A Novel Mechanism to Afford Photosensitivity to Unfunctionalized Polyimides:
Negative-tone Reaction Development Patterning

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A film of commercially available polyetherimide (PEI, Ultem®) containing
diazonaphthoquinone (DNQ) and N-phenylmaleimide (PMI) was irradiated by UV light
from high-pressure mercury lamp through a photomask and developed with a solution
containing tetramethylammonium hydroxide (TMAH) to give negative-tone patterns
with high sensitivity. PMI was found to retard dissolution of the exposed areas. PEI was
dissolved into the developer as poly(amic acid) resulted from reaction of the imide
groups in PEI with OH⁻. PMI is considered to react with OH⁻ in the developer to give
anionic intermediates, and at unexposed areas, the intermediates would regenerate OH⁻
by reaction with water in the developer. At exposed areas, the regeneration would be
inhibited by reaction with acid generated by photo-rearrangement of DNQ, and this
would be the reason for the preferential dissolution at the unexposed areas.

Keywords: negative-tone reaction development patterning, polyetherimide,
diazonaphthoquinone, N-phenylmaleimide

1. Introduction

Photosensitive polymers have been widely used in various industries, such as photoresists for
patterning of integrated circuits (ICs), buffer coat layers for IC chips and interlayer dielectric films
in electronics industry, manufacturing of printing plates, color filters, optical waveguides, and so on
[1,2]. Different properties are desired for such the applications of photosensitive polymers, and the
most appropriate molecular designs should be adopted for each application. In electronics
packaging (Jisso) like buffer coat layers and interlayer dielectrics, though requirement for
resolution is not strict, high thermal, mechanical and insulating properties are required for
photosensitive polymers due to permanent utilization of patterns prepared from the polymers
without removing. Therefore, photosensitive polymers based on engineering plastics, known as
high-performance polymers, have been studied, and especially, photosensitive polyimides have
received extensive attentions due to excellent properties of polyimide [3]. Conventional
strategies in order to give photosensitivity to polyimides have been utilization of polyimide
precursor, poly(amic acid), and/or functionalization of polyimide structure [4-8]. However, these molecular designs lead to
complicated synthetic routes and the resulting high-cost preparation of the polymers. In addition,
high temperature post-curing is needed for imide ring formation when poly(amic acid)s are used as the
polymer component.

We have developed a novel pattern-forming mechanism, reaction development patterning
(RDP), for unfunctionalized polyimides and other engineering plastics having -C(=O)-X- linkages in
the main chain [9-15]. RDP realizes positive-tone
pattern formation from the unfunctionalized polymers only by photo-irradiation onto the polymer films containing diazonaphthoquinone (DNQ) and the following development with amine-containing solution. RDP uses main chain scission by nucleophilic acyl substitution between the -C(=O)-X- linkages and amines in the developer as a key reaction for pattern formation. Though RDP has an advantage of no need for functionalization of polymer, there are still several drawbacks such as necessity of large amount of DNQ (~30 wt% for polymer), low sensitivity (~1000 mJ/cm² at 10 μm thickness) and use of organic amines as a component of developer.

Recently, we found that photo-irradiation to polyetherimide (PEI) films containing N-phenylmaleimide in addition to DNQ and the following development with a solution containing tetramethylammonium hydroxide (TMAH) enabled negative-tone pattern formation with large increase in sensitivity, reduction of the amount of DNQ, and development with the solution containing industrially-used aqueous TMAH. The pattern formation was found to be based on reaction at development process as well as RDP, and thus, we named this novel pattern forming process as negative-tone RDP (NRDP). In this paper, we report effect of addition of PMI on dissolution behavior of unexposed and exposed PEI films containing DNQ, examination of conditions for pattern formation, and model reactions of PEI and PMI with the developer. Pattern-forming mechanism of NRDP is also discussed.

