

Synthesis and Characterization of Novel Hydrogenated Poly(norbornene bisimide)s Prepared from Ring Opening Metathesis Polymerization[†]

Kyung-Hwan Yoon, Seung Beom Park, Insook Park,[‡] and Do Y. Yoon*

Department of Chemistry, Seoul National University, Seoul 151-747, Korea. *E-mail: dyoon@smu.ac.kr

[‡]E&A Center, Kolon Central Research Institute, Yongin 446-797, Korea

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We synthesized three novel poly(norbornene bisimide)s by ring opening metathesis polymerization (ROMP) and subsequent hydrogenation. Their thermal, mechanical and optical properties were investigated with TGA, DMA, UV-Vis spectrometer, and optical reflectometer. The new polymers showed high glass transition temperatures over 260 °C and good thermal stability with 5% wt-loss temperature higher than 390 °C. When solvent casted, they yielded optically transparent and dimensionally stable films with a relatively low coefficient of thermal expansion of about 50 ppm K⁻¹. Therefore, the bisimide moieties substantially enhanced thermal and dimensional stabilities, as compared with normal ROMP-prepared polynorbornene films. Though the water uptake was increased to 0.6 wt-%, this water uptake is still considerably lower than that for polyethersulfones (1.4 wt-%) or polyimides (2.0 wt-%). Hence, the new poly(norbornene bisimide)s may become attractive candidates for flexible substrates of optoelectronic devices such as displays and photovoltaic solar cells.

Key Words : Polynorbornene, Poly(norbornene imide), Poly(norbornene bisimide), ROMP, Flexible substrates

Introduction

Polymeric films have been considered as a good candidate for flexible substrates of optoelectronic devices, such as displays and photovoltaic solar cells, due to their light weight, low cost, and roll-to-roll processability.¹ Flexible substrates require high thermal stability (glass transition temperature (T_g) > 200 ~ 250 °C), excellent dimensional stability (coefficient of thermal expansion (CTE) < 20 ppm K⁻¹), good optical transparency (total light transmittance at 400 ~ 800 nm > 85%), and low water-vapor permeability (< 0.01 g/m²/day).² Currently, polyethersulfones and colorless polyimides approach these requirements more closely than other polymers. However, their high water transmission rates are still unsolved problems (208 g/m²/day for polyethersulfone, 54 g/m²/day for polyimide). Polynorbornenes prepared from ring opening metathesis polymerization (ROMP) followed by hydrogenation exhibit an extremely good water-barrier characteristics (0.1 g/m²/day), but their thermal and dimensional stabilities are not satisfactory for flexible substrates (T_g of 140 ~ 170 °C, CTE of around 70 ppm K⁻¹). For this reason, some research groups introduced an imide moiety to the monomer of polynorbornene and succeeded in increasing T_g of the polymer to 200 ~ 230 °C.³⁻⁵ The imide moiety was therefore considered to be the major source of the enhanced thermal and dimensional stabilities.

N-Amino-imide has been synthesized for a rather long period,^{6,7} but its application to polymer synthesis was reported very rarely. So far, there is no report on polymers

