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(71) Applicant (for all designated States except US): **KOLON INDUSTRIES, INC.** [KR/KR]; 1-23, Byeoryang-dong, Gwacheon-si, Gyeonggi-do 427-800 (KR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BAEK, Soo Min** [KR/KR]; 102-104 Jeil Family Apart, Sammun-dong Miryang-si, Gyeongsangnam-do 627-754 (KR). **KIM, Hyun Jin** [KR/KR]; 105-1506 Hyundai Morningside 2-cha, Bora-ri Giheung-eup Yongin-si, Gyeonggi-do 449-583 (KR).

(74) Agent: **WOO YUN IP & LAW FIRM**; 3F Maru Bldg., 942-20, Daichi-dong Kangnam-ku, Seoul 135-845 (KR).

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(54) Title: NORBORNENE-ESTER POLYMER CONTAINING BULKY SUBSTITUENTS

(57) Abstract: This invention provides a norbornene- ester polymer, obtaining by a norbornene- ester monomer having a total number of carbons of the ranges from 19 to 80, having a bulky substituent.

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【DESCRIPTION】

【Invention Title】

NORBORNENE-ESTER POLYMER CONTAINING BULKY SUBSTITUENTS

5 【Technical Field】

The present invention relates to a norbornene-ester polymer having an ester group, and more particularly, to a norbornene-ester polymer, which is obtained from a norbornene monomer having a bulky substituent.

10

【Background Art】

In general, as material for insulating elements, inorganic material, such as silicon oxide or silicon nitride, has been mainly used. However, the increased demand for
15 smaller devices having high efficiency has led to the requirement for polymers that are low in dielectric constant and hygroscopicity and are superior in metal adhesion, strength, thermal stability, and light transmittance, and have a high glass transition temperature.

20 Presently, polyimide or BCB (bis-benzocyclobutene) has been used as a low dielectric substance for electronic materials. Polyimide has excellent thermal stability and oxidation stability, a high glass transition temperature, and superior mechanical properties, and thus has been widely used

for electronic materials. However, polyimide suffers because it has problems related to element corrosion and an increase in dielectric constant due to high moisture absorption, anisotropic electric properties, a need for pretreatment to
5 decrease its reactivity with copper lines, and adhesion to metal. Further, although BCB has lower hygroscopicity and a lower dielectric constant than polyimide, it also has problems in which metal adhesion is poor and a curing process should be conducted at high temperatures.

10 Therefore, attempts to use cyclic olefin polymers have been made.

Cyclic olefin polymers, which are polymers obtained through the polymerization of a cyclic olefin monomer, such as norbornene, have superior transparency, heat resistance,
15 and chemical resistance, and furthermore, have much lower birefringence and moisture absorption, compared to conventional olefin polymers. Accordingly, this polymer may be used for insulating films of semiconductors or TFT-LCDs, protecting films for polarizing plates, multi-chip modules,
20 ICs, printed circuit boards, sealants for electronic materials, or low dielectric coating materials, films, and packages for flat panel displays or optics, and may also be used as material for plastic substrates for flexible displays.

However, in order to apply the norbornene polymer to the above end uses, high optical properties and thermal stability must be assured. The norbornene polymer, which is presently commercially available, has light transmittance of
5 about 80~90% and a glass transition temperature (T_g) of 100~180°C, which does not satisfy the requirements for properties for realizing the above end uses.

In the case where the cyclic olefin monomer contains a polar functional group, such as an ester group, this polar
10 functional group plays a role in increasing intermolecular packing and increasing adhesion to metal substrates or other polymers, and may be efficiently used for information electronic materials, and therefore, polymerization or copolymerization of norbornene, having an ester group, is
15 steadily receiving increasing attention (US Patent No. 3,330,815, EP 0445755A2, US Patent No. 5,705,503, US Patent No. 6,455,650).

However, even though such a polar functional group is contained, there are problems in which optical properties and
20 thermal stability are not assured.

Korean Unexamined Patent Publication No. 2004-5593 discloses a norbornene-ester addition polymer having a low dielectric constant, low hygroscopicity, a high glass transition temperature, excellent thermal stability and

oxidation stability, and high chemical resistance and metal adhesion, and a method of preparing the same. The norbornene-ester addition polymer comprises at least 50 mol% of norbornene-ester monomer, which is an exo isomer, as a
5 repeating unit, and has a molecular weight of at least 20,000.

Whereas the metal adhesion and surface tension of the addition polymer and the adhesion and birefringence of the film using the addition polymer are measured, hygroscopicity,
10 stability, including thermal stability, and optical properties are not mentioned in the above patent. Ultimately, the above patent is unsuitable for solving the above-described problems. Further, although the norbornene-ester monomer, which is an exo isomer, should be used in an
15 amount of 50 mol% or more, it is difficult to assure this amount of monomer.

【Disclosure】

【Technical Problem】

20 According to an embodiment of the present invention, there is provided a norbornene-ester polymer, in which a norbornene-ester monomer comprises a bulky substituent to thereby increase a glass transition temperature, and thus an

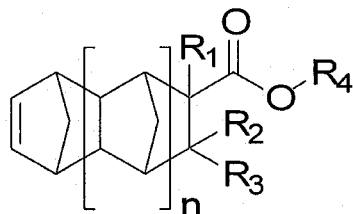
optical material comprising the same provides exhibit excellent optical properties and thermal properties.

