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Novel Partial Esterification Reaction in Poly(amic acid) and Its Application for Positive-Tone Photosensitive Polyimide Precursor

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We found novel quantitative esterification in poly(amic acid) (PAA) by reacting with *N*,*N*-dimethylformamide dialkyl acetals (DFAs). Different alkyl ester was obtained by changing the alkyl group in DFAs. The esterification ratio was determined by amount of DFAs. The reaction proceeds under mild condition without any catalysis. It has not been reported such a kind of quantitative partial esterification before. The partial esterification allowed us to control the solubility of PAA to alkaline solutions. The strict solubility rate control to alkaline solution of PAA was quite important for positive tone photosensitive polyimide (posi PSPI). The partial esterification of PAA gave us a way to strict dissolution control. By using it, we could obtain posi PSPI just mixing with diazonaphthoquinone compound.

KEY WORDS: Dimethylformamide-Dialkyl Acetals / Esterified Poly(amic acid) / Partial Esterification / Photosensitive Polyimide / Diazonaphthoquinone Compound /

Polyimides are widely used for semiconductor applications such as inter-layer dielectrics, protection layers (buffer coatings), and re-distribution layers for wafer level package.[1] For these applications, polyimide is required to make a fine pattern by photo-lithographic technique. In early times polyimide was patterned by chemical etching through photo-resist pattern. In order to simplify the polyimide pattering process, several groups developed the addition of photosensitivity to polyimide precursor namely PSPI.[2,3] Most of the PSPIs were negative tone type, which made exposed area insoluble by photo-reaction. In order to progress semiconductor, polyimide is required fine pattern such as 5 μm or less. To realize such a fine pattern, posi PSPI was desired. First posi PSPI was reported by Loprest *et al.*[4] The posi PSPI was composed of PAA and naphthoquinone diazide compound which is popular for novolak photo resist system. But it was not realized due to high solubility of PAA to alkaline solution. In order to obtain suitable solubility of PAA, Simmons reported partial protection by reaction with 1,4-dihydropyrane.[5] There were few drawbacks for this reaction. One was that the reaction did not proceed quantitatively. Another was that reaction condition needs acidic catalyst. Excess amount of 1,4-dihydropyrane with acidic catalyst and long reaction time were required. Posi PSPI from special PAA structure was reported by Sakayori *et al.*[6]

On the other hand, Rubner reported positive tone photosensitive polybenzoxazole precursor.[7] Polybenzoxazole precursor was poly(hydroxyamide) which has phenolic groups in the polymer chain. The acidity of phenol group was much weaker than that of aromatic carboxylic acid. The positive tone photosensitive polybenzoxazole precursor was applied for buffer coating of semiconductor devices.[8] Recently Watanabe *et al.* reported the negative tone photosensitive polybenzoxazole precursor by using acid catalysis cross linking.[9]

From the point of polyimide base development, Kubota reported a different posi PSPI by introduction of o-nitirobenzyl group to carboxylic acid in PAA.[10] Omote reported chemical amplification system by mixing with t-butyl protected PAA and photo-acid-generators.[11] Okabe invented the posiPSPI by mixing with phenolic group containing poly(amic ester) and dinaphthoquinone diazide to reduce the dissolution of polyimide precursor.[12] Those posi PSPIs, however, were difficult to synthesize. Therefore simple PAA base posi PSPI was desired. Tamura *et al.* developed an image-reversed technique by using negative ionic bonded PSPI.[13] The technique utilized the glass transition temperature (T_g) difference between exposed area and unexposed area. However this technique required very strict control of post exposure baking temperature.

Oyama *et al.* reported to obtain various types of posi PSPI by new reaction method.[14] This patterning process required to use strong base and organic solvent. Those PSPIs progress was summarized by Fukukawa and Ueda.[15]

In order to obtain posi PSPI which could be patterned in the wide process window, it was important to control the dissolution rate of PAA to the alkaline solution. In this article, we reported finding of novel partial quantitative esterification of PAA and the dissolution rate control to the alkaline solution. In addition, we prepared the posi PSPI by using the quantitative esterified PAA. This method was easy to obtain various types of posi PSPI.

