. The effective method for synthesis of aliphatic polyimides has not been reported. Therefore, we tried to find a good synthetic method. A one-pot PI synthesis without isolation of PAA at high reaction temperature would be a useful method for preparing high-molecular-weight aliphatic polyimides, because the amines used for the salt formation can be generated during the formation of imide. High temperature polymerization was carried out in an aprotic solvent, such as NMP or DMAc. The APIs with inherent viscosities of 0.07–0.08 dL g⁻¹ were obtained, however. One-step synthesis of PIs is successfully carried out in *m*-cresol. Therefore, the APIs were synthesized from the combination of rigid and flexible diamines with BODA by the one-step procedure through the ring-opening



Scheme 2.



polyaddition and subsequent thermal cyclodehydration in *m*-cresol (Scheme 4). The polymerizations proceeded in the homogeneous state to produce **APIs** quantitatively with inherent viscosities up to 0.53 dL g⁻¹. These results are summarized in Table I. The polymerizations from rigid amines proceeded with polymer precipitations, which limited the molecular weights. **PI-1** and **-2** were prepared from BODA with DCHM and CHDA, respectively, in *m*-cresol through the same procedure, to compare the properties with **APIs**.

Characterization of APIs

The **APIs** were identified as the expected PIs by IR spectroscopy and elemental analyses. The IR spectra showed two characteristic absorptions at 1695 and around 1760 cm⁻¹ due to the imide

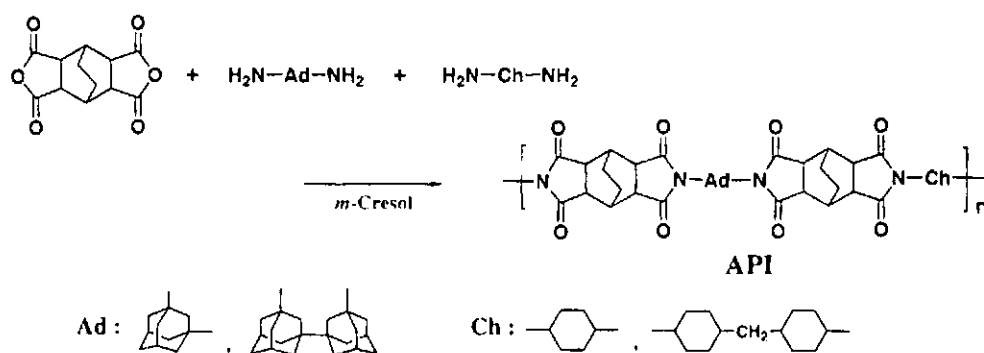
carbonyl groups. Elemental analyses also supported the formation of the expected PIs.

Solubilities

The solubilities of **APIs** are summarized in Table II. Copolymerization of rigid and flexible diamines with BODA produced soluble **APIs** even in haloalkanes at room temperature. On the other hand, **APIs** obtained from DAA · 2HCl or DABA were only soluble in *m*-cresol and sulfuric acid due to the rigidity of **API** backbones. Several **APIs** could be cast into transparent and colorless films from NMP or haloalkane solutions.

Thermal Stability

The thermal behavior of the **APIs** was evaluated by TGA and differential scanning calorimetry



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Table I. Syntheses of Polyimides^a

Rigid Diamine	Flexible Diamine	Polymer	Inherent Viscosity η (dl g ⁻¹)
	4,4'-DCHM	PI-1	0.51 ^b
	1,4-CHDA	PI-2	—
DAA · 2HCl		API-1	0.28 ^b
DABA		API-2	0.24 ^b
DAA · 2HCl	4,4'-DCHM	API-3	0.34 ^c
DABA	4,4'-DCHM	API-4	0.53 ^c
DAA · 2HCl	1,4-CHDA	API-5	0.32 ^b
DABA	1,4-CHDA	API-6	0.19 ^b

^a Polymerizations were carried out in *m*-cresol at 100–200°C.
^b Measured at a concentration of 0.5 g dl⁻¹ in H₂SO₄ at 30°C.
^c Measured at a concentration of 0.5 g dl⁻¹ in NMP at 30°C.