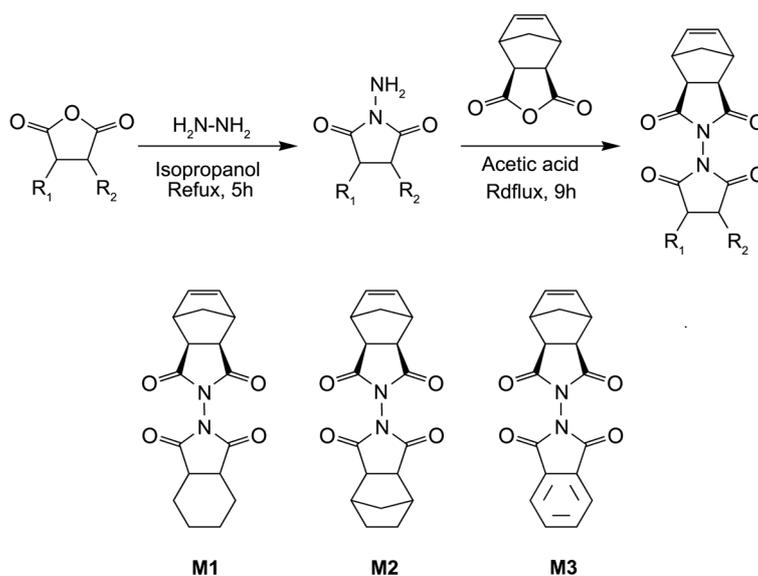
based on bisimides, in which two imides groups are connected to each other via N-N linkage. Recently, Kas'yan and his coworkers succeeded in systematic synthesis of various bisimides based on N-amino-imidization of 5-norbornene-2,3-dicarboxylic anhydride (Scheme 1).⁸ In this work, we introduced bisimide moieties in the norbornene based monomers for ROMP, in order to obtain new polymers with significantly increased thermal and dimensional stabilities. Since polynorbornenes prepared from ROMP become chemically stable after hydrogenation of backbones,⁹⁻¹¹ we also carried out hydrogenation experiments of ROMP-prepared polymers. The thermal, mechanical, and optical properties of the resulting polymers were then investigated in details. To our knowledge, this is the first preparation and characterization of hydrogenated poly(norbornene bisimide)s.

Experimental Section

Materials. *cis*-1,2-Cyclohexanedicarboxylic anhydride (CHDA), 5-norbornene-2,3-*endo,endo*-dicarboxylic anhydride (*endo*-NDA), phthalic anhydride (PA), hydrazine monohydrate, ethyl vinyl ether and Pd/C (5%) were purchased from TCI. Grubbs 1st generation catalyst (**G1**), Grubbs 2nd generation catalyst (**G2**), dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)bis(3-bromopyridine) ruthenium(II) (**G3**), and *p*-toluenesulfonyl hydrazide (*p*-TSH) were purchased from Sigma-Aldrich. Isopropanol, ethyl acetate, ethanol, chloroform, N,N-dimethylformamide (DMF), methanol, sodium carbonate were purchased from Duksan Chemical.

Synthesis of N-amino-imide. *Endo*-NDA was thermally isomerized to *exo*-NDA by heating at 185 °C for 4 hrs,

[†]This paper is dedicated to Professor Eun Lee on the occasion of his honourable retirement.



Scheme 1. Method of monomer synthesis.

followed by recrystallization with ethyl acetate twice (Scheme 2). For the monomer **M1** (Scheme 1), 15.4 g of CHDA was dissolved in 100 mL of isopropanol. Into the solution, 1.2 equimolar amount of hydrazine hydrate (6.1 mL) was added dropwise, and the solution was heated to reflux at 90 °C for 5 hrs. The resulting solution was kept at -15 °C until the product was fully precipitated. The precipitant was then filtered and dried under high vacuum. Product yield was 82%. For the monomer **M2**, the same procedures were performed except for the addition of 16.4 g of *exo*-NDA, instead of CHDA, in the first step. The product (13.3 g) and Pd/C (0.1 g) were dissolved in ethanol (100 mL), and hydrogen balloon was applied for 1 day. The catalyst was filtered off and the solution was rotary evaporated. Product yield was 70%. For the monomer **M3**, 14.8 g of PA and 0.6 equimolar amount of urea (3.6 g) were dissolved in 100 mL of xylene, and heated to reflux at 140 °C for 2 hrs. After cooling, the precipitant (phthalimide) was filtered and dried fully under vacuum. Phthalimide and 1.1 equimolar amount of hydrazine hydrate were dispersed in methanol/water (50/50) mixture kept at 0 °C and stirred for 9 hrs. The resulting precipitant was filtered and dried fully under high vacuum. Product yield was 31%. Purity and molecular mass of all products were confirmed with GC-MS: *m/z* 168, 180 and 162, respectively.