EXPERIMENTAL

Materials

4,4′-Diaminodiphenylether(oxy-dianiline, ODA) was obtained from Wakayama-Seika. 3,3′,4,4′-Diphenylether tetracarboxylic acid dianhydride (ODPA) was obtained from

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Manac. 3-Amino phenol (AMP) was purchased from Tokyo-Kasei. DMF dialkyl acetals (DFAs) were purchased from Tokyo-Kasei. *N*-methyl-2-pyrolidone (NMP) and γ-butylolactone (GBL) were obtained from Mitsubishi-Chemical. Diazonaphthoquinone compound (DNQ) was purchased from Toyo Gosei. Tetramethyl ammonium hydroxide (TMAH) solution was obtained from Mitsubishi Gas Chemical. Other chemicals were purchased from Tokyo-Kasei. All the chemicals were used without any treatment.

Synthesis of *N*-Phenylphthalamic Acid (1). Phthalic anhydride (14.80 g, 100 mmol) was added to aniline (9.30 g, 100 mmol) with 50 mL of NMP and stirred vigorously at room temperature under nitrogen flow for 4 h. The solution was poured into 500 mL of water. The white precipitate was collected by filtration. The precipitate was washed by water several times. The washed precipitate was dried under vacuo at 50 °C for 72 h. The yield was 19.63 g (85%). m.p. 170–172 °C (lit. 169–172 °C, 172 °C[16,17]).

Esterification of 1 by Dimethylformamide Diethyl Acetal (DMFDEA). *N*-Phenylphthalamic acid (**1**) (2.41 g, 10 mmol) was dissolved into 10 mL of NMP. DMFDEA (1.47 g, 10 mmol) was added to the solution with 2 mL of NMP and stirred vigorously under fixed conditions. Reaction compounds ratio was determined by HPLC method. (Shimadzu LC-10, flow rate: 0.5 mL/min, Detector: SPD-10A (254 nm, Shimadzu), Column: Shim-Pack VP-ODS (150 mm × 4.6 mm) (Shimadzu), Eluent; CH_3CN, 0.1 M H_3PO_4 9:1 (in volume))

Synthesis of Partial Esterified PAA by DFAs. ODA (18.02 g, 90 mmol) was dissolved into 100 mL of NMP at room temperature under nitrogen flow. ODPA (31.01 g, 100 mmol) was added to the solution at one time with 40 mL of NMP. The solution was stirred vigorously at room temperature for 2 h. Then AMP (3.18 g, 20 mmol) was added to the solution. Then the solution was heated to 40 °C and stirred for 4 h.

Equivalent mole amount of DFAs to carboxylic acid in PAA were added to the PAA solution with 10 mL of NMP gradually. Then the solution was stirred under 50 °C for 2 h. After the reaction, the solution was poured into 2 L of water. The precipitate was collected by filtration. The precipitate was washed by water several times. The washed precipitate was dried under vacuo at 80 °C for 72 h.

Molecular weight of the polymer was measured by Model1510 GPC (Waters). (Column TSK-GEL α2500, TSK-GEL α4000 (Toso), Column temperature: 40 °C, Eluent: NMP containing 0.05 M LiCl and 0.05 M H_3PO_4. Flow rate 0.4 mL/min) Standard mono disperse polystylene (Toso) was used as molecular weight calibration.

Measurement of Esterification

Esterification ratio was determined from titration method by using 702SM Titrino (Metrohm) with 1*N*-tetra-butyl-ammonium hydroxide in methanol.

Measurement of Dissolution Rate

The esterifed PAA to be measured was dissolved into GBL at 20%. The solution was filtered by 0.45 µm pore-size poly(tetrafluoroethylene) filter (Milipore). The filtrate solution was coated on 6 inch Silicone wafer (Shin-Etsu-Chemical) by spin coating and baked at 120 °C for 3 min using by Tokyo Electron Mark-7. The coated thickness was about 2 µm after the 120 °C baking. The coated thickness was measured by STM-602 (Dainippon Screen) with material refractive index 1.64. The coated wafer was placed in dissolution rate monitoring apparatus (RDA-760, Lithotech Japan). The film thickness change in 2.38% TMAH solution was measured *in situ* by using the apparatus.

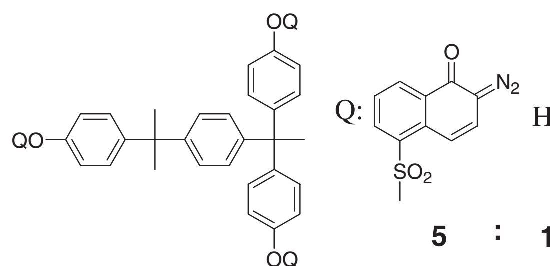

Figure 1. Chemical structure of naphthoquinone diazide compound (DNQ).

