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Article

High-Performance Liquid Chromatographic Method of Photoactive Compounds Based on Diazonaphthoquinone for Positive Photoresists

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An analytical method for the compositional and quantitative analysis of photoactive compounds (PACs) in positive photoresist (Posi PR) has been developed by high-performance liquid chromatography (HPLC). Under optimum HPLC conditions, various types of PACs consisting of a mixture of isomers were satisfactorily separated with no interference. This method was applied to the quantitative analysis of PACs in Posi PR. All correlation coefficients were better than or equal to 0.998. The precision and accuracy showed no significant deviation and were measured with acceptable values. The intra-batch precision and accuracy (%) of quality control samples ranged from 0.80 to 1.46% and from 101.7 to 102.8%. Consequently, the method was demonstrated to be acceptable for the analysis of PACs in Posi PR. We believe that the HPLC method developed in this work can be used for the compositional and quantitative analysis of PACs in Posi PR.

Introduction

Lithography not only plays an important role in the fabrication of micoelectronic devices such as integrated circuits (IC), large-scale integration (LSI) devices, liquid crystal devices (LCD) and light emitting diodes (LED), but is also a key technology in many electronic industries (1). Furthermore, microlithographic technology in conjunction with biomaterials has been used to print neuropeptide features for artificial networks of neuronal cells and to obtain protein patterning for the development of high-throughput analytical devices (2–4). Fabrication consisting of film deposition, lithography, etching and metallization are required to repeat processes for the production of electronic devices (1).

Photopatternable polymers, so-called photoresists, are key materials for the constructing complex of multi-layer electronic devices through fabrication processes (5–7). The circuit element density of semiconductors has rapidly increased, roughly quadrupling every three years, and such a steep improvement of technology has primarily been achieved by improving the resolutions of photoresist and light-exposure tools (8). Negative photoresists (Nega PRs) swell during development because the developer is an organic solvent. To overcome these problems, the use of positive photoresists (Posi PRs) that can use aqueous base solutions as the developer have been increasing. Generally, Posi PR consists of novolac resins with photoactive compounds (PACs) based on diazonaphthoquinone (DNQ), in which DNQ acts as the dissolution inhibitor for the aqueous base developer. It is well known that DNQ compounds are photochemically or thermally converted to indenylidene ketene via a Wolff rearragement reaction under exposed areas. The unstable ketenes react readily with water in ambient conditions and yield corresponding indenecarboxylic acid. In a resulting conversion, exposed areas exhibit solubility in alkaline solutions such as aqueous tetramethylammonium hydroxide. Therefore, positive patterns exhibit from solubility differences between exposed and unexposed areas (8, 9).

According to the isomer and esterification ratio of PACs, varying quantities of DNQ change the photoresist properties such as the photospeed of exposed areas and the retention ratio of unexposed areas. Additionally, in the case of varying kinds of PACs, the inhibition power of dissolution and the taper angle of the pattern have been changed during the lithographic process. Therefore, it is important to achieve an adequate analytical method for the compositional and quantitative analysis of PACs in manufacturing and benchmarking Posi PR. Many papers evaluated photoresist properties through photochemical reactions such as mass spectrometry (10–12), Fourier transform–infrared spectrometry (1, 13–16), ultraviolet-visible spectrometry (9, 14, 17, 18), broad-band nuclear magnetic resonance spectroscopy (19), gel-permeation chromatography (20), thermal analysis (5, 9, 13, 14, 18) and contact angle measurement (21), respectively. However, it is difficult to find corresponding literature regarding the compositional and quantitative analysis of PACs. To utilize the compositional analysis of PACs, it is necessary to establish an adequate analytical method.

In this study, we have developed an analytical method for PACs based on DNQ for Posi PR by HPLC and we describe the results of quantitative analysis of PACs in Posi PR.

Experimental

Chemicals and reagents

In this study, commercially available PACs were used, such as benzophenone (BP) PAC 3xx and BP PAC 4xx comprising benzophenone ballast, TPPA 3xx comprising trisphenol PA (α,α-Bis(4-hydroxyphenyl-4-(4-hydroxy-α, α-dimethylbenzyl)-ethylbenzene) ballast and THPE 3xx comprising 1,1,1-tris-(p-hydroxyphenylethane) ballast, as shown in Figure 1.