An object of the present invention is to provide a norbornene-ester polymer, which is able to increase thermal
5 stability and light transmittance and to minimize moisture absorption.

【Technical Solution】

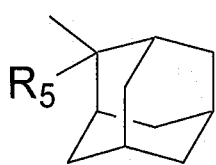
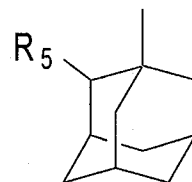
According to an embodiment of the present invention,
10 the invention provides a norbornene-ester polymer, i)
comprising a repeating unit of a norbornene-ester compound
having a total number of carbons of the ranges from 19 to 80,
represented by Formula 1 below; and ii) having light
transmittance of 0.9 or higher which is determined in a
15 manner such that the polymer is formed into a casting film,
which is then measured for intensity of normal incident light
on a substrate, light absorption intensity to the substrate,
and light reflection intensity from the substrate at a
wavelength ranging from 400 nm to 800 nm using a hazemeter,
20 and then the light transmittance is determined according to
Equation 1 below:

Formula 1

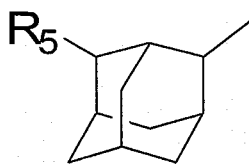


wherein R_1 , R_2 and R_3 , which are the same as or different from each other, are each a hydrogen atom, a C_{1-10} linear or branched alkyl group, or a C_{5-12} cyclic alkyl group, at least one of R_1 , R_2 and R_3 is not a hydrogen atom, and R_4

has a structure selected from among



and



, in which R_5 is a hydrogen

atom, a C_{1-10} linear or branched alkyl group, or a C_{5-12} cyclic alkyl group, and n is an integer of 0 or more; and

Equation 1

$$\frac{l_0 - (l_a + l_r)}{l_0} = T$$

wherein l_0 is the intensity of normal incident light on a substrate, l_a is the light absorption intensity to the substrate, and l_r is the light reflection intensity from the substrate.

According to the present invention, the norbornene-ester polymer may have a glass transition temperature (T_g) ranging from 200°C to 300°C.

The norbornene-ester polymer may have a number average
5 molecular weight (M_n) of 10,000 or more and a molecular weight distribution of 1.0~4.0.

In addition, the present invention provides an optical material, comprising the norbornene-ester polymer.

The optical material is characterized in that it has light
10 transmittance of 0.9 or higher which is determined according to Equation 1.

The optical material may be a film.

【Advantageous Effects】

15 According to the present invention, a norbornene-ester polymer has a high glass transition temperature, to thus exhibit excellent thermal stability, has good metal adhesion, has increased light transmittance, to thus realize superior optical properties, and has minimal moisture absorption, thus
20 making it easy to prepare electronic material.

【Best Mode】

Hereinafter, the present invention is described in detail.

The norbornene-ester polymer of the present invention is obtained by polymerizing a norbornene-ester monomer having from 19 to 80 carbons, represented by Formula 1, which is introduced an ester group and a bulky substituent to a cyclic
5 norbornene monomer.

If polymer chains become tangled with each other or become stacked, light transmittance may be decreased. The polymer of the present invention is characterized in that the monomer itself, constituting the repeating unit, is added
10 with the bulky substituent, and thereby the chains of the resultant polymer are stacked less extensively, or stacking spaces are increased, thus preventing a tangling phenomenon and leading to increased light transmittance.

The term 'norbornene-ester monomer' means a monomer
15 containing at least one norbornene (bicyclo[2,2,1]hept-2-ene) unit represented by Formula 2 below:

Formula 2



The norbornene-ester monomer represented by Formula 1
20 may be obtained by subjecting an alkyl group-substituted or unsubstituted cyclopentadiene (CPD), dicyclopentadiene (DCPD), or mixture thereof, and alkylacrylate, having an adamantyl group, to Diels-Alder reaction.

Specifically, an alkyl group-substituted or unsubstituted CPD, DCPD or mixture thereof and alkylacrylate having an adamantyl group are reacted at a molar ratio of 1:0.5~10, and preferably 1:0.5~4, yielding the norbornene-
5 ester monomer.

As such, the reaction temperature is set to 180~220°C and the reaction pressure is set to atmospheric pressure or higher.

When the monomer of Formula 1 is synthesized, a
10 polymerization inhibitor may be added in order to adjust n of Formula 1 to a desired numerical value. Specific examples of the polymerization inhibitor include, but are not limited to, aniline, cyclohexane, phenol, 4-epoxyphenol, nitrobenzene, hydroquinone, benzoquinone, copper dichloride, and 2,2-di(4-
15 tert-octylphenyl)-1-picrylhydrazyl, and hydroquinone or benzoquinone is preferably used.

The polymerization inhibitor is added so that the molar ratio of the alkyl group-substituted or unsubstituted CPD, DCPD or mixture thereof to the polymerization inhibitor
20 is 1:0.001~0.05, and preferably 1:0.002~0.04.

The monomer thus obtained is represented by Formula 1, and preferably may have a structure in which, in Formula 1, at least one of R₁ to R₃, in particular, R₁ is not a hydrogen atom. Such a structure is included as the repeating unit in

the polymer to thus function to increase the amorphous properties of the polymer, leading to increased light transmittance.

When the above monomer is polymerized to a polymer, a
5 polymerizable monomer and a catalyst are mixed with an organic solvent according to a typical norbornene polymerization process, and furthermore, a cocatalyst may be added, if necessary.