Formulation of Positive PSPI

Partial esterified PAA (10.0 g), DNQ (2.0 g) shown in Figure 1 and *N*-phenyl-3-aminopropyl trimethoxy silane (0.2 g, KBM-573, Shin-Etsu Silicones) were dissolved into 30 mL of GBL at room temperature. The solution was filtered by 0.45 µm pore-size poly(tetrafluoroethylene) filter.

Patterning of Positive PSPI

The filtered sample was coated on 6 inch Silicone wafer about 3 µm thickness after 120 °C for 3 min soft-baking by spin-coating method (Mark-7). The coated wafer was soft-baked by a hot plate at 120 °C for 3 min using by Mark-7. Coated thickness was measured by STM-602. The baked wafer was exposed through a patterned mask by i-line stepper (GCA DSW-8750, exposure wave length: 365 nm) with a 100 mJ/cm^2 to 1000 mJ/cm^2. The exposed wafer was developed with 2.38% TMAH solution by a puddle development (Mark-7) for 1 min. The obtained pattern thickness was measured by STM-602. Cross sectional photos were obtained by a Scanning Electron Microscopy (SEM, Hitachi S-4800). The developed wafer was heated to 320 °C for 1 h under nitrogen flow to convert patterned polyimide film (Koyo-thermo System INH-9).

RESULTS AND DISCUSSION

Esterification of 1

DFAs were prepared by Meerwein *et al.*[18] Those reagents were developed for use of alkylating agent which converted lower molecular carboxylic acid into ester without any catalysis.[19] Especially dimthylformamide dimethyl acetal and DMFDEA were known as esterification reagent for GC-pretreatment.[20] However, no one has not applied the reagents for esterification of carboxylic acid in polymer side branch.

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Table I. Reaction results of Model compound

	Starting Material	Ester Compound	Imide Compound
Before Reaction	100	0	0
50 °C for 2 h	2	88	10
80 °C for 15 min	5	77	18
80 °C for 2 h	2	64	34

% by HPLC area at 254nm absorption.

Ester Compound

Imide Compound

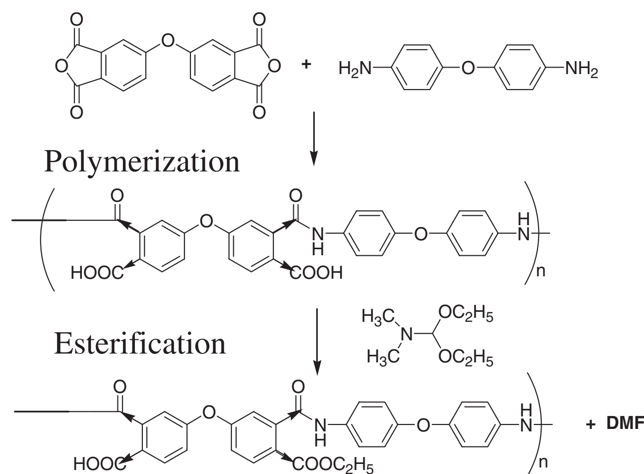

Figure 2. Reaction scheme of this work.

Esterification of **1** by use of DMFDEA was investigated as a model reaction of PAA. The results were summarized in Table I. From our experimental data, 50 °C for 2 h was suitable reaction condition. Esterification reaction proceeded smoothly. As shown in table, reaction at higher temperature gave lower selectivity of esterification from imidizaiton. The selectivity from imidization was quite important to suppress UV absorption of polyimide precursor. From the result of the low molecular model reaction, the esterification method seemed to be meaningful to apply the esterification of PAA.

Esterification of PAA

Partial esterification of PAA was known as very difficult due to its competition with imidization reaction. To obtain partial esterified PAA, Simmons reported partial protection by reaction with excess amount of 1,4-dihydropyrane and acidic catalyst at 85 °C for 6 h.[5] Yu reported the partial esterified PAA by using ethyl-iodide and potassium carbonate.[21] However those reactions were difficult to apply for practical use because of low yield and need for alkali metal and halogenated compounds. Choi obtained partial esterified PAA by using glycidyl methacrylate with a presence of triethylamine.[22] This reaction conversion was less than 50% from their results. In addition, the imidization was faster than esterification in those studies.

The esterification reaction scheme by using DMFDEA was shown in Figure 2. Esterification was done after polymerization continuously. The number average molecular weight of the PAA in this work was about 9000 by GPC. Esterification occurred in the case of PAA with good yield also. The reaction revealed high selectivity from imidization also. As shown in Figure 3, the reaction proceeded in proportion with DMFDEA amount. As much as we knew, this was first case to control the esterification ratio of PAA just by changing amount of reaction agent. The esterification reaction we found was quite unique from the point of polymer reaction and useful for convenient partial esterification of PAA.