PACs and Posi PR were of industrial grades and PACs were purchased from Miwon Commercial Company (South Korea). All solvents used in this study were HPLC grade and purchased from J.T. Baker (Phillipsburg, NJ). Trifluoroacetic acid (TFA) was purchased from Aldrich. Distilled and deionized water was used in this study (Milli-Q water purification system, Millipore, Milford, MA).

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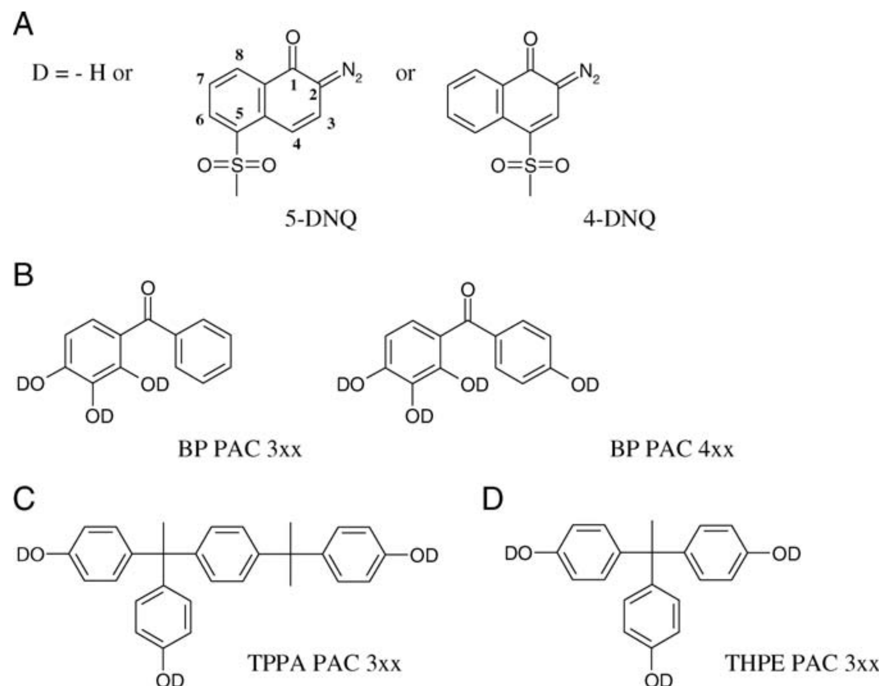

Figure 1. Chemical structures of photoactive compounds for Posi PR: 5-DNQ and 4-DNQ (A); DNQ derivatives with BP ballast (B); DNQ derivatives with TPPA ballast (C); DNQ derivatives with THPE ballast (D).

Sample preparation

PAC samples were dissolved in tetrahydrofuran (THF) at a concentration of 1 mg/mL for the determination of optimum separation conditions. To apply composition and quantitation analysis of PACs in Posi PR, sample preparation was employed by using the following procedures: a primary stock standard of BP PAC 430 was accurately prepared at the concentration of 1.0 mg/mL in THF. Further dilutions were performed at desired concentrations. The working standards were prepared at concentrations of 50, 100, 200, 300, 400 and 500 μg/mL, respectively. Posi PR samples composed of BP PAC 430 were prepared at a concentration of 5 mg/mL in THF. Working standard solution was added into Posi PR samples to prepare quality control samples to evaluate the accuracy of this analytical method. Quality control samples were prepared at concentrations of approximately 50, 100 and 150 μg/mL. All sample preparations required amber glassware, owing to the photosensitive property of PACs under various exposure sources. All standards and samples were analyzed immediately after sample preparation.

Chromatographic conditions

An Alliance 2695 HPLC system with 2996 photo diode array detector was connected to an electrospray interface, which included a 3100 mass spectrometer (Waters, Milford, MA). Instrument control and data process were performed by MassLynx software (Version 4.1, Waters). Electrospray positive mode was chosen as the ionization mode and detection was set to scan mode ranging from 50 to 2,000 m/z. Source conditions were typically as follows: capillary voltage, cone voltage, extractor and RF lens were 3.0 (kV), 30 (V), 3 (V) and 0.1 (V), respectively. Source temperature and desolvation temperature were 150 and 350°C. Desolvation gas and cone gas flow rate were 600 and 50 L/h. The analytical column was a Capcell-pak C18 (4.6 mm i.d. × 150 mmL, particle size 5 μm, Shiseido, Japan) in all experiments.

