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In this paper, simple, effective, and stereo-selective syntheses of 5-norbornene-2-carboxylic acid (NBMA) and its derivatives were reported. The properties as a resist material were also investigated. In order to obtain exo-rich isomer at high yield, methyl 5-norbornene-2-carboxylate (MNBC) was synthesized via Diels-Alder reaction as a starting material at first. Then, the isomerization and exo-selective hydrolysis of MNBC were performed in a basic condition to synthesize exo-rich NBMA. Exo-rich t-butyl 5-norbornene-2-carboxylate (tBNBC) was prepared by non-selective esterification. After purification, exo-tBNBC was isolated. The random copolymers consisting of exo- or endo-rich tBNBC (endo-rich tBNBC was synthesized by classic Diels-Alder reaction) and maleic anhydride were synthesized as resist materials via free radical polymerization. The resulting copolymers were characterized by GPC and $^1$H NMR. Furthermore, the acidic deprotection behavior of exo- and endo-tBNBC was monitored using $^1$H NMR for the model reaction of resist system. In this study, it is suggested that the endo/exo ratio of norbornene derivatives affect reactivity, rate of reaction, property of polymer and monomer, and lithographic performance. Keywords: 2-substituted norbornene, stereo-selective synthesis, maleic anhydride, random copolymer, 193 nm lithography

1. Introduction
Poly(norbornene) synthesized via the vinyl addition polymerization process has good physical properties such as high thermal stability, high glass transition temperature and high optical transparency [1-3]. Therefore, norbornene is important as a monomer for industrial chemistry. Norbornene derivatives are also useful as a monomer or intermediate for photosensitive materials with high dry etching resistance which comes from alicyclic structure [4-7].

2-Substituted norbornene compounds consist of endo- and exo-isomers which show different properties. For example, exo-isomers show higher reactivity in living ring opening metathesis polymerization (ROMP) than endo-isomers [8]. In the case of photosensitive monomer synthesis, endo-isomer provides undesired lactone by intermolecular cycloaddition resulting in a low yield of desired photoresist monomer [9]. Furthermore, the ratio of endo- and exo-isomers in norbornene units in a resist polymer influences resist performance such as a dissolution rate [10]. Therefore, the control of ratio of endo- and exo-isomer is very important.

2-Substituted norbornene compounds are synthesized via Diels-Alder cycloaddition reaction. It is well-known that Diels-Alder cycloaddition reaction is endo-selective due to the secondary overlap and the selectivity is enhanced by Lewis acid (>99 %). Some of exo-selective synthesis of norbornene have been reported. However, exo-selective synthesis requires antibody catalyst or chiral dieneophile, which are difficult or costly to access [11-14]. Exo-isomer can be purified by removing endo-isomer through lactonization. While the ratio of exo-isomers can increase, the total yield of both isomers reduces [15,16].

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Niwayama reported exo-selective monohydrolysis of norbornene dicarboxylic diester, which suggests that exo-norbornene carboxylic acid can be synthesized by exo-selective hydrolysis of norbornene carboxylic ester [17]. However, the total yield of exo-carboxylic acid would be low unless exo-rich mixture of norbornene carboxylic ester was used as the starting material. Otake reported exo-selective synthesis of NBCA via endo/exo isomerization and exo-selective hydrolysis of MNBC [18]. But the reaction mechanism was not explained in detail. Here, the purpose of this paper is to establish the simple, effective, and stereo-selective synthesis of exo-norbornene derivatives and to discuss the reaction mechanism of thermodynamic isomerization and kinetically exo-selective hydrolysis. Besides the influence of endo/exo ratio of the resulting monomer for any characteristics such as reactivity, polymer properties, and lithographic performance, was evaluated. Finally, exo-tBNBC/maleic anhydride (MAH) random copolymer was synthesized as a resist polymer for 193 nm lithography.

2. Experimental
2.1 Materials

Dicyclopentadiene, methyl acrylate, 2-methyl propene, and 2,2-azobisisobutyronitrile (AIBN), and propylene glycol monomethyl ether acetate (PGMEA) were obtained from Tokyo Chemical Industry Co. Ltd. Sulfuric acid was obtained from Aldrich. Tetrahydrofuran (THF) was dehydrated. All other materials were purchased from Wako Pure Chemical Industries, Ltd. and used without any further purification unless otherwise mentioned.