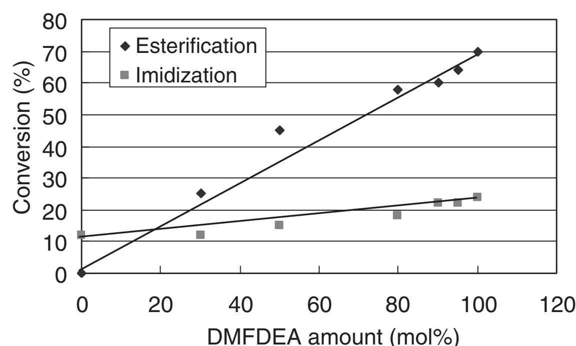

Figure 3. DMFDEA amount dependency on esterification and imidization.

Table II. Effect of alkyl groups of DFAs in PAA

Alkyl group	Esterification	Imidization	Ester/Imide ratio
Methyl	65%	30%	2.2
Ethyl	70%	25%	3.0
iso-Propyl	60%	10%	6.0
None*	0%	10%	—

Reaction condition: 50 °C 2 h. *: No reaction with DFAs.

Effect of Alkyl Groups in DFAs

In previous section, we found that DMFDEA was effective for PAA esterification. To understand the effect of alkyl groups in DFAs, esterifications using by various DFAs were investigated. Those results were summarized in Table II. In the Table, "none" means that we did not react anything with PAA. As shown in the table, acetals with larger alkyl groups gave lower conversion. On the other hand, larger alkyl containing acetals showed higher esterification selectivity from imidization. Larger alkyl group interfered with imidization due to steric hinderance. Including the imidization and esterification, methyl or ethyl acetals converted carboxylic acid of PAA almost completely.

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Table III. Effect of reaction temperature on esterification

Reaction Temperature (°C)	Esterification (%)	Imidization (%)
30	50	8
40	71	10
50	70	15
60	50	33
70	53	52

DMFDEA amount: Equivalent to carboxylic acid in PAA. Esterification and Imidization were determined by titration and FT-IR respectively.

Effect of Reaction Condition

The reaction mechanism of alkylation by DFA was thought to be generation of an oxo-stabilized carbenium ion.[19] We thought that the success of PAA esterification by DFA is following reason. Strong basicity of DFA due to existence of aliphatic amine group allowed forming ion pair with carboxylic group of PAA and DFA. The complex formation made the esterification effectively. After completion of the reaction, DFA was changed to DMF which is very weak base and good solvent of PAA. The change of basicity of DFA was thought to be important for suppressing imidization.

We investigated the reaction condition of the esterification summarized in Table III. The higher temperature condition gave higher imidization ratio. As expressed in previous section, higher imidization was not preferable due to UV absorption of PAA. It was concluded that 40–50 °C was suitable temperature for the reaction to obtain high selectivity from imidization. The esterification reaction could be done after polymerization consequently.

The quantitative partial esterification might be applied for not only PAA but poly(acrylic acid) or other carboxyl-group branch polymers. Reasons for usefulness of the esterification we found were as follows: The reaction did not need catalyst. The reaction proceeded under mild condition. In addition, by-product arising from the reaction was DMF which was good solvent for most of polymers. And the most important thing was that we could control the esterification ratio by changing the amount of DFA.

Posi PSPI from the Partial Esterified PAA

The use of the esterification of PAA made us easily control the carboxylic concentration in PAA. The nature of controlling carboxylic group made us to obtain alkaline solubility control in polyimide precursor. Strict control of solubility to alkaline solution is one of most important factor for positive photo-sensitive materials using DNQ compound.

In semiconductor industries, 2.38% THAM solution was standard alkaline developer. We tried to control the posi PSPI 2.38% TMAH developable. Basically most of PAAs showed very high dissolution rate to 2.38% TMAH solution due to those high concentrations of carboxylic acid groups. The high dissolution rate of PAA made difficult to obtain polyimide based positive photosensitive materials. The quantitative esterification we found would realize to control the dissolution rate of polyimide precursor to optimal value. In most case, optimal dissolution rate was 40 to 1000 nm/min by Kato *et al.*[23]

In order to obtain suitably dissoluble polyimide precursor, we measured the esterification ratio and dissolution rate of various partial esterified PAA. Those results were summarized in Figure 4. As shown in the Figure, we were able to control the dissolution rate of polyimide precursor by amount of DMFDEA. From the Figure, desired range of dissolution rate is achived in the range of between 90 to 95 mol % of DMFDEA to carboxylic acid group in PAA.