The mobile phase consisted of solvent A [0.08% TFA in acetonitrile (ACN)] and solvent B (0.1% TFA in water). The mobile phase was filtered and degassed through a 0.45-μm membrane filter. The flow rate was performed at 1.0 mL/min and the column temperature was maintained at 40°. Gradient elution was employed as follows: 40% of A at initial condition, 60% of A at 15 min, 80% of A at 35 min, 80% of A at 40 min and 40% of A at 40.01 min. The equilibration time of column initialization was 10 min until the next sample analysis. The detection of the photo diode array detector was set at 350 nm. The injection volume of PAC samples dissolved in THF was 10 μL.

Results and Discussion

In general, PACs based on DNQ are prepared by reacting 2-diazo-1-naphthol-5-sulfonylchloride (5-NAC) with the desired ballast under base catalysis conditions. NAC is prepared by reacting 2-diazo-1-naphthol-5-sulfonic acid sodium salt monohydrate (5-NAS) with thionyl chloride and chlorosulfonic acid, because NAC does not have thermally sufficient stability to be commercially available (8). The 5- and 4-isomer forms of DNQ, which exist in 4-, 5- and 6-isomers according to the position of the sulfonate group, have primarily been used in photoresist. As shown in Figure 1, ballasts consisting of PACs exist in the substitution site of DNQ ranging from 3 to 4. Hence, PACs are known to be esterified as the mixture of several kinds of isomers. Their isomers consist of mono-substituted (m),

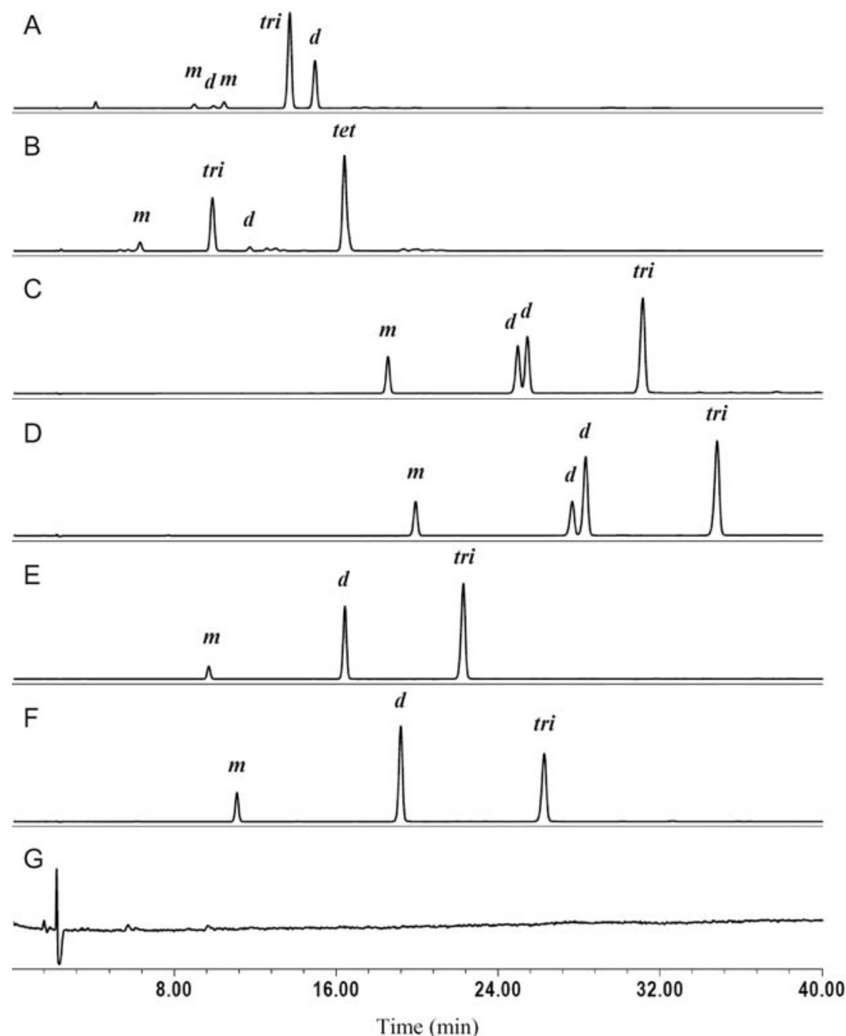

Figure 2. Chromatograms of various types of photoactive compounds: BP PAC 320 (5-DNQ) (A); BP PAC 430 (5-DNQ) (B); TPPA PAC 320 (5-DNQ) (C); TPPA PAC 320 (4-DNQ) (D); THPE PAC 323 (5-DNQ) (E); THPE PAC 320 (4-DNQ) (F); Posi PR excluding PACs (G); m, mono-DNQ substituted PAC; d, di-DNQ substituted PAC; tri, tri-DNQ substituted PAC; tet, tetra-DNQ substituted PAC; detection wavelength, 350 nm.

di-sustituted (di), tri-sustituted (tri) and tetra-sustituted (tet) forms according to the esterification ratio of DNQs.