2.2 Monomer synthesis
2.2.1 Synthesis of methyl 5-norbornene-2-carboxylate (MNBC)

Solid dicyclopentadiene (26.4 g, 0.20 mol) was added into 100 mL flask equipped with distillation condenser. Dicyclopentadiene was heated at 170 °C to generate cyclopentadiene by pyrolysis. Cyclopentadiene was cooled at distillation condenser and added directly and dropwisely into a 100 mL three-necked flask charged with excess amount of methyl acrylate (40.1 g, 0.45 mol) and methanol (14 mL) at 40 °C. After addition, the mixture stirred 12 h at 40 °C, and the excess methyl acrylate and methanol were removed under the reduced pressure to give crude MNBC. The crude products was purified by vacuum distillation to give MNBC (48.7 g, 79 %, exo ; 20 %).

2.2.2 Synthesis of endo-rich t-butyl 5-norbornene-2-carboxylate (tBNBC)

Endo-rich mixture of tBNBC was obtained by the similar procedure as described above using t-butyl acrylate (yield 81 %, exo ; 20 %).

2.2.3 Synthesis of exo-rich 5-norbornene-2-carboxylic acid (NBCA)

Sodium t-butoxide (6.34 g, 66.0 mmol) and dehydrated THF (66 mL) were added into a 100 mL two-necked flask equipped with dropping funnel under nitrogen atmosphere. MNBC (4.56 g, 30.0 mmol, endo : 80 %) was added into the flask and stirred at room temperature for 3 h. An equivalent amount of deionized water (540 µL) diluted with dehydrated THF (27 mL) was added into the reaction mixture dropwise, and the reaction was continued for 24 h at room temperature. Furthermore, the same amount of water was added again, and the mixture was stirred 3 h. Then, excess amount of deionized water (5.40 mL) was added to complete the hydrolysis. The reaction mixture was stirred for 1 h at room temperature and was neutralized with acetic acid until pH was adjusted to 7.5. The excess solvent was removed under reduced pressure. After the addition of 35% HCl until pH was adjusted to 2.0, the reaction mixture was extracted with toluene (30 mL) three times. Toluene was removed under reduced pressure, and the product was dried in vacuo over night to give NBCA (2.81 g, 67 %, exo ; 82 %).

2.2.4 Synthesis of exo-t-butyl 5-norbornene-2-carboxylate (tBNBC)

Exo-rich mixture of NBCA (5.34 g, 38.7 mmol, exo ; 82 %), dichloromethane (21.5 mL) and sulfuric acid (0.721 mL, 13.5 mmol) were added into 50 mL three-necked flask equipped with capillary. The mixture was stirred well at room temperature and isobutene gas was introduced from capillary. After isobutene bubbling for 4 h, the mixture was stirred for 24 h at room temperature, then the reaction mixture was neutralized with a solution of 5 % K₂CO₃. The mixture was extracted by diethyl ether and the organic layer was washed with K₂CO₃ (saturated solution), 10 % hydrochloric acid, and H₂O each three times. The organic layer was dried with MgSO₄ over night, filtered, and concentrated (6.47
The crude product was purified by column chromatography on a silica gel column with toluene as an eluent. Toluene was removed under reduced pressure, and the product was dried in vacuo over night to obtain pure exo-tBNBC (1.98 g, 26%).

2.3 Synthesis of tBNBC/MAH random copolymer

A dry 20 mL-three necked flask equipped with a stirring bar, condenser, and stop-cock was charged with AIBN (98.5 mg, 0.600 mmol) and MAH (588 mg, 6.00 mmol) was under nitrogen. After the evacuation for 30 min followed by backfilling of nitrogen, THF (4.85 mL) and tBNBC (1.12 mL, 6.00 mmol) were added with syringe under nitrogen flow. After four freeze-pump-thaw cycles, the mixture was allowed to stir at room temperature for 10 min. Then, the flask was placed in 70 °C oil bath for 24 h under nitrogen flow. After the reaction mixture was cooled to room temperature, resulting polymer was precipitated into hexane/diethyl ether (1/1). The obtained polymer was washed again, and dried overnight in vacuo. The resulting polymer was obtained as white powder (0.692 g, 39%).

2.4 Characterization

The monomers were characterized by NMR and HPLC. The ratio of endo- and exo-isomers of MNBC, NBCA and tBNBC were determined from peak intensities of each isomer by 1H NMR in chloroform-d at 25 °C. The ratio of MNBC and NBCA were also determined by HPLC ; JASCO C-Net /ADC system ; UV-detector ; JASCO UV-2075 (224 nm), column ; SC PEGASIL ODS-2352 (4.6 mm i.d., 18 cm), eluent ; deionized water/methanol = 4/6 (1 mL/min), pH was adjusted to 3 by phosphate buffer, retention time ; exo-isomer 7.4 min, endo-isomer 8.6 min. The ratio determined by HPLC was calibrated by NMR.