As the organic solvent, alcohol may be used alone, or
10 may be used in combination with water or an organic solvent other than alcohol, such as tetrahydrofuran, examples of alcohol including methanol, ethanol, isopropanol, and butanol.

Examples of the catalyst include transition metal
15 catalysts, such as nickel and palladium, as well as metallocene compounds.

While the polymerization temperature, which varies depending on the type of solvent, is maintained at 20~100°C, the reaction is conducted for 1~24 hours, thus preparing a
20 norbornene-ester polymer.

The norbornene-ester polymer having bulky substituents thus prepared has a number average molecular weight (M_n) of 10,000 or more. Under typical polymerization conditions, M_n

ranges from 20,000 to 1,000,000, and the molecular weight distribution is 1.0~4.0.

Since the norbornene-ester polymer has a glass transition temperature of 200~300°C, it is able to be applied
5 to highly thermally stable materials, and also has metal adhesion equal to or higher than conventional norbornene-ester polymers.

Further, the norbornene-ester polymer having bulky substituents is dissolved in a solvent, and is then prepared
10 into a film or a sheet through a solvent casting process. As such, the polymer may be used in mixtures of one or more. The prepared film has a thickness of 50~500 μm and has light transmittance of 0.9 or higher, which is determined according to Equation 1 below:

15 Equation 1

$$\frac{l_0 - (l_a + l_r)}{l_0} = T$$

wherein l_0 is the intensity of normal incident light on a substrate, l_a is the light absorption intensity to the substrate, and l_r is the light reflection intensity from the
20 substrate.

Moreover, the film or the sheet has low moisture absorption, and therefore superior dimensional stability is realized.

【Mode for Invention】

A better understanding of the present invention may be obtained through the following examples, which are set forth to illustrate, but are not to be construed as the limit of the present invention.

Synthesis of Norbornene-Ester Monomer (Synthesis Examples 1~8, Comparative Synthesis Examples 1~2)

<Synthesis Example 1> Synthesis of 2-Methyl-2-Adamantyl-5-Norbornene-2-Methyl-2-Carboxylate

Into a 0.25 L autoclave, DCPD (dicyclopentadiene, Aldrich, 10.2 mL, 0.0757 mol), 2-methyl-2-adamantylmethacrylate (42.6 g, 0.18 mol), and hydroquinone (0.83 g, 0.1 mol) were added, and were then allowed to react at 180°C for 12 hours, after that the reaction product was cooled, transferred into a distillation apparatus, and then distilled at a reduced pressure of 1 torr using a vacuum pump, thus obtaining a final product at 110°C (yield: 25%). This product had a molar ratio (mol%) of exo isomer to endo isomer of 48.5:51.5.

¹H-NMR (500MHz, CDCl₃), endo: δ 6.20 (dd, 1H), 6.18 (dd, 1H); exo: δ 6.12 (m, 2H)

<Synthesis Example 2> Synthesis of 2-Ethyl-2-Adamantyl-5-Norbornene-2-Methyl-2-Carboxylate

Into a 0.25 L autoclave, DCPD (dicyclopentadiene, Aldrich, 10.2 ml, 0.0757 mol), 2-ethyl-2-adamantylmethacrylate (44.3 g, 0.18 mol), and hydroquinone (0.83 g, 0.1 mol) were added, and were then allowed to react at 200°C for 12 hours, after that the reaction product was cooled, transferred into a distillation apparatus, and then distilled at a reduced pressure of 1 torr using a vacuum pump, thus obtaining a final product at 120°C (yield: 27%). This product had a molar ratio (mol%) of exo isomer to endo isomer of 45.5:54.2.

¹H-NMR (500MHz, CDCl₃), endo: δ6.22 (dd, 1H), 6.19 (dd, 1H); exo: δ 6.18 (m, 2H)

<Synthesis Example 3> Synthesis of 2-Methyl-2-Adamantyl-5-Norbornene-2-Ethyl-2-Carboxylate

Into a 0.25 L autoclave, DCPD (dicyclopentadiene, Aldrich, 10.2 ml, 0.0757 mol), 2-methyl-2-adamantylethacrylate (44.3 g, 0.18 mol), and hydroquinone (0.83 g, 0.1 mol) were added, and were then allowed to react at 210°C for 12 hours, after that the reaction product was cooled, transferred into a distillation apparatus, and then distilled at a reduced pressure of 1 torr using a vacuum pump, thus obtaining a final product at 117°C (yield: 34%). This product had a molar ratio (mol%) of exo isomer to endo isomer of 40.2:59.5.

¹H-NMR (500MHz, CDCl₃), endo: δ6.20 (dd, 1H), 6.18 (dd, 1H); exo: δ6.14 (m, 2H)

<Synthesis Example 4> Synthesis of 1-Adamantyl-5-Norbornene-2-Methyl-2-Carboxylate

Into a 0.25 L autoclave, DCPD (dicyclopentadiene, Aldrich, 10.2 mL, 0.0757 mol), 1-adamantylmethacrylate (40.0 g, 0.18 mol), and hydroquinone (0.83g, 0.1 mol) were added, and were then allowed to react at 200°C for 12 hours, after that the reaction product was cooled, transferred into a distillation apparatus, and then distilled at a reduced pressure of 1 torr using a vacuum pump, thus obtaining a final product at 100°C (yield: 85%). This product had a molar ratio (mol%) of exo isomer to endo isomer of 40.0:59.1.