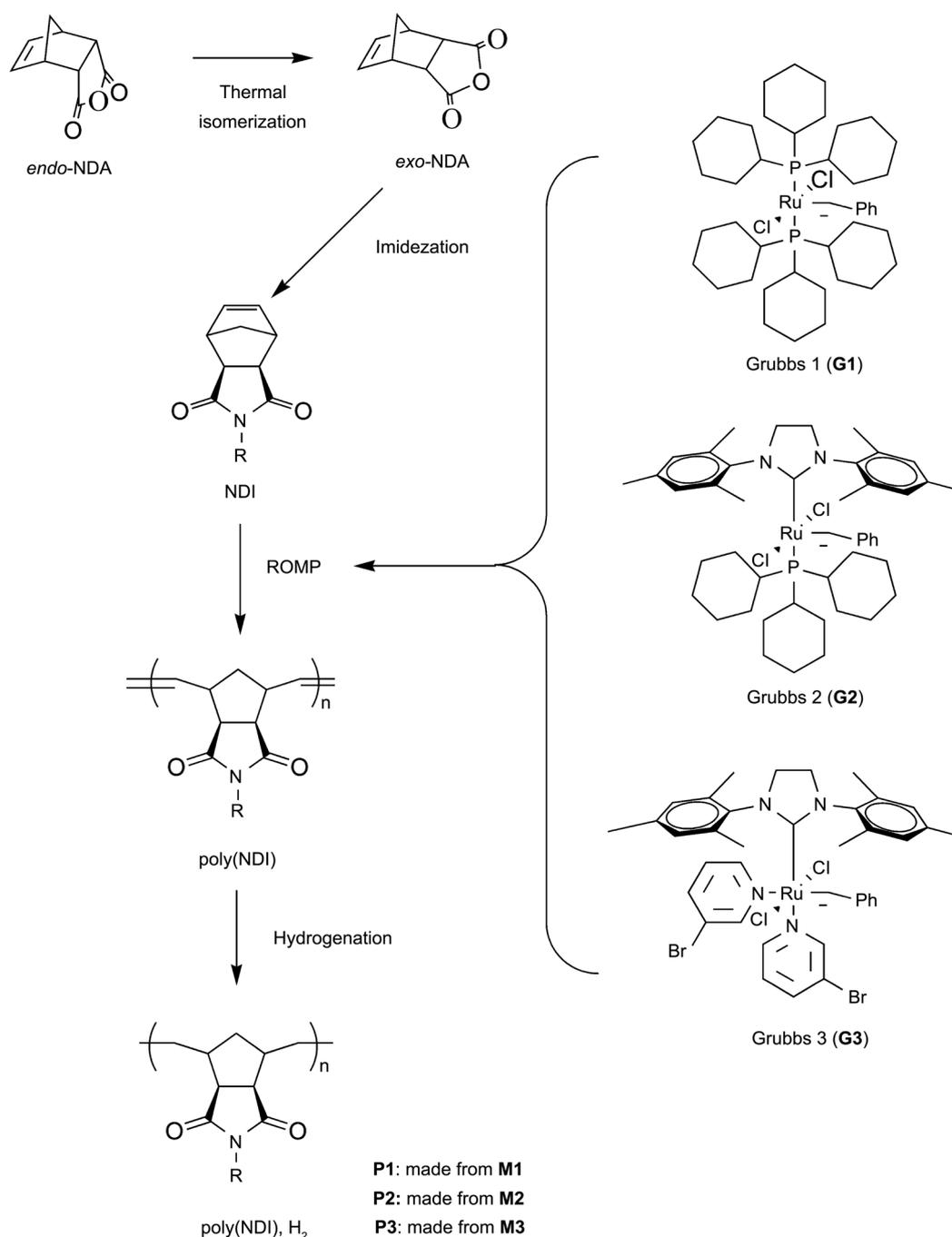
Synthesis of Monomers (NDI). Each N-amino-imide and equimolar amount of *exo*-NDA were dissolved in acetic acid (1 M concentration), and the solution was heated to reflux at 140 °C for 9 hrs (Scheme 1). The solution was then poured into cold water, and the colorless precipitant (**M1**, **M2**, **M3**) was filtered, washed with sodium carbonate solution and water, and then dried completely under high vacuum. Product yields were higher than 70%. Purity and molecular mass of all products were confirmed with MALDI-TOF-MS: [*m* + 1]*z* 315, 327 and 309, respectively, together with

¹H NMR; the ¹H NMR data (400 MHz, CDCl₃) for the three monomers are presented in Supporting Information.