The polymer was characterized by NMR and GPC. NMR spectra were recorded on a JEOL ECX 400 spectrometer operating at 400 MHz for 1H. The molecular weight and its distribution of synthesized polymers were estimated by gel permeation chromatography using a column packed with styrene-divinylbenzene gel beads. Chloroform was used as an eluent and the molecular weight was calibrated using polystyrene standards (Shodex).

2.5 Model reaction for deprotection

The 0.1 mL of endo- or exo-tBNBC, 50 µL of sulfuric acid, and methanol-d₄ were charged into 5 mmφ-NMR tube with the meniscus adjusted to 4 cm. The NMR tube was placed in a 400 MHz 1H NMR probe at 25 °C. After the monitoring for 30 min, the probe was heated at 50 °C. The signals of free induction decay were recorded about every 4 min for about 1.5 hour [20]. The peak intensity of t-butyl resonance at 1.4 ppm normalized to integration of vinylene proton at 5.90-6.20 ppm was recorded.

3. Results and discussion

3.1 Monomer synthesis

3.1.1 Synthesis of MNBC

MNBC was synthesized via a conventional Diels-Alder cycloaddition as a starting material. The ratio of endo/exo was determined as 80/20 by comparing the integral ratios of protons of olefin at 6.19 to 5.93 ppm in 1H NMR spectrum (Figure 1). In HPLC, the ratio of peak intensity for endo/exo isomer was estimated as 71/29. Although the UV absorption coefficients at 224 nm is different between endo- and exo-isomers, it is possible that HPLC data are converted into the ratio of endo/exo. Therefore, peak ratio of MNBC and NBCA determined by HPLC were calibrated by NMR estimation.

3.1.2 Synthesis of NBCA

In order to obtain exo-tBNBC in a high yield, we synthesized NBCA as precursor via hydrolysis of MNBC. MNBC formed endo/exo isomerized equilibrium under a basic condition due to continuous inversion of the carbanion that is generated by elimination of the active proton at α-position of carbonyl group. By utilizing the inversion, the mixture comprising mainly endo-isomer of MNBC can be isomerized to endo/exo mixture and the ratio is ruled by thermodynamic equilibrium. Scheme 1 represents the reaction path...
for exo-selective hydrolysis.

Figure 2 shows time dependence of the content of exo-isomer for MNBC in the presence of a base. The exo-content was determined by HPLC calibrated with $^1$H NMR analyses. In the case of sodium methoxide, the exo-content increased to about 35% from 20% at 25 °C. At this temperature, when THF or methanol was used as a solvent, both exo-content at equilibrium and isomerized rate were almost same (not shown). At higher temperature, the isomerization seemed to be fast and accelerated, but maximum exo-content remained at 55% even at 67 °C (not shown). It is noteworthy that strong base (sodium t-butoxide) drastically shortened the time needed to reach thermodynamic equilibrium, which increased exo-content to 55% even at 25 °C. When the isomerization was started with exo-rich mixture, the ratio of exo-isomer also reached at the same content (about 55%). These results suggest that strong base (sodium t-butoxide) accelerates the isomerization reaction, but the endo/exo ratio depends only on thermodynamical stability of isomers. Moreover, endo- and exo-isomer of MNBC have almost the same thermodynamical stability.

Hydrolysis of exo-isomer is expected to be faster than that of endo-isomer due to steric hindrance of norbornene ring. Therefore, exo-rich NBCA can be synthesized by exo-selective hydrolysis of MNBC under a basic condition. Table 1 shows results of the hydrolysis. The ratio of exo-isomer increased to about 63% at 60 °C with sodium methoxide. We performed hydrolysis at 25 °C, because it is expected that the slower hydrolysis, the higher exo-selectivity, however, ratio of exo-isomer was very low (29%). The decline of ratio was caused by two reasons. One is a decline of isomerization rate. Since kinetically exo-selective hydrolysis consumes exo-isomer of ester faster, the hydrolysis should be accompanied by the fast thermodynamic isomerization from endo- to exo-isomer to maintain exo-rich equilibrium in order to obtain exo-rich mixture of carboxylic acid in a high yield. According to Figure 2, isomerization at 25 °C can not reach thermodynamic equilibrium for 2 h due to slower rate of isomerization. Therefore, the ratio of endo-MNBC becomes higher and higher through the reaction. In addition, the other reason is that the hydrolysis is so slow at this condition that all of MNBC can not be consumed even after 24 h. As a result, when excess water was provided to quench the reaction, the remaining endo-rich MNBC was converted to NBCA, which gives the low ratio of exo-MNBC. In contrast, the ratio of exo-NBCA could be increased to about 82% at 25 °C with sodium t-butoxide (Figure 3). The strong base makes isomerization fast, therefore, exo-MNBC