¹H-NMR (500MHz, CDCl₃), endo: δ6.18 (dd, 1H), 6.04 (dd, 1H); exo: δ6.12 (dd, 1H), 6.04 (dd, 1H)

<Synthesis Example 5> Synthesis of 2-Methyl-2-Adamantyl-9-Tetracyclododecene-4-Methyl-4-Carboxylate

Into a 0.25 L autoclave, DCPD (dicyclopentadiene, Aldrich, 10.2 mL, 0.0757 mol) and 2-methyl-2-adamantylmethacrylate (42.6 g, 0.18 mol) were added, and were then allowed to react at 180°C for 12 hours, after that the resultant reaction solution was added with DCPD (dicyclopentadiene, Aldrich, 5.1 mL, 0.0379 mol), and was then allowed to react at 200°C for 8 hours. The reaction product was cooled, transferred into a distillation apparatus, and then distilled at a reduced pressure of 1 torr using a vacuum

pump, thus obtaining a final product at 110°C (yield: 25%). This product had a molar ratio (mol%) of exo isomer to endo isomer of 47.5:52.5.

¹H-NMR (500MHz, CDCl₃), endo: δ6.30 (dd, 1H), 6.18 (dd, 1H), 2.32 (dd, 2H); exo: δ6.20 (m, 2H), 2.40 (dd, 2H)

<Synthesis Example 6> Synthesis of 2-Ethyl-2-Adamantyl-9-Tetracyclododecene-4-Methyl-4-Carboxylate

Into a 0.25 L autoclave, DCPD (dicyclopentadiene, Aldrich, 10.2 ml, 0.0757 mol) and 2-ethyl-2-adamantylmethacrylate (44.3 g, 0.18 mol) were added and were then allowed to react at 200°C for 12 hours, after that the resultant reaction solution was added with DCPD (dicyclopentadiene, Aldrich, 5.1 ml, 0.0379 mol), and was then allowed to react at 200°C for 8 hours. The reaction product was cooled, transferred into a distillation apparatus, and then distilled at a reduced pressure of 1 torr using a vacuum pump, thus obtaining a final product at 120°C (yield: 27%). This product had a molar ratio (mol%) of exo isomer to endo isomer of 43.7:56.3.

¹H-NMR (500MHz, CDCl₃), endo: δ6.32 (dd, 1H), 6.20 (dd, 1H), 2.32 (dd, 2H); exo: δ6.25 (m, 2H), 2.40 (dd, 2H)

<Synthesis Example 7> Synthesis of 2-Methyl-2-Adamantyl-9-Tetracyclododecene-4-Ethyl-4-Carboxylate

Into a 0.25 L autoclave, DCPD (dicyclopentadiene, Aldrich, 10.2 ml, 0.0757 mol) and 2-methyl-2-adamantylethacrylate (44.3 g, 0.18 mol) were added and were then allowed to react at 210°C for 12 hours, after that the
5 resultant reaction solution was added with DCPD (dicyclopentadiene, Aldrich, 5.1 ml, 0.0379 mol), and was then allowed to react at 210°C for 8 hours. The reaction product was cooled, transferred into a distillation apparatus, and then distilled at a reduced pressure of 1 torr using a vacuum
10 pump, thus obtaining a final product at 117°C (yield: 34%). This product had a molar ratio (mol%) of exo isomer to endo isomer of 50.1:49.9.

¹H-NMR (500MHz, CDCl₃), endo: δ6.31 (dd, 1H), 6.23 (dd, 1H), 2.30 (dd, 2H); exo: δ6.27 (m, 2H), 2.39 (dd, 2H)

15 **<Synthesis Example 8> Synthesis of 1-Adamantyl-9-Tetracyclododecene-4-Methyl-4-Carboxylate**

Into a 0.25 L autoclave, DCPD (dicyclopentadiene, Aldrich, 10.2 ml, 0.0757 mol) and 1-adamantylmethacrylate (40.0 g, 0.18 mol) were added and were then allowed to react at
20 200°C for 12 hours, after that the resultant reaction solution was added with DCPD (dicyclopentadiene, Aldrich, 5.1 ml, 0.0379 mol), and was then allowed to react at 200°C for 8 hours. The reaction product was cooled, transferred into a distillation apparatus, and then distilled at a reduced

pressure of 1 torr using a vacuum pump, thus obtaining a final product at 100°C (yield: 75%). This product had a molar ratio (mol%) of exo isomer to endo isomer of 45.2:54.8.

¹H-NMR (500MHz, CDCl₃), endo: δ6.34 (dd, 1H), 6.27 (dd, 1H), 2.32 (dd, 2H); exo: δ6.31 (m, 2H), 2.34 (dd, 2H)

<Comparative Synthesis Example 1> Synthesis of Norbornene-2-Carboxylic Acid Methyl Ester

Into a 0.5 L autoclave, DCPD (dicyclopentadiene, Aldrich, 67 mL, 0.5 mol), methylacrylate (Aldrich, 94.6 mL, 1.05 mol), and hydroquinone (2.3 g, 0.02 mol) were added, and were then allowed to react at 200°C for 12 hours, after that the reaction product was cooled, transferred into a distillation apparatus, and then distilled at a reduced pressure of 1 torr using a vacuum pump, thus obtaining a final product at 50°C (yield: 89%). This product had a molar ratio (mol%) of exo isomer to endo isomer of 52.8:47.2.