Polymerization. In a nitrogen-filled round bottomed flask, 5 g of **M1** was dissolved in 100 mL of chloroform. Reaction temperature was maintained at 60 °C. **G3** catalyst was prepared in 1 mL of chloroform with the monomer to catalyst molar ratio of 120 to 1, and injected into the monomer solution at once (Scheme 2). After 5 min of reaction, 1 mL of ethyl vinyl ether was added dropwise and the solution was stirred for overnight. The polymer solution was passed through a short silica column, and precipitated into cold methanol. The colorless polymer was filtered and dried completely in a vacuum oven at 130 °C. The procedure for polymerizing **M2** was identical to that for **M1**. For **M3**, only the solvent was changed to DMF instead of chloroform. Product yields were higher than 90% for **P1** from **M1** and **P2** from **M2**, but less than 50% for **P3** from **M3**.

Hydrogenation. About 3 g of polymer and *p*-TSH (2.2 equimolar amount of double bond calculated) were dissolved in DMF at a concentration of 5 wt-% (Scheme 2, 3). After the solution was heated to reflux at 140 °C for 6 hrs, it was concentrated to higher than 7.5 wt-% in a rotary evaporator and precipitated into cold methanol or ethanol. The precipitant was filtered, washed with methanol or ethanol overnight, and dried completely in a vacuum oven at 130 °C. Product yields were higher than 85%. Degree of hydrogenation was checked with ¹H NMR.

Characterization. All ¹H NMR measurements were performed on Eclipse +400 spectrometer (JEOL, Japan) using CDCl₃ except for **P3** in DMSO-*d*₆. Degree of hydrogenation was calculated with the area ratio of double bond peaks between 5 and 6 ppm against the other peaks. Gel permeation chromatography, comprised of a CM4000 pump (Milton Roy, USA), tandemly connected MixedBed B and D columns (Agilent, USA) and a 2410 refractive index



Scheme 2. Method of polymer synthesis.

detector (Waters, UK), was used to measure molecular weight (MW). The eluent was DMF containing 50 mM lithium bromide, and the flow rate was 0.8 mL/min. The values of MW were determined from the polystyrene-standard calibration curve. The refractive index of a polymer film coated on a silicon wafer was measured with an optical reflectometer (Filmetrics F20, USA). Thermogravimetric analysis was carried out by TGA Q50 (TA instruments, USA) at a heating rate of 10 °C/min. The values of T_g were measured by dynamic mechanical analyzer (DMA 2890, TA instruments, USA) with a single cantilever clamp at a single

frequency mode (1 Hz), on polymer samples coated on glass fibers heated at a rate of 2 °C/min. To measure the tensile modulus and CTE values, a number of films with ca. 100 μm thickness were prepared from chloroform or DMF solutions by a conventional solution-casting method. For tensile modulus measurements, polymer films were held at a film tension clamp in DMA 2890 and the tension force was increased at a rate of 5 N/min. For CTE measurements, polymer films were also held at a film tension clamp in DMA with a static force of 0.1 N, and the temperature was increased at a rate of 2 °C/min. For light transmission

measurements, polymer films were characterized by V-530 spectrometer (JASCO, Japan). To estimate the water absorption, the polymer films were dipped into a water reservoir at 30 °C for 1 day. Weight changes of the films were then measured to calculate the water uptake.

