Synthesis of New Ladder Cyclic Materials (Noria Derivatives) with Photo-Reactive Groups and Their Application to EUV-Resists, EB-Resists and Photo-Curable Materials

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ABSTRACT

Noria derivatives containing protective groups such as *t*-BOC group, *t*-butyl ester group (*t*-BAc), adamantyl group (Ad) were synthesized and evaluated as alkaline developable positive-type EB- and EUV-resists. As the result, it was cleared that Noria-*t*-BOC and Noria-*t*-BAc showed 50 nm and 70 nm resolutions as EB-resists, respectively. Noria-Ad also showed clear line and space pattern with 22-24 nm resolution as alkaline developable positive-type EUV-resists using SEFT exposure tool (X-slit) on Selete (Tsukuba, Japan).

Noria derivatives containing certain polymerizable groups, such as methacryloyl (MA), 2-hydroxy-3-methacryloylpropanoxy (HMPA), vinyl ether (VE), and oxetanyl (OX) groups were synthesized and evaluated as UV-curable materials. As the result, it was found that these photo-cured Noria derivatives have excellent thermal stability.

Keywords: Noria. Noria derivatives. Protective groups. Positive-type EB- and EUV-resists. Photo-polymerizable groups. Photo-curable resins. Negative-type EB- and EUV resists.

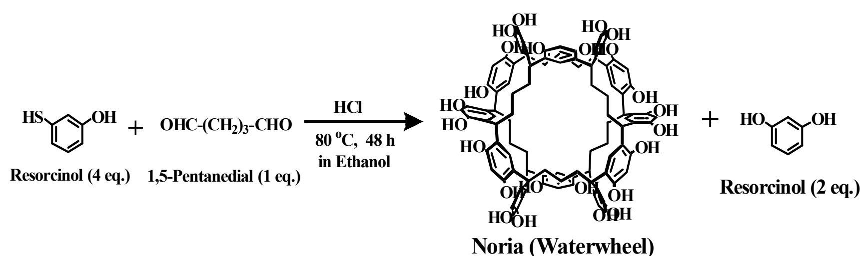
1. INTRODUCTION

Molecular resists have been of great interest as next generation's materials to achieve high resolution beyond polymeric resists. As the first molecular resist[1], calixarene (CA) derivatives have been proposed and achieved about 10 nm resolution as negative-type EB-resist.

On the other hand, the authors studied the synthesis of CA derivatives containing acryloyl, methacryloyl, vinyl ether, propargyl ether, oxirane, oxetane, or spiro ortho ester groups as high performance photo-curable materials[2]. Then, it was found that these CA derivative had high *Tg*s and excellent thermal stabilities, and could be used as high performance photo-curable materials. We also examined the synthesis and evaluation of CA derivatives containing *t*-BOC, *t*-butyl ester, cyclohexenyl ether, or trimethylsilyl ether groups as a positive-type EB-resist. However, calix[4]resorcinearene (CRA) derivative with *t*-butyl ester, which had the highest reactivity among

AC derivatives, could not achieve 100 nm resolution as positive-type EB-resist, because falling down of the resist pattern has occurred on the development process and following processes. It seems that the mechanical property of CRA derivative is not enough as a positive-type molecular resist to achieve nm level resolution. This result means that the mechanical property is an important factor for molecular resist.

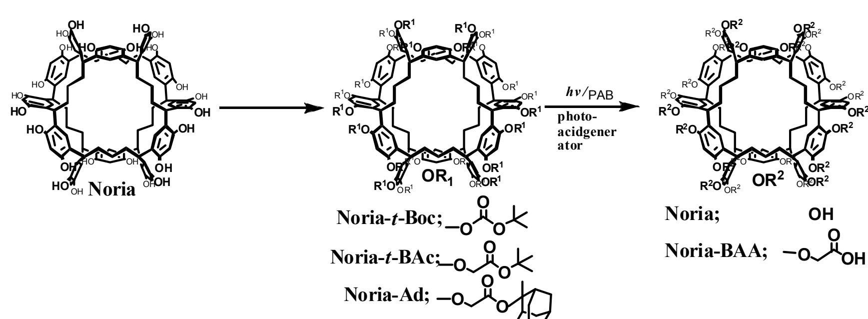
Therefore, we examined the synthesis of new molecular material with good mechanical property to achieve high resolution. Then, it was found that a ladder cyclic compound was obtained in satisfactory high yield by the polycondensation reaction of resorcinol with 1,5-pentanedial $[(CH_2)_3(CHO)_2]$. The structure of this molecule was confirmed by X-ray crystallography. This molecule has 24 hydroxyl groups, 6 hydrophilic cavities in the side, and a large hydrophobic central hole[3]. Therefore, we named this compound as “Noria” in Latin (Waterwheel in English) (Scheme 1). Then, we examined the synthesis and patterning-properties of the Noria derivatives containing suitable photo-induced deprotective groups for positive-type EB- or extreme ultraviolet (EUV)-resist systems. We also examined the synthesis and photo-crosslinking reaction of Noria derivatives containing suitable photo-curable groups as UV-curable resins.