¹H-NMR (500MHz, CDCl₃), endo: δ6.17 (dd, 1H), 5.91 (dd, 1H), 3.60 (s, 3H), 3.17 (b, 1H), 2.91 (m, 1H), 2.88 (b, 1H), 1.28 (m, 1H); exo: δ6.09 (m, 2H), 3.67 (s, 3H), 3.01 (b, 1H), 2.88 (b, 1H), 2.20 (m, 1H), 1.88 (m, 1H), 1.51 (d, 1H), 1.34 (m, 2H)

<Comparative Synthesis Example 2> Synthesis of 2-Adamantyl-5-Norbornene-2-Carboxylate

Into a 0.25 L autoclave, DCPD (dicyclopentadiene, Aldrich, 10.2 ml, 0.0757 mol), 2-adamantylacrylate (37.1 g, 0.18 mol), and hydroquinone (0.83 g, 0.1 mol) were added, and were then allowed to react at 200°C for 12 hours, after that
5 the reaction product was cooled, transferred into a distillation apparatus, and then distilled at a reduced pressure of 1 torr using a vacuum pump, thus obtaining a final product at 120°C (yield: 40%). This product had a molar ratio (mol%) of exo isomer to endo isomer of 50.2:49.8.
10 ¹H-NMR (500MHz, CDCl₃), endo: δ6.22 (dd, 1H), 6.19 (dd, 1H); exo: δ6.17 (m, 2H)

Synthesis of Norbornene-Ester Polymer (Examples 1~10, Comparative Examples 1~2)

<Example 1> 2-Methyl-2-Adamantyl-5-Norbornene-2-Methyl-2-Carboxylate Homopolymer
15

0.13 g (1.0 mmol) of nickel chloride (NiCl₂) was added with 3 ml of ethanol, after that 20 g (6.73 mmol) of 2-methyl-2-adamantyl-5-norbornene-2-methyl-2-carboxylate, synthesized in Synthesis Example 1, was added thereto while
20 the temperature was maintained at 60°C, to thus conduct the reaction for 12 hours. After the completion of the reaction, the temperature of the reactor was decreased to room temperature, and the resultant reaction solution was added in droplets to excess methanol, thus forming a first precipitate

that deposited. The first precipitate was dissolved in 5 ml of ethanol, after that the precipitate solution was added in droplets to excess methanol to thus deposit a second precipitate. The second precipitate was filtered, and was
5 then dried in a vacuum oven at 60°C for 24 hours, yielding a 5-norbornene-2-carboxylic acid methyl ester homopolymer. The obtained polymer was purified through vacuum drying. As the results of the present example, the yield of the resultant polymer was determined to be 12 g (60%), the molecular weight
10 thereof was determined to be 35,000, and the molecular weight distribution thereof was determined to be 2.0.

<Example 2> 2-Ethyl-2-Adamantyl-5-Norbornene-2-Methyl-2-Carboxylate Homopolymer

Polymerization was conducted in the same manner as in
15 Example 1, with the exception that 20 g (6.47 mmol) of 2-ethyl-2-adamantyl-5-norbornene-2-methyl-2-carboxylate, synthesized in Synthesis Example 2, was used, instead of 2-methyl-2-adamantyl-5-norbornene-2-methyl-2-carboxylate. The catalyst and the monomer were used in the same molar ratio as
20 in Example 1. As the results of the present example, the yield of the resultant polymer was determined to be 10 g (50%), the molecular weight thereof was determined to be 22,000, and the molecular weight distribution thereof was determined to be 1.48.

**<Example 3> 2-Methyl-2-Adamantyl-5-Norbornene-2-Ethyl-
2-Carboxylate Homopolymer**

Polymerization was conducted in the same manner as in Example 1, with the exception that 20 g (6.47 mmol) of 2-methyl-2-adamantyl-5-norbornene-2-ethyl-2-carboxylate, synthesized in Synthesis Example 3, was used, instead of 2-methyl-2-adamantyl-5-norbornene-2-methyl-2-carboxylate. The catalyst and the monomer were used in the same molar ratio as in Example 5. As the results of the present example, the yield of the resultant polymer was determined to be 9.2 g (46%), the molecular weight thereof was determined to be 21,000, and the molecular weight distribution thereof was determined to be 1.72.

**<Example 4> 1-Adamantyl-5-Norbornene-2-Methyl-2-
Carboxylate Homopolymer**

Polymerization was conducted in the same manner as in Example 1, with the exception that 20 g (6.99 mmol) of 1-adamantyl-5-norbornene-2-methyl-2-carboxylate, synthesized in Synthesis Example 4, was used, instead of 2-methyl-2-adamantyl-5-norbornene-2-methyl-2-carboxylate. The catalyst and the monomer were used in the same molar ratio as in Example 1. As the results of the present example, the yield of the resultant polymer was determined to be 16 g (80%), the molecular weight thereof was determined to be 26,000, and the

molecular weight distribution thereof was determined to be 1.42.