Results and Discussion

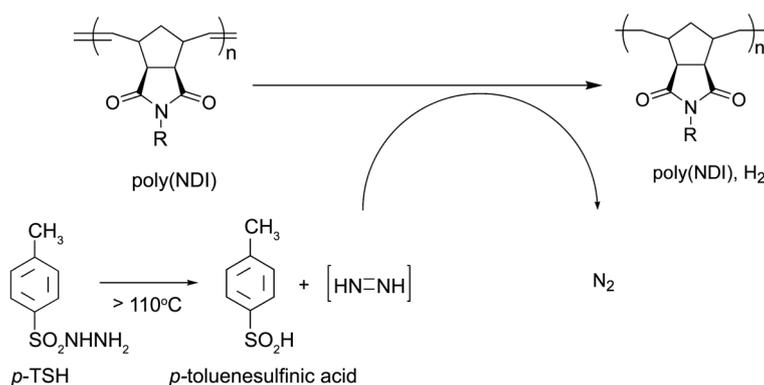
Since *exo*-isomer is more reactive for ROMP catalysts,¹²⁻¹⁴ commercially available *endo*-NDA was thermally isomerized to *exo*-NDA according to the previously reported methods.^{4,12,15} N-amino-imidization of CHDA and NDA can be achieved by propanol solvent method,^{6,7} benzene dispersion method,¹⁶ or acetic acid solvent method.¹⁷ Because the benzene dispersion method and the acetic acid solvent method were originally designed for hydrazine derivatives, they only resulted in dimer molecules in our case. N-amino-imidized NDA should be hydrogenated to remove a double bond in order to avoid any cross-linking during ROMP. N-amino-imidization of PA is more complicated, because N-amino-phthalimide easily isomerizes to 2,3-dihydro-1,4-phthalazinedione under heat.^{16,17} Therefore, PA was first turned into phthalimide via reaction with urea, and then reacted with hydrazine to obtain N-amino-phthalimide.¹⁸ The temperature of reaction between phthalimide and hydrazine should be kept at 0 °C to avoid thermal isomerization.¹⁹⁻²¹ An alternative route for **M3** is the reaction between N-amino-imidized NDA and phthalic anhydride, which was also successful. Imidization of a dicarboxylic anhydride by the reaction with a primary amine is easily achievable either by refluxing in acetic anhydride/sodium acetate solution^{3,4,12} or by refluxing in acetic acid.²² Both methods worked well.

Grubbs and his coworkers have developed very powerful ROMP catalysts, called Grubbs 1 (**G1**), Grubbs 2 (**G2**) and Grubbs 3 (**G3**) (Scheme 2).²³ **G1** did not work for norbornene bisimide monomers (**NDI** in Scheme 2), whereas **G2** and **G3** worked quite effectively in either chloroform or DMF. When polymerization of **M1** or **M2** was attempted in chloroform with **G2**, it always resulted in polymeric gels. In contrast, **G3** in case of **M1** and **M2** could be used for polymerization without any gels in chloroform with the monomer to catalyst

ratio less than 120:1. However, at a higher catalyst ratio, **G3** also resulted in polymeric gels. For **M3**, both **G2** and **G3** produced polymeric gels immediately in chloroform. Therefore, polymerization of **M3** was performed in DMF. In DMF, rather higher monomer to catalyst ratio up to 200:1 was allowed. A problem with polymerizing in DMF is that the purification is not as clean as that in chloroform, since the silica column cannot trap catalyst due to the high polarity of DMF. Therefore, the solution had to be concentrated to higher than 7.5 wt-% in a rotary evaporator prior to precipitation in order to avoid too fine precipitants. The properties of these unhydrogenated polymers are summarized in Table 1.