Posi PSPI was prepared from the quantitative esterified PAA and DNQ shown in Figure 1. To obtain suitable dissolution rate to 2.38% TMAH solution, 93 mol % of DMFDEA amount to carboxylic acid in PAA ($M_n = 9000$) was chosen from Figure 4.

The posi PSPI was coated by spin coating method on Si wafer and baking on hot plate at 120 °C for 3 min. The soft-baked PSPI was exposed by UV with high pressure Hg lamp (365 nm). The exposed PSPI was developed by 2.38% TMAH solution and heated to 320 °C for 1 h. As shown in Figure 5, we obtained good pattern shape. By using our quantitative partial esterified PAA, we were able to obtain various kinds of posi PSPI. This process was quite unique and useful for PSPI development. In addition, various types of posi PSPI for different alkaline developer was able to be designed just by changing the amount of DFA.

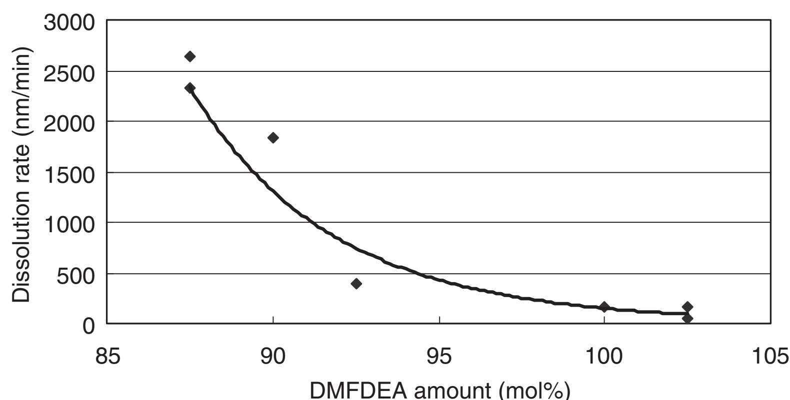

Figure 4. DMFDEA amount depecdency on dissolution rate of PAA to 2.38% TMAH solution.

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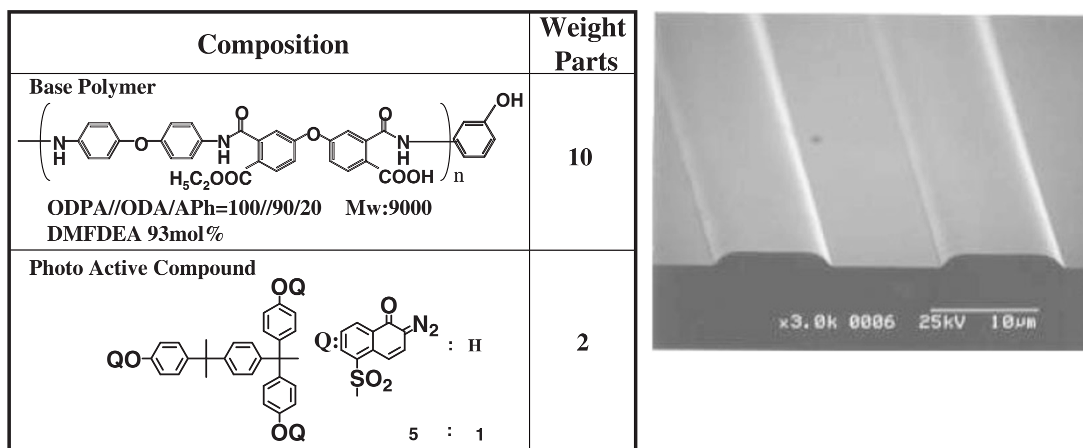

Figure 5. Composition of obtained positive photosensitive polyimide and patterning photo by scanning electron microscope (10 μm line and space).

CONCLUSIONS

We developed novel convenient partial esterification reaction for PAA by using DFAs. The reaction proceeds quantitatively under mild condition without any catalyst. Esterification ratio of PAA was determined by amount of DFA. The partial esterification allowed us to control a dissolution rate of partially esterified PAA to alkali solution precisely.

Novel posi PSPI was prepared by mixing the partially esterified PAA and DNQ successfully. The posi PSPI obtained in this work was easy to prepare. The reaction we found was quite useful for a base resin of posi PSPI.

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