<Example 5> 2-Methyl-2-Adamantyl-9-Tetracyclododecene-4-Methyl-4-Carboxylate Homopolymer

5 Polymerization was conducted in the same manner as in Example 1, with the exception that 20 g (5.46 mmol) of 2-methyl-2-adamantyl-9-tetracyclododecene-4-methyl-4-carboxylate, synthesized in Synthesis Example 5, was used, instead of 2-methyl-2-adamantyl-5-norbornene-2-methyl-2-carboxylate. The catalyst and the monomer were used in the
10 same molar ratio as in Example 1. As the results of the present example, the yield of the resultant polymer was determined to be 15 g (81%), the molecular weight thereof was determined to be 31,500, and the molecular weight
15 distribution thereof was determined to be 1.92.

<Example 6> 2-Ethyl-2-Adamantyl-9-Tetracyclododecene-4-Methyl-4-Carboxylate Homopolymer

Polymerization was conducted in the same manner as in Example 1, with the exception that 20 g (5.26 mmol) of 2-ethyl-2-adamantyl-9-tetracyclododecene-4-methyl-4-carboxylate, synthesized in Synthesis Example 6, was used, instead of 2-methyl-2-adamantyl-5-norbornene-2-methyl-2-carboxylate. The catalyst and the monomer were used in the
20 same molar ratio as in Example 1. As the results of the

present example, the yield of the resultant polymer was determined to be 9 g (45%), the molecular weight thereof was determined to be 14,000, and the molecular weight distribution thereof was determined to be 1.83.

5 **<Example 7> 2-Methyl-2-Adamantyl-9-Tetracyclododecene-4-Ethyl-4-Carboxylate Homopolymer**

Polymerization was conducted in the same manner as in Example 1, with the exception that 20 g (5.26 mmol) of 2-methyl-2-adamantyl-9-tetracyclododecene-4-ethyl-4-carboxylate, synthesized in Synthesis Example 7, was used, instead of 2-methyl-2-adamantyl-5-norbornene-2-methyl-2-carboxylate. The catalyst and the monomer were used in the same molar ratio as in Example 1. As the results of the present example, the yield of the resultant polymer was
10 determined to be 12 g (60%), the molecular weight thereof was determined to be 27,000, and the molecular weight distribution thereof was determined to be 1.27.

15 **<Example 8> 1-Adamantyl-9-Tetracyclododecene-4-Methyl-4-Carboxylate Homopolymer**

20 Polymerization was conducted in the same manner as in Example 1, with the exception that 20 g (5.68 mmol) of 1-adamantyl-9-tetracyclododecene-4-methyl-4-carboxylate, synthesized in Synthesis Example 8, was used, instead of 2-methyl-2-adamantyl-5-norbornene-2-methyl-2-carboxylate. The

catalyst and the monomer were used in the same molar ratio as in Example 1. As the results of the present example, the yield of the resultant polymer was determined to be 9.5 g (48%), the molecular weight thereof was determined to be 34,000, and the molecular weight distribution thereof was determined to be 1.53.

<Example 9> 2-Methyl-2-Adamantyl-5-Norbornene-2-Methyl-2-Carboxylate and 2-Ethyl-2-Adamantyl-9-Tetracyclododecene-4-Methyl-4-Carboxylate Copolymer

1.0 mmol of nickel chloride (NiCl_2) was added with 10 ml of ethanol, after that 2-methyl-2-adamantyl-5-norbornene-2-methyl-2-carboxylate, synthesized in Synthesis Example 1, and 2-ethyl-2-adamantyl-9-tetracyclododecene-4-methyl-4-carboxylate, of Synthesis Example 5, were added at a molar ratio of 1:1 while the temperature was maintained at 60°C, to thus conduct the reaction for 15 hours. After the completion of the reaction, the temperature of the reactor was decreased to room temperature, and the resultant reaction solution was added in droplets to excess methanol, thus forming a first precipitate that deposited. The first precipitate was dissolved in 5 ml of ethanol, after that the precipitate solution was added in droplets to excess methanol to thus deposit a second precipitate. The second precipitate was

filtered, and was then dried in a vacuum oven at 60°C for 24 hours, yielding a 5-norbornene-2-carboxylic acid methyl ester homopolymer. The obtained polymer was purified through vacuum drying. As the results of the present example, the
5 yield of the resultant polymer was determined to be 62%, the molecular weight thereof was determined to be 42,000, and the molecular weight distribution thereof was determined to be 2.2.

<Example 10> 1-Adamantyl-5-Norbornene-2-Methyl-2-Carboxylate and 2-Ethyl-2-Adamantyl-9-Tetracyclododecene-4-Methyl-4-Carboxylate Copolymer

Polymerization was conducted in the same manner as in Example 9, with the exception that 1-adamantyl-5-norbornene-2-methyl-2-carboxylate, synthesized in Synthesis Example 4,
15 and 2-ethyl-2-adamantyl-9-tetracyclododecene-4-methyl-4-carboxylate, synthesized in Synthesis Example 6, were used. As the results of the present example, the yield of the resultant polymer was determined to be 48%, the molecular weight thereof was determined to be 37,600, and the molecular
20 weight distribution thereof was determined to be 2.53.

<Comparative Example 1> Norbornene-2-Carboxylic Acid Methyl Ester Homopolymer

Polymerization was conducted in the same manner as in Example 1, with the exception that 50 g (0.33 mmol) of

norbornene-2-carboxylic acid methyl ester, synthesized in Comparative Synthesis Example 1, was used, instead of 2-methyl-2-adamantyl-5-norbornene-2-methyl-2-carboxylate. The catalyst and the monomer were used in the same molar ratio as in Example 1. As the results of the present comparative example, the yield of the resultant polymer was determined to be 40 g (80%), the molecular weight thereof was determined to be 60,000, and the molecular weight distribution thereof was determined to be 1.7.