Hydrogenation of polymer backbones can be achieved either by heterogeneous [Pd] or [Ru] catalyst,^{24,25} homogeneous [Ru] catalyst,²⁶⁻²⁸ or *p*-TSH method.^{29,30} In case of aromatic solvent (xylene, toluene, etc.) used in previous studies,^{29,30} *p*-toluenesulfonic acid, a side product from thermal degradation of *p*-TSH (Scheme 3), caused chemical degradation of polymers, resulting in decrease of MW. Therefore, a basic reagent such as tripropylamine was often added to neutralize *p*-toluenesulfonic acid.³⁰ In our case, MWs were not reduced by more than 5% (compare MWs in Table 1 and 2) even without a basic reagent, due to the basic nature of DMF. As seen in Fig. 1, the reduction of cis-bonds is much lower than the reduction of trans-bonds (Table 2). In case of the polymer from **M1** monomer, **P1**, 93.4% of trans-bonds were reduced, whereas only 51.6% of cis-bonds were reduced. This tendency is also observed for other polymers (Table 2). In the case of poly(norbornene imide)s, we achieved the hydrogenation to higher than 99.9% with the same method. Therefore, the reason of the incomplete hydrogenation of poly(norbornene bisimide)s lies in the polymer sample itself rather than the method, and the details are under investigation.

Figure 2 shows the thermogravimetric results of the hydrogenated polymers. All three polymers were stable up to 400 °C, and the thermal stability was enhanced after hydrogenation (compare T_d values in Table 1 and 2) as already pointed out in previous studies.⁹⁻¹¹ Although the values of T_g were decreased somewhat after hydrogenation (compare T_g values in Table 1 and 2), they are still



Scheme 3. Hydrogenation method.

Table 1. Properties of the polymers before hydrogenation

	P1 before H ₂	P2 before H ₂	P3 before H ₂
Weight-average MW [PDI]	220,000 [1.49]	146,000 [1.25]	190,000 [1.18]
T _{d, 5%} (°C) ^a	381	380	388
T _g (°C) ^b	293	319	297
Refractive index (633 nm)	1.54	1.56	1.62

^aThe temperature at which the TGA data show a weight loss of 5% upon heating at 10 °C/min (Fig. 2).

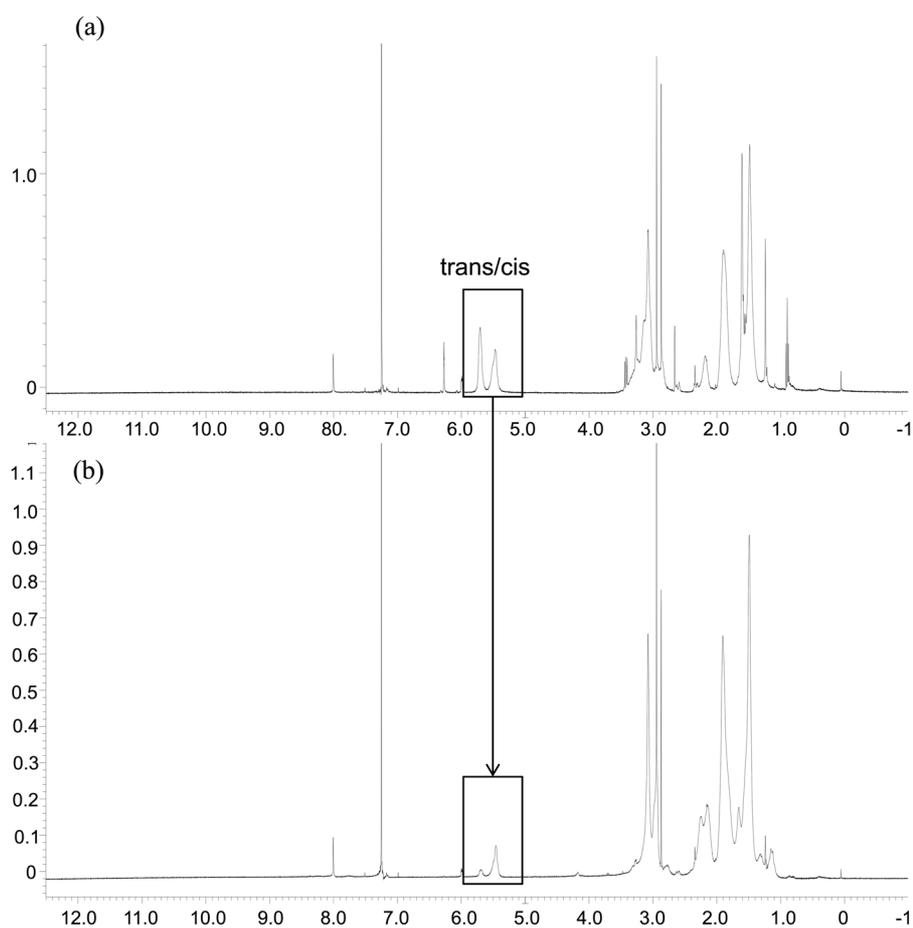
^bThe T_g value is taken to be the peak temperature in mechanical loss tangent δ vs. temperature plot (Fig. 2).