2. Experimental
2.1 Materials
Polyetherimide (PEI, Ultem® (Scheme 1), Mₙ = 28,000, Mₘ/Mₙ = 1.6) was purchased from Aldrich. 1,2-Naphthoquinonediazide-5-sulfonic acid p-cresol ester (PC-5®) as DNQ (Scheme 2) was purchased from Toyo Gosei Kogyo Co., Ltd. N-phenylmaleimide (PMI, Scheme 2) was purchased from Wako Pure Chemical Industries, Ltd. Other reagents and solvents were commercially available.

![Scheme 1 Chemical structure of PEI](image)

![Scheme 2 Chemical structures of DNQ and PMI](image)

2.2 Measurement
Molecular weight was determined using a GPC (TOSOH TSK-gel GMHHR-M column, eluting rate 1.0 mL/min) equipped with a UV detector (TOSOH, UV-8020) at room temperature using polystyrene standards and DMF containing LiBr (30 mmol/L) and phosphoric acid (60 mmol/L) as a mobile phase. ¹H-NMR spectra were recorded on a JEOL JNM-270 spectrometer (270 MHz) at room temperature or 60°C using DMSO-d₆ as a solvent and tetramethylsilane as an internal standard. Film thickness was measured with a contact-type thickness analyzer (Nikon, DIGIMICRO MFC-101). Photo-irradiation was conducted by a UV exposure apparatus equipped with ultra high-pressure mercury lamp (ORC, JP-2000-EXC), and exposure dose was measured in the wavelength of 320-390nm (ORC, UV-331AP2). Scanning electron micrograph (SEM) was taken with a HITACHI S-2600N instrument.

2.3 Pattern formation
15–30 wt% of PEI was dissolved in N-methylpyrrolidone (NMP). The DNQ compound PC-5® as a photosensitive agent (15–30 wt% for PEI) and PMI (1–20 wt%) was dissolved in the NMP solutions. The resulting photosensitive PEI solutions were degassed and spin-coated onto a shiny side of copper foil, and the photosensitive PEI films with 10–15 μm in thickness were obtained after prebaking at 90°C for 10 min in a far-infrared oven. The films were irradiated with an ultra high-pressure mercury lamp without any filter at both i and g lines through a negative photomask in a contact technique. The exposed films were developed in a mixture of TMAH / H₂O / NMP / alcohol at room temperature or 50°C under ultrasonication or by dipping, and rinsed with pure water.

2.4 Model reactions
2.4.1 Reaction of PEI
To a 100 mL three-necked flask were added 1.00 g of PEI and 20.0 g of developer (TMAH / H₂O /
NMP / CH₂OH = 2 / 5 / 5 / 18 (by weight)) and the mixture was stirred at 50°C for 2 h. The resultant solution was poured into a large excess amount of diethyl ether and the obtained precipitate was dried in vacuo at 80°C. The solid was crashed, washed with pure water, and dried again in vacuo at 80°C to give 1.32 g of a pale yellow solid. The solid was then treated with 2M aqueous HCl solution for acidification.

2.4.2 Reaction of PMI
To a 100 mL three-necked flask were added 1.00 g of PMI and 20.0 g of a mixture of TMAH / H₂O / acetone / CH₂OH = 2 / 5 / 5 / 18 (by weight) and the mixture was stirred at 50°C for 2 h. The volatile components in the resultant solution were evaporated and the residue was dried in vacuo at 80°C to give 1.66 g of an orange sticky solid.

3. Results and Discussion
3.1 Dissolution behavior
To clarify effect of PMI on dissolution behavior of the photosensitive PEI films based on NRDP, change in normalized film thickness during development with TMAH / H₂O / NMP / CH₂OH mixture was measured with or without irradiation in the presence or absence of PMI (Figure 1). Little difference in dissolution behavior between the exposed and unexposed areas was observed when no PMI was added to the system. On the other hand, the addition of 10-20 wt% of PMI was found to slow dissolution of the exposed area to a great extent. Relationship between exposure dose and dissolution behavior was also examined (Figure 2), and exposure dose of 100 mJ/cm² proved sufficient for differentiation between the exposed and unexposed areas. These results suggest that negative-tone pattern based on NRDP can be formed with smaller exposure dose than that in conventional RDP (more than 1000 mJ/cm² at ~10 μm film thickness) [9].