![Scheme 1 Exo-selective hydrolysis.](image)

![Figure 2 Isomerization of MNBC at 25 °C in basic condition](image)

![Figure 3 $^1$H NMR spectrum of NBCA recorded at 400 MHz at 25 °C in CDCl$_3$. (olefin proton -CH=CH-)](image)
can be provided sufficiently and hydrolysis can proceed stereo-selectively. These results suggest that better hydrolysis condition to obtain exo-NBCA in a high yield is strong base and low temperature.

3.1.3 Synthesis of tBNBC

**Endo-rich tBNBC** was synthesized via a classical Diels-Alder reaction. The *endo/exo* ratio of tBNBC was determined as 80/20 by $^1$H NMR.

We synthesized *exo-rich* tBNBC from *exo-rich* NBCA. The *endo/exo* ratio of crude tBNBC was determined as 15/85 by $^1$H NMR. The ratio was almost same as a starting material. (*Exo-rich* MNBC was also synthesized from this NBCA via Fischer-esterification.) Furthermore, tBNBC was purified by column chromatography and *exo-*tBNBC was isolated (Figure 4). (*Exo-isomer eluted faster than endo-isomer in the examined condition.)

![Figure 4  $^1$H NMR spectrum of *exo-*tBNBC recorded at 400 MHz at 25 °C in CDCl$_3$.](image)

**Table 2 Characteristic of polymers.**

<table>
<thead>
<tr>
<th>Run</th>
<th>tBNBC$^*$</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_M/M_n$</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>1300</td>
<td>1500</td>
<td>1.2</td>
<td>39.5</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>1300</td>
<td>1700</td>
<td>1.3</td>
<td>44.4</td>
</tr>
</tbody>
</table>

* Monomer ratio

![Scheme 2 Polymerization of tBNBC/MAH random copolymer](image)

![Figure 5 $^1$H NMR spectrum of *exo-*tBNBC/MAH random copolymer recorded at 400 MHz at 25 °C in CDCl$_3$.](image)

Molecular weight and yield of copolymer of Run 1 was slightly lower than that of Run 2. It seems that the polymerization behavior is different between *exo*-isomer and *endo*-isomer.

3.3 Deprotection behavior

Acidic deprotection behavior of *t*-butyl group in tBNBC was investigated as a model reaction of exposure using $^1$H NMR. The ratio of deprotection were calculated from the integral ratio of the *t*-butyl proton (*endo-isomer ; $\delta$=1.40 ppm, *exo*-isomer ; $\delta$=1.45 ppm) compared with vinylene proton (*endo-isomer ; $\delta$=5.90-6.19 ppm, *exo*-isomer ; $\delta$=6.11 ppm). At first, the mixture was measured at 25 °C (t=0 min) and this ratio of deprotection was normalized as 1. After the sample was heated at 50 °C, the data acquisitions were carried out about every 4 min.

Figure 6 shows time dependence of the ratio of deprotection. Acidic deprotection of *exo-*tBNBC is faster than that of *endo-*tBNBC, since steric hindrance of norbornene ring affect reactivity of...
tBNBC. This results suggest that endo/exo ratio affect lithographic performance, for example, dissolution rate and sensitivity. Therefore, control of the ratio is important to enhance the lithographic performance.

4. Conclusion

Exo-NBCA and its esters were synthesized via endo/exo isomerization and selective hydrolysis in a basic condition. It was found that isomerization behavior of MNBC significantly depends on strength of base. In order to increase the ratio of exo-isomer, endo/exo isomerization must be fast. The isomerization can be accelerated using stronger base (sodium tert-butoxide). Although the higher temperature also increased the rate of isomerization, it afforded poor exo-selectivity for hydrolysis. The optimized condition for exo-selective synthesis is considered to be fast isomerization and slow hydrolysis, which allows us to prepare highly exo-rich NBCA up to 82% of the exo ratio. Finally, the obtained exo-rich NBCA can be converted to the desired esters without changing the endo/exo ratio slightly.

The rate of polymerization of exo-tBNBC is slower than endo-tBNBC. Furthermore, the acidic deprotection rate of exo-tBNBC is faster than that of endo-tBNBC. These results suggest that endo/exo ratio of norbornene derivatives greatly affect the reactivity and lithographic performance. Therefore, the stereo-selective synthesis of norbornene derivatives is significant from the practical view point.

References