Table 2. Properties of the polymers after hydrogenation

	P1	P2	P3
Total degree of hydrogenation (%) [trans/cis]	73.9 [93.4/51.6]	76.7 [89.9/61.2]	62.7 [72.4/51.6]
Weight-average MW [PDI]	210,000 [1.54]	140,000 [1.28]	200,000 [2.21]
T _{d, 5%} (°C)	422	420	392
T _g (°C)	273	303	263
Refractive index (633 nm)	1.52	1.53	1.61
Tensile modulus (GPa)	1.5	1.3	1.6
CTE (ppm K ⁻¹) ^a	52	51	51
Total light transmittance (%) ^b	90.8	87.0	67.2
Water absorption (wt-%)	0.6	0.6	1.2

^acalculated between 55 °C and 125 °C

^bnormalized to 100 μ m thickness

**Figure 1.** ¹H NMR spectra of **P1** before (a) and after hydrogenation (b).

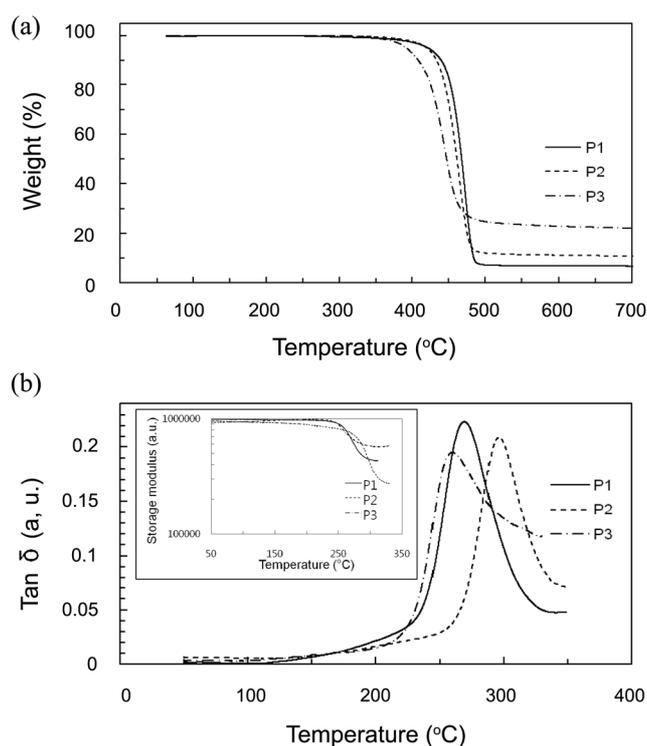


Figure 2. Thermal properties of polymers after hydrogenation: TGA results of weight loss (a) and DMA results of mechanical loss tangent δ and storage modulus (arbitrary unit) (b). The T_g value is taken to be the peak temperature in tangent δ vs. temperature plot.

considerably higher compared to those reported for poly(norbornene imide)s.³⁻⁵ This may be due to the stronger intermolecular interactions induced by the imides groups as well as the increased bulkiness of pendant groups. The slight decrease in refractive index upon hydrogenation, which indicates that the polymer packing becomes less dense, is consistent with the decrease in T_g .