10 **<Comparative Example 2> 2-Adamantyl-5-Norbornene-2-Carboxylate Homopolymer**

Polymerization was conducted in the same manner as in Example 1, with the exception that 20 g (7.3 mmol) of 2-adamantyl-5-norbornene-2-carboxylate, synthesized in Comparative Synthesis Example 2, was used, instead of 2-methyl-2-adamantyl-5-norbornene-2-methyl-2-carboxylate. The catalyst and the monomer were used in the same molar ratio as in Example 1. As the results of the present comparative example, the yield of the resultant polymer was determined to be 8.8 g (44%), the molecular weight thereof was determined to be 23,000, and the molecular weight distribution thereof was determined to be 2.1.

Preparation of Film

<Examples 11~20, Comparative Examples 3~4>

Using the polymer of each of Examples 1~10 and Comparative Examples 1 and 2, a film was prepared. Specifically, the polymer of each of Examples 1~10 and Comparative Examples 1 and 2 was mixed with an organic solvent having the composition shown in Table 1 below to thus prepare a coating solution, which was then cast on a glass substrate using an applicator (YOSHIMITSU YBA-4), dried at room temperature for 1 hour, further dried at 100°C for 18 hours in a nitrogen atmosphere, and then allowed to stand at -10°C for 10 sec. Thereafter, the resultant film was removed from the glass substrate using a knife, thus obtaining the transparent film of each of Examples 11~20 and Comparative Examples 3 and 4, having a uniform thickness, with a thickness variation less than 5%, as shown in Table 1 below.

15 **【Table 1】**

No.	Polymer	Solvent	Thickness (μm)
Ex. 11	Polymer of Ex. 1	THF:PGMEA=1:4	124
Ex. 12	Polymer of Ex. 2	THF:PGMEA=1:4	105
Ex. 13	Polymer of Ex. 3	THF:PGMEA=1:4	122
Ex. 14	Polymer of Ex. 4	THF:PGMEA=1:5	130
Ex. 15	Polymer of Ex. 5	THF:PGMEA=1:5	134
Ex. 16	Polymer of Ex. 6	THF:PGMEA=1:5	151
Ex. 17	Polymer of Ex. 7	THF:PGMEA=1:4	118
Ex. 18	Polymer of Ex. 8	THF:PGMEA=1:5	129
Ex. 19	Polymer of Ex. 9	THF:PGMEA=1:5	131
Ex. 20	Polymer of Ex. 10	THF:PGMEA=1:5	129
C. Ex. 3	Polymer of C. Ex. 1	THF:PGMEA=1:5	115
C. Ex. 4	Polymer of C. Ex. 2	THF:PGMEA=1:5	106
* THF : <u>tetrahydrofuran</u>			
* PGMEA : <u>propyleneglycol methyletheracetate</u>			

<Evaluation of Properties>

(1) Glass Transition Temperature

The glass transition temperature of the polymer of
 5 each of Examples 1~10 and Comparative Examples 1 and 2 was
 measured using TGA (Thermogravimetric Analyzer) and DSC
 (Differential Scanning Calorimeter).

The results are shown in Table 2 below.

【Table 2】

No.	Glass Transition Temp. (°C)
Ex. 1	233
Ex. 2	215
Ex. 3	234
Ex. 4	240
Ex. 5	230
Ex. 6	246
Ex. 7	237
Ex. 8	225
Ex. 9	231
Ex. 10	239
C. Ex. 1	280
C. Ex. 2	222

(2) Metal Adhesion

In order to evaluate the metal adhesion of the polymer of each of Examples 1~10 and Comparative Examples 1 and 2, the polymer was dissolved in 10 wt% of toluene and was then applied to a thickness of 1 μ m on each of glass plates which had been coated with chromium, aluminum and tungsten patterns. The thin film was cross-cut in the form of a grid of squares, each square having a width of 5 mm x a length of 5 mm, and was then subjected to a 180°tape test. As the results, no squares of the test pieces of Examples 1~10 and Comparative Examples 1 and 2 were separated from the glass plate coated with the pattern.

(3) Light Transmittance

The film of each of Examples 11~20 and Comparative Examples 3 and 4 was measured for the intensity of normal

incident light on the substrate, the light absorption intensity to the substrate, and the light reflection intensity from the substrate at a wavelength ranging from 400 nm to 800 nm using a hazemeter (NIPPON DENSHOKU 300A), and
5 then light transmittance was determined according to Equation 1 below. The results are shown in Table 3 below.

Equation 1

$$\frac{l_0 - (l_a + l_r)}{l_0} = T$$

wherein l_0 = the intensity of normal incident light on
10 a substrate,

l_a = the light absorption intensity to a substrate,

and

l_r = the light reflection intensity from a substrate.

(4) Moisture Absorption

15 The film of each of Examples 11~20 and Comparative Examples 3 and 4 was cut to a size of 10 cm × 10 cm, and was then allowed to stand in water at 25°C for 24 hours, after that moisture absorption was determined through weight changes. The results are shown in Table 3 below.