Scheme 1. Synthesis of Noria (Water-wheel)

2. SYNTHESIS AND EVALUATION OF NORIA DERIVATIVES WITH SUITABLE PHOTO=INDUCED DEPROTECTING GROUPS AS EB- OR -EUV RESISTS

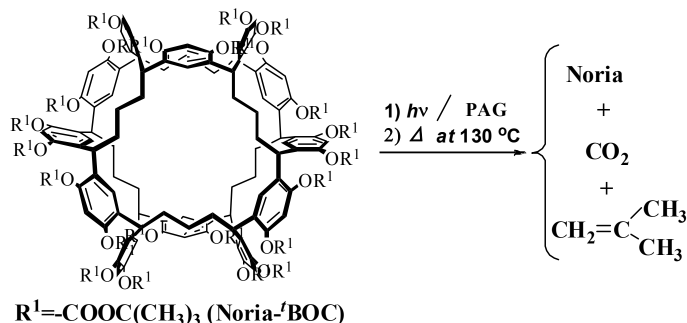
Noria-*t*-BOC and Noria-*t*-BAc with 100 mol-% of protecting groups were synthesized by the reaction of Noria with di-*t*-butyl dicarbonate (DiBOC) and *t*-butyl α-bromoacetate, respectively (Scheme 2). These Noria derivatives containing such as *t*-BOC and *t*-BAc groups were soluble in common organic solvents; however, these compounds were insoluble in water, methanol, and tetramethylammonium hydride (TMAH) aq. solution. These Noria derivatives have good film forming property, although Noria did not have good thin film forming property. Furthermore, it was found that Noria-*t*-BOC[4] with 100 % of *t*-BOC groups and Noria-*t*-BAc[5] with partly (about 50 mol %) *t*-butyl ester groups have good film forming property and soluble in TMAH aq. solution. Noria-*t*-BOC and Noria-*t*-BAc also showed 50 nm and 80 nm resolutions, respectively, as positive-type EB-resists.



Scheme 2. Noria derivatives as positive-type EB- and EUV-resists

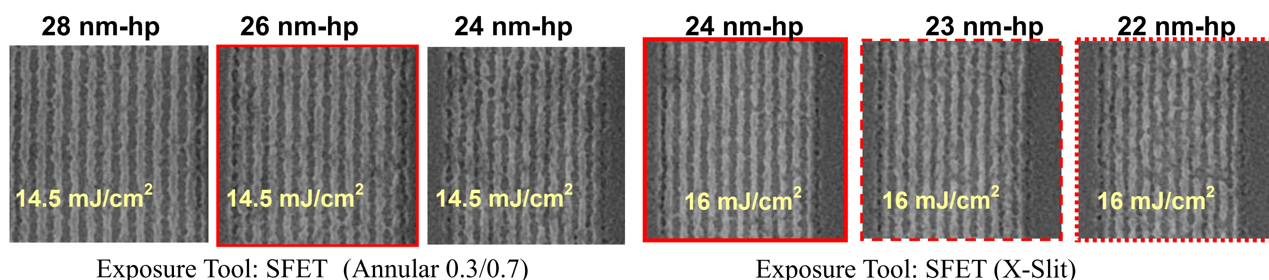
However, *t*-BOC and *t*-BAc groups in Noria molecules are not suitable protecting groups for EUV-resist, because, as shown in Scheme 3, low molecular weight gas *iso*-butane was produced after UV or EUV irradiation and following process.

From this background, we examined the synthesis and evaluation of new Noria derivative Noria-Ad containing certain adamantyl (Ad) groups[6].



Scheme 3. Photo-induced deprotection of Noria-*t*-BOC

As the results, Noria-Ad$_{23}$ containing 23 mol-% of Ad groups showed clear line and space pattern with 26 and 23 nm resolutions as positive-type EUV-resists, respectively, when the evaluation was performed on Selete (Tsukuba, Japan) using SEFT exposure tool annular and X-slit, respectively.