Values of tensile modulus of the films were somewhat lower as compared commercial polynorbornene films (2.1 ~ 2.4 GPa),¹⁰ but this may be due to different film fabrication techniques, such as film stretching, which result in molecular orientation. The results on dimensional changes with temperature (Fig. 3) show lower CTEs (ca. 50 ppm K⁻¹) (Table 2) for the hydrogenated poly(norbornene bisimide)s as compared with polycarbonate film (75 ppm K⁻¹).² By stretching during film fabrication, for example, the CTE values may be reduced to the desired range of less than 20 ppm K⁻¹. Concerning the optical properties, the films of **P1** and **P2** are very optically transparent with the overall transmittance > 85%, normalized to the 100 μ m thickness, whereas the film of **P3** exhibits a considerably lower transmittance of 67% and brownish color, consistent with the absorption tails into the visible frequency range (Fig. 4). **P3** film also absorbs twice as large amount of water as compared with **P1** and **P2** (Table 2), for which the values are similar to poly(ethylene naphthalate) (PEN) (0.4 wt-%). As compared with currently promising polymer candidates for flexible substrate, polyethersulfones (1.4 wt-%) and

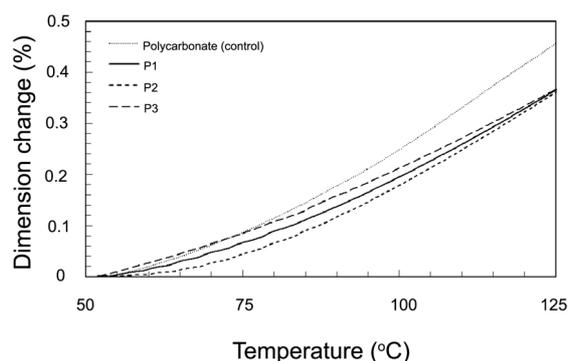


Figure 3. Dimensional changes of polymer films with temperature. The value of CTE is estimated by the linear slope between 55 °C and 125 °C. A polycarbonate film was used as a control sample to confirm reliability of the instrument.

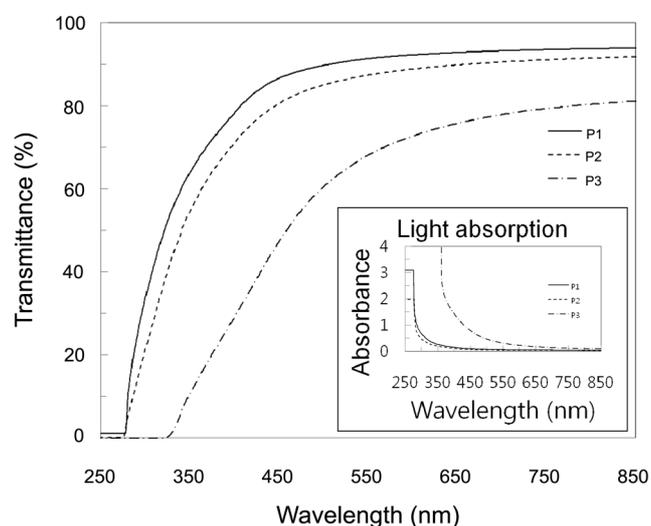


Figure 4. UV-Vis transmittance and absorption spectrum of polymer films with ca. 100 μ m thickness after hydrogenation.

polyimides (2.0 wt-%), the water absorption characteristics of hydrogenated poly(norbornene bisimide)s represents a substantial improvement.²

Conclusion

We successfully synthesized three novel hydrogenated poly(norbornene bisimide)s and characterized their thermal, mechanical, and optical properties. They are very stable both thermally ($T_d > 390$ °C, $T_g > 260$ °C) and dimensionally (CTE ≈ 50 ppm K⁻¹), and are optically transparent. The values of tensile modulus and CTE are expected to be improved with better film fabrication methods. Although these polymers show somewhat higher water uptake than normal polynorbornenes, their water absorption is still substantially lower than those of currently promising polymer candidates for flexible substrates of optoelectronic devices.

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