20 **【Table 3】**

No.	Light Transmittance (T)	Moisture Absorption (%)
Ex. 11	0.93	0.037
Ex. 12	0.97	0.035
Ex. 13	0.95	0.032
Ex. 14	0.94	0.034
Ex. 15	0.93	0.026
Ex. 16	0.92	0.028
Ex. 17	0.93	0.025
Ex. 18	0.92	0.030
Ex. 19	0.93	0.031
Ex. 20	0.93	0.027
C. Ex. 3	0.85	0.022
C. Ex. 4	0.88	0.041

As is apparent from the above evaluation results, the norbornene-ester polymer, having an adamantyl group as a bulky substituent, has a glass transition temperature of 200°C or higher to thus exhibit high thermal stability, and therefore is suitable for use in electronic materials, and also has good metal adhesion.

The film, which is prepared with the use of the norbornene-ester polymer having an adamantyl group as a bulky substituent, can be seen to have further increased light transmittance, compared to films prepared without the use thereof. In addition, the film has low moisture absorption, and consequently, superior dimensional stability is realized.

【CLAIMS】

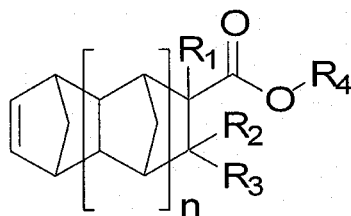
【Claim 1】

A norbornene-ester polymer:

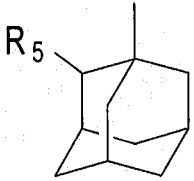
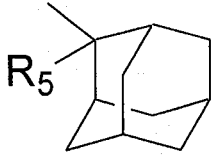
i) comprising a repeating unit of a norbornene-ester
 5 compound having a total number of carbons of the ranges from
 19 to 80, represented by Formula 1 below; and

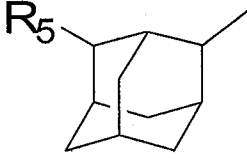
ii) having light transmittance of 0.9 or higher which
 is determined in a manner such that the polymer is formed
 into a casting film, which is then measured for intensity of
 10 normal incident light on a substrate, light absorption
 intensity to the substrate, and light reflection intensity
 from the substrate at a wavelength ranging from 400 nm to 800
 nm using a hazemeter, and then the light transmittance is
 determined according to Equation 1 below:

15 Formula 1



wherein R_1 , R_2 and R_3 , which are same as or different
 from each other, are each a hydrogen atom, a C_{1-10} linear or
 branched alkyl group, or a C_{5-12} cyclic alkyl group, at least
 20 one of R_1 , R_2 and R_3 is not a hydrogen atom, and R_4 has a

structure selected from among ,  and

, in which R₅ is a hydrogen atom, a C₁₋₁₀

linear or branched alkyl group, or a C₅₋₁₂ cyclic alkyl group, and n is an integer of 0 or more; and

5 Equation 1

$$\frac{l_0 - (l_a + l_r)}{l_0} = T$$

wherein l₀ is the intensity of normal incident light on a substrate, l_a is the light absorption intensity to the substrate, and l_r is the light reflection intensity from the
10 substrate.

【Claim 2】

The norbornene-ester polymer according to claim 1, which has a glass transition temperature (T_g) ranging from
15 200°C to 300°C.

【Claim 3】

The norbornene-ester polymer according to claim 1, which has a number average molecular weight (Mn) of 10,000 or more and a molecular weight distribution of 1.0~4.0.

5 **【Claim 4】**

An optical material, comprising the norbornene-ester polymer of any one of claims 1 to 3.

【Claim 5】

10 The optical material according to claim 4, which has light transmittance of 0.9 or higher which is determined in a manner such that the optical material is measured for the intensity of normal incident light on a substrate, the light absorption intensity to the substrate, and the light
15 reflection intensity from the substrate at a wavelength ranging from 400 nm to 800 nm using a hazemeter, and then the light transmittance is determined according to Equation 1 below:

Equation 1

$$\frac{l_0 - (l_a + l_r)}{l_0} = T$$

20

wherein l_0 is the intensity of normal incident light on a substrate, l_a is the light absorption intensity to the

substrate, and l_r is the light reflection intensity from the substrate.

【Claim 6】

- 5 The optical material according to claim 4, wherein the optical material is a film.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2007/001047**A. CLASSIFICATION OF SUBJECT MATTER***C08G 61/06(2006.01)i*

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC8 C08G 61/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Utility models and applications for Utility models since 1975

Japanese Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKIPASS, PAJ "norbornene", "ester"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004/254318 A1 (Sung-Ho Chun et al.) 16.12.2004 See the whole document(especially, claim 18)	1-6
A	DE 10047023 A1(BASF AG) 11.04.2002 See the whole document	1-6
A	JP 12-169558 A(NIPPON ZEON Co., Ltd.) 20.06.2000 See the whole document	1-6
A	JP 12-219725 A(NIPPON ZEON Co., Ltd.) 08.08.2000 See the whole document	1-6

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

12 JUNE 2007 (12.06.2007)

Date of mailing of the international search report

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Korean Intellectual Property Office
920 Dunsan-dong, Seo-gu, Daejeon 302-701,
Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

JWA, Seung Kwan

Telephone No. 82-42-481-5537



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2007/001047

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JP 12-169558 A	20.06.2000	NONE	
JP 12-219725 A	08.08.2000	NONE	