To obtain the optimum analysis conditions, we performed several kinds of gradient elution by HPLC. Acetonitrile and methanol as organic solvents of the mobile phase were employed for the determination of optimum HPLC conditions. Similar separation results were obtained under both conditions using gradient elution. ACN was chosen to reduce column pressure. The initial conditions of gradient elution were varied from 20 to 50% of ACN. The best separation result was found at 40% of ACN as an initial condition of gradient elution. However, a tri-DNQ substituted isomer [retention time (RT): 13 min)] and di-DNQ substituted isomer (RT: 14 min) of BP PAC 320 (5-DNQ) were overlapped in this condition. To separate both isomers of BP PAC 320 (5-DNQ), TFA was added to the mobile phase. TFA used in the mobile phase allowed both isomers to separate successfully. Figure 2 shows the HPLC chromatograms of various types of PACs at optimum analysis conditions. At the same HPLC condition, each isomer was confirmed by using a liquid chromatography–electrospray mass spectrometer (LC–ESI-MS), as shown in Figure 3. The esterification ratio of PACs determines their polarity owing to residual hydroxyl groups of ballast. In most cases, various types of PACs were satisfactorily separated according to their degree of polarity. Additionally, each isomer of PACs was eluted without interference, compared with the Posi PR sample excluding PACs, and good peak shape was achieved. However, elution sequences of each isomer were not found according to the substitution ratio of DNQs. It has been considered that different polarities appear in equimolar substituted isomers according to the position of substitution. In general, commercial names of PACs were represented by PAC xyy, where x and yy indicate the number of substitution sites and average substitution ratios. For example, PAC 325 consists of three substitution sites and 2.5 average substitution ratios. It was found that the average substitution ratio is the sum of the HPLC area ratio of each isomer multiplied by the number of substitution, in which the HPLC area ratio was obtained from this analytical method.

To evaluate the reproducibility and repeatability of this method, we examined quantitative analysis of PACs in Posi PR,