3.2 Lithographic evaluation
Actual line and space (L/S) pattern formation based on NRDP was then attempted. Photosensitive PEI varnish was easily prepared just by dissolving PEI (Scheme 1), a photosensitive DNQ compound PC-5⁰ (Scheme 2) and PMI (Scheme 2) into NMP. The varnish was spin-coated onto copper foil and prebaked, and the resulting film was irradiated by UV light through a photomask and developed with TMAH / H₂O / NMP / CH₂OH mixture. A SEM photograph of the patterns formed from the film with 30 wt% of PC-5⁰ and 20 wt% of PMI is shown in Figure 3a. Clear negative-tone L/S patterns were successfully prepared.

Reduction of the additives from NRDP system was then examined. Negative-tone patterns were formed from the PEI film with 15wt% of PC-5⁰ and 10 wt% of PMI (Figure 3b), but further decrease in the amount of PC-5⁰ resulted in unsuccessful pattern formation. On the other hand, application of NRDP to the film with 15wt% of PC-5⁰ and 1 wt% of PMI afforded negative-tone patterns (Figure 3c), while 10 μm pattern could not be obtained. Then, use of ethanol instead of methanol as a component of developer was carried out. The result of pattern formation was shown in Figure 3d and negative-tone pattern was successfully prepared with shorter development time despite no ultrasonic treatment during
development. Ethanol has more carbons than methanol and would have higher affinity for the organic polymer films than methanol [14]. This would result in successful pattern formation with shorter time and milder condition in the ethanol-containing developer. By further optimization of development condition, we achieved pattern formation using developer without NMP, that is, a mixture of aqueous TMAH / alcohols (poly(ethylene glycol) (PEG400, $M = 400$) + ethanol) (Figure 4). Sensitivity curve for this system was shown in Figure 5, and the sensitivity ($E_{50}$), the exposure dose where 50% of the film remained, was found to be 31 mJ/cm$^2$ for the film with 9.2 μm initial thickness. This value is largely improved from those of conventional positive-tone RDP (∼1000 mJ/cm$^2$) [9].

![Figure 3 SEM images of NRDP-based photosensitive PEIs (~10 μm L/S patterns).](image)

PC-5® (wt% for PEI): a) 30, b–d) 15
PMI (wt% for PEI): a) 20, b) 1, c,d) 1
Initial thickness (μm): a) 10.0, b,c) 11.7, d) 12.3
Exposure dose: 100 mJ/cm$^2$
Developer (TMAH / H$₂$O / NMP / CH$_₃$OH (EtOH in d) (by weight)): a,c,d) 2 / 8 / 5 / 18, b) 2 / 5 / 5 / 18
Development condition: a–c) 50 °C / ultrasonication, d) 50°C / dipping
Development time: a) 9 min 27 sec, b) 6 min 50 sec, c) 10 min 30 sec, d) 8 min
Residual thickness at exposed areas after development (%): a) 95, b) 93, c) 58, d) 60

![Figure 4 SEM image of NRDP-based photosensitive PEI with 15 wt% of PC-5® and 1 wt% of PMI (~10 μm L/S patterns).](image)

Initial thickness: 11.1 μm, Exposure dose: 100 mJ/cm$^2$, Development: TMAH / H$₂$O / PEG400 / EtOH = 2 / 8 / 5 / 12 (by weight), 50°C / dipping for 8 min 20 sec. Residual thickness at exposed areas after development: 88%

![Figure 5 Sensitivity curve of NRDP-based photosensitive PEI with 15 wt% of PC-5® and 1 wt% of PMI.](image)

Initial thickness: 9.2 μm, Development: TMAH / H$₂$O / PEG400 / EtOH = 2 / 8 / 5 / 12 (by weight), 50°C / dipping