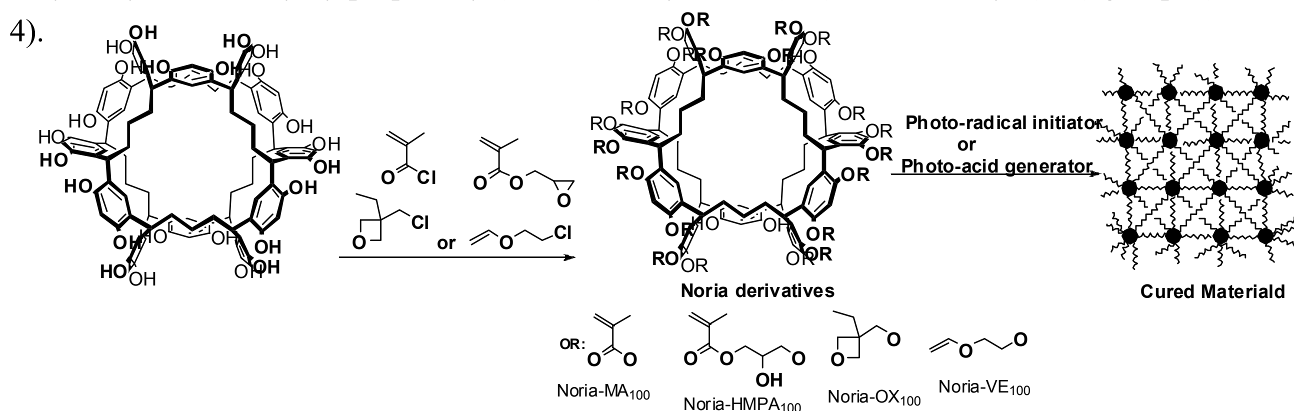


Exposure Tool: SFET (Annular 0.3/0.7) Exposure Tool: SFET (X-Slit)

Figure 1. 26 and 23 nm line/spaces obtained using 'Noria-Ad (23)' resist after EUV exposure (13.5 nm, 5 % triphenylsulphonium nonaflate, PAB 130 °C/ 60 s, PEB 110 °C/ 60 s).

3. SYNTHESIS AND EVALUATION OF NORIA DERIVATIVES WITH SUITABL PHOTO-CURABLE GROUPS AS EB- OR -EUV RESISTS, AND UV-CURABLE MATERIALS

It is well known that CA and CRA derivatives have high *Tg*s and excellent thermal stabilities, and could be used as high performance photo-curable materials, we also examined[7] the synthesis of Noria derivatives containing various polymerizable groups, such as methacryloyl (MA), 2-hydroxy-3-methacryloylpropanoxy (HMPA), vinyl ether (VE), and oxetanyl (OX) groups (Scheme 4).



Scheme 4. Noria derivatives containing photo-curable groups

The synthesized above Noria derivatives have good solubility, good film-forming property, and excellent thermal stability. The photochemical reactions of these derivatives were also examined in the film state in the presence of appropriate photo-radical initiator or photo-induced acid generator under irradiation with a 250 W high-pressure mercury lamp. As shown in Figure 2, photo-chemical reaction of these compounds proceeded affording the corresponding cured gel materials. This result also showed that Noria-oxetane (Noria-OX) has higher photochemical reactivity than other Noria derivatives under the same irradiation conditions.

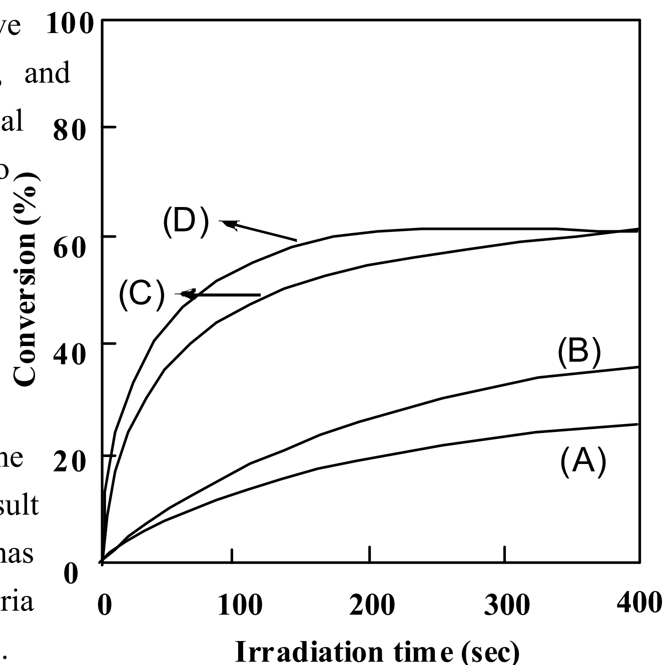


Figure 2. Photochemical reaction of Noria derivatives with certain photo-curable groups: (A) Noria-MA_{100}. (B) Noria-$HMPA_{100}$. (C) Noria-VE_{100}. (D) Noria-OX_{100}.

4. REFERENCES

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