(DSC). The results are listed in Table III. Typical TGA curves of **API-4** are shown in Figure 1. The polymer showed a 5% weight loss at 460 and 470°C in air and nitrogen, respectively. The 5% weight loss temperatures of polyimides from aromatic dianhydrides and 1,3-diaminoadamantane were at approximately 480°C in nitrogen.¹¹ Therefore, the **APIs** exhibited lower thermal stability than did the aforementioned polyimide, but

Table III. Thermal Properties of Polyimides

Polymer	T_d (5%) ^a (°C)		T_d (10%) ^b (°C)	
	In N ₂	In air	In N ₂	In air
PI-1	445	360	460	375
PI-2	440	410	470	445
API-1	390	380	460	410
API-2	385	380	420	425
API-3	460	415	470	435
API-4	460	430	470	450
API-5	465	385	480	405
API-6	425	400	455	430

^a Temperature at 5% weight loss recorded with TG at heating rate of 10°C min⁻¹.
^b Temperature at 10% weight loss recorded with TG at heating rate of 10°C min⁻¹.

still have good thermal stability for electronics applications.

UV-vis. Spectra

The UV-vis spectra of 15 μm-thick films of **PI-1** and **API-2**, **-3**, and **-4** are shown in Figure 2. The transmittance of **APIs** was more than 95% above 300 nm. This indicates that the adamantyl units

Table II. Solubilities of Polyimides

Solvents	Solubility							
	PI-1	PI-2	API-1	API-2	API-3	API-4	API-5	API-6
Acetone	—	—	—	—	—	—	—	—
Methanol	—	—	—	—	—	—	—	—
2-Propanol	—	—	—	—	—	—	—	—
Acetonitrile	—	—	—	—	—	—	—	—
Dioxane	—	—	±	±	±	±	—	—
2-Butanone	—	—	—	—	—	—	—	—
Cyclohexanone	±	—	±	±	±	±	—	—
2-Methoxyethanol	—	—	—	—	—	—	—	—
<i>m</i> -Cresol	++	—	+	++	++	++	—	+
Dichloromethane	++	—	±	±	++	++	+	±
Chloroform	++	—	±	++	—	++	±	±
THF	—	—	±	—	±	±	—	±
γ-Butyrolactone	—	—	±	—	—	—	—	—
DMF	—	—	±	—	—	—	—	—
DMAc	—	—	±	—	±	—	—	—
DMSO	±	—	±	—	—	—	—	—
NMP	±	—	±	+	++	++	—	—
H ₂ SO ₄	++	±	++	++	++	++	++	++

Key: ++, soluble at room temperature; +, soluble at heating; ±, partially soluble or swelling; —, insoluble.

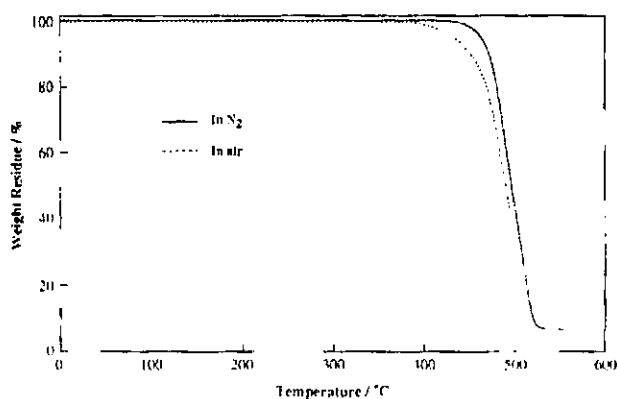


Figure 1. TGA/DTA curves of API-4 in nitrogen and air.

enhance the transparency of APIs due to their bulkiness. This excellent transparency will enable application of the APIs in the optoelectric industry. The glass transition temperatures (T_g 's) of the APIs were not observed by DSC up to 300°C.

CONCLUSIONS

We successfully synthesized APIs by poly(addition/condensation) of alicyclic dianhydride BODA

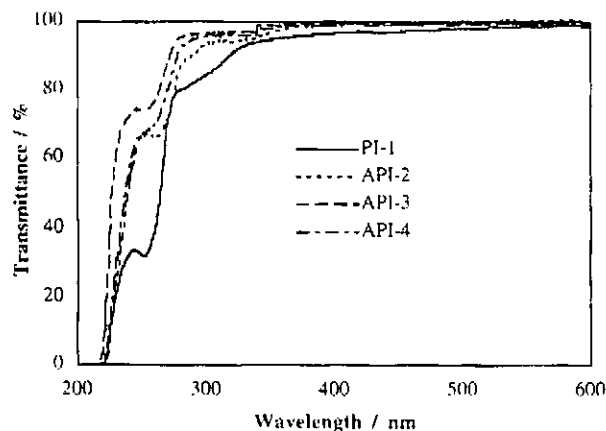


Figure 2. UV-vis spectra of polyimides.

with a rigid diamine, DAA or DABA, and a flexible diamine, 4,4'-DCHM or 1,4-CHDA, in *m*-cresol at high temperature. The APIs obtained had inherent viscosities of 0.19–0.53 dL g⁻¹ and showed good solubility, thermal stability, and transparency above 300 nm.

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