3.3 Pattern-forming mechanism
In order to elucidate pattern-forming mechanism, a PEI film containing 30 wt% of PC-5® and 20 wt% of PMI was irradiated through a photomask
and developed with TMAH / H₂O / NMP / CH₃OH solution (2 / 5 / 5 / 18 by weight), and molecular weight of the component dissolved into the developer was measured (Figure 6). No decrease in molecular weight after development was observed, and this indicates that pattern-forming mechanism in NRDP would be different from that in conventional RDP, where molecular weight of polymers was decreased as a result of main chain scission during development process [10,13,15]. Reaction of PEI with solution of TMAH / H₂O / NMP / CH₃OH in a flask was also carried out. Although the mixture was heterogeneous at first, 30-min stirring at 50 °C made the system homogenous. After the reaction for 2 h at 50°C, the polymer was isolated and characterized by GPC and ¹H-NMR spectrum. In GPC measurement, just like the experiment using the film, little decrease in molecular weight was observed. ¹H-NMR spectrum of the isolated polymer after HCl treatment showed the peaks assigned to amide and carboxylic acid protons. These results suggest that PEI was dissolved into the developer as a form of poly(amic acid), generated by nucleophilic attack of OH⁻ from TMAH to imide groups in PEI (Scheme 3).

![Figure 6 GPC trances of PEI (a) and the component dissolved into the developer (b). 30 wt% of PC-5® and 20 wt% of PMI for PEI were added and developed with TMAH / H₂O / NMP / CH₃OH = 2 / 5 / 5 / 18 (by weight) at 50°C for 4 min under ultrasonication.](image)

Scheme 3 Ring-opening reaction of imide group in PEI with hydroxyl anion

Model reaction of PMI with TMAH-containing solution in a flask was also conducted. ¹H-NMR spectrum of the products from the reaction of PMI with TMAH / H₂O / acetone / CH₃OH is shown in Figure 7. The peaks assignable to protons of asymmetric double bonds, probably those of amic acids from ring-opening reaction of PMI, were observed (Hₐ in Figure 7 and Scheme 4). In addition, the peaks assignable to methine protons of Michael addition products between PMI and OH⁻ were also observed (Hₐ+Hᵦ in Figure 7 and Scheme 4). In addition, there is no identifiable peak for the double bond of PMI (ca. 6.8 ppm). Therefore, it can be considered that PMI is reacted with hydroxyl anion in developer as shown in Scheme 4 during development process in NRDP. Unfortunately, attempts to separate the products from the model reaction were unsuccessful.

![Figure 7 ¹H-NMR spectrum of the products from the model reaction of PMI with TMAH / H₂O / acetone / CH₃OH = 2 / 5 / 5 / 18 (by weight) at 50°C for 2 h.](image)

![Scheme 4 Reaction products deduced from the model reaction of PMI with hydroxyl anion](image)

From these results, we propose the pattern-forming mechanism in NRDP as Scheme 5. In unexposed areas, an anionic intermediate in Michael addition between PMI and hydroxyl anion abstract a proton from H₂O (or alcohol) to give a product and regenerate hydroxyl anion. On the other hand, the intermediates in exposed areas can
abstract a proton from indenecarboxylic acid generated by photo-rearrangement of DNQ, and the reaction with the acid does not regenerate hydroxyl anions. This difference in degree of the regeneration of hydroxyl anions would realize preferential formation of poly(amic acid) at the unexposed areas, and the resulting poly(amic acid) was dissolved into the alkaline developer to give negative-tone patterns. Further examinations for elucidation of detailed pattern forming mechanism are in progress.

4. Conclusion
Negative-tone pattern formation based on NRDP from films of commercially available PEI containing DNQ and PMI was accomplished with 10 µm resolution. Addition of PMI was found to retard dissolution of photo-irradiated areas. Much higher sensitivity than conventional positive-tone RDP and development with TMAH-containing solution were achieved by NRDP. The patterns in NRDP were prepared by preferential formation of poly(amic acid) at unexposed areas, which would be realized by difference in degree of regeneration of hydroxyl anions between exposed and unexposed areas.

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References