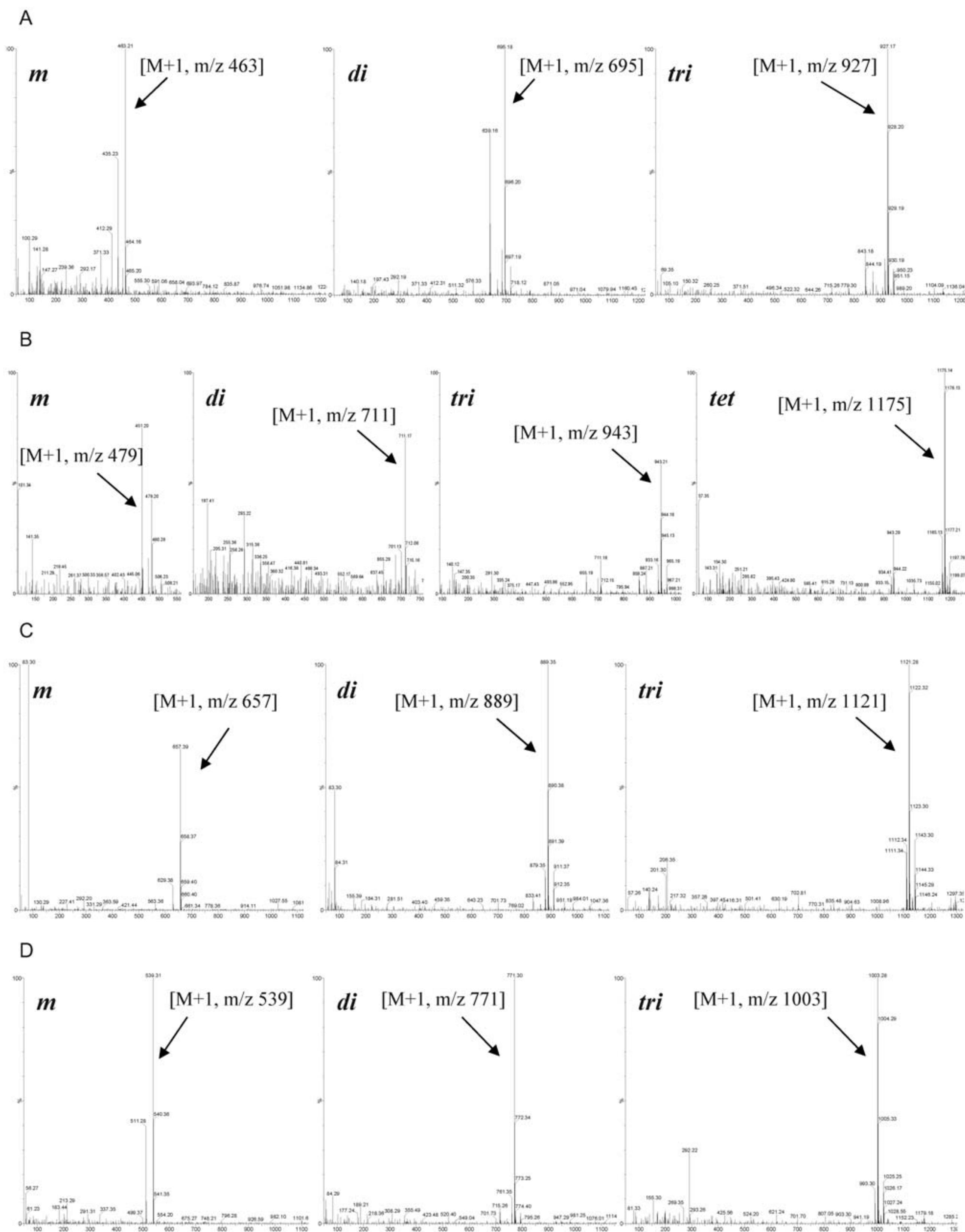

Figure 3. Mass spectra of various types of photoactive compounds: BP PAC 320 (5-DNQ) (A); BP PAC 430 (5-DNQ) (B); TPPA PAC 320 (5-DNQ) (C); THPE PAC 323 (5-DNQ) (D); m, mono-DNQ substituted PAC; d, di-DNQ substituted PAC; tri, tri-DNQ substituted PAC; tet, tetra-DNQ substituted PAC; detection, HPLC–ESI-MS.

Table I
Precision and Accuracy for the BP PAC 430 in Posi PR

Analytes	Added concentration (μg/mL)	Found concentration (mg/mL)*	± SD	Precision (%)[†]	Accuracy (%)[‡]
BP PAC 430	51.4	52.4	0.08	1.46	101.9
	102.8	105.7	0.10	0.92	102.8
	154.2	156.8	0.13	0.80	101.7

*Mean values of three replicate analyses.
[†]Expressed as % RSD.
[‡]Calculated as % [found concentration / added concentration] × 100.

including BP PAC 430. The intra-day and inter-day concentrations (w/w, %) of were found to be 3.88 and 3.85%. Also, intra-day and inter-day precisions [relative standard deviation (RSD)] were 0.28 and 1.35%. This method was found to be reproducible and repeatable through intra-day and inter-day assays. Six calibration standards were employed over the range of 50 to 500 μg/mL and determined by the calibration for three separate days. All correlation coefficients (r^2) were better than or equal to 0.998 ($y = 13696x - 22318$, $y = 14325x - 13803$, $y = 14644x - 33552$). The precision and accuracy showed no significant deviation and were measured with acceptable values, as shown in Table I. Intra-batch precision (% RSD) and accuracy (%) of quality control samples ranged from 0.80 to 1.46% and from 101.7 to 102.8%.

Conclusions

We have developed a liquid chromatographic method for the compositional and quantitative analysis of PACs in Posi PR. Good separation of various types of PACs consisting of a mixture of isomers has been achieved at the same gradient elution. No interfering peaks were present in the chromatograms corresponding to the retention times of PACs. This method was found to be repeatable and reproducible for the measurement of PACs in Posi PR. Additionally, the method has been demonstrated to show acceptable precision and accuracy through the concentration range, over which good linearity was observed. It is expected to be quite useful for the analysis of PACs in manufacturing photoresists.

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