A New Positive-Type Photosensitive Alkaline-Developable Alicyclic Polyimide Based on Poly(amic acid silylester) as a Polyimide Precursor and Diazonaphthoquinone as a Photosensitive Compound

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A new positive working photosensitive alicyclic polyimide precursor based on poly(amic acid *tert*-butyldimethylsilylester) (**3**) and 2,3,4-tris[2-diazo-1-(2*H*)-naphthalenone-4-sulfonyloxy]benzophenone (**D4SB**) as a photosensitive compound has been developed. Polymer **3** was prepared by ring-opening polyaddition of bicyclo[2.2.1]heptane-2-methanecarboxylic-3,5,6-tricarboxylic-2,3:5,6-dianhydride (**2**) with 5-*tert*-butyldimethylsilylamino-*N*-*tert*-butyldimethylsilyl-1,3,3-trimethylcyclohexanemethylamine (**1**) in toluene/*N*,*N*-dimethyl acetamide (DMAc) (2/1 weight ratio) at 20 °C for 3 h. The film of polymer **3** showed excellent transparency at the wavelengths above 250 nm. The dissolution behavior of polymer **3** containing 30 wt % **D4SB** after exposure was studied, and it was found that the difference of dissolution rate between the exposed and unexposed areas was enough to obtain a high contrast due to the photochemical reaction of **D4SB** in the polymer film. The photosensitive polyimide precursor containing 30 wt % **D4SB** showed a sensitivity of 60 mJ/cm^2 and a contrast of 1.7 when it was exposed to 365-nm light and developed with a 2.38 wt % aqueous tetramethylammonium hydroxide solution at 25 °C. A fine positive image of 10-μm-line and space patterns was also printed in a film which was exposed to 300 mJ/cm^2 by contact mode. The positive image in polymer **3** was converted to the positive image in the polyimide (**PI**) film by thermal treatment. The optically estimated dielectric constants of the polyimides with and without **D4SB** are 2.45 and 2.44, respectively. These values are significantly lower than those of conventional aromatic polyimides.

Introduction

Polyimides (**PIs**) have been widely used as the protection and insulation layers for very large scale integration circuits (VLSI) and multichip modules for computers because of their high thermal stability and excellent mechanical property. Photosensitive PIs (**PSPIs**) have been developed to simplify the processing steps.

Recently, **PIs** having low dielectric constants are required to increase the circuit speed. Especially, aliphatic and alicyclic **PIs** are interesting as optoelectronic and interlayer dielectric materials. Therefore, partially aliphatic **PIs** derived from aliphatic dianhydrides and aromatic diamines or vice versa have been developed as **PIs** with low dielectric constants.[1−13] Several reports have been published on the synthesis of wholly aliphatic PIs (**APIs**). However, the reported **APIs** were of low molecular weight. Quite recently, we developed a synthetic method to give wholly alicyclic **PIs** with high molecular weights via poly(amic acid silyl ester)s, which can be employed as a **PSPI** precursor.[14] These findings prompted us to develop a new alicyclic PSPI having a lower dielectric constant.

In this study, we report a new positive working alkaline developable thermally stable and photosensitive polymer based on poly(amic acid *tert*-butyldimethylsilylester) (**3**) and 2,3,4-tris[2-diazo-1-(2*H*)-naphthalenone-4-sulfonyloxy]benzophenone (**D4SB**) as a photoreactive compound.

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Experimental Section

Materials. *N*,*N*-Dimethyl acetamide (DMAc) was distilled from CaH_2 and stored over 4-A molecular sieves. Toluene was distilled from Na/benzophenone under N_2 and stored over sodium wire. 5-Amino-1,3,3-trimethylcyclohexanemethylamine was purified by distillation. Triethylamine (TEA) was distilled from KOH and stored over KOH. Dianhydride, bicyclo[2.2.1]heptane-2-methanecarboxylic-3,5,6-tricarboxylic-2,3:5,6-dianhydride (**2**) was heated to 90 °C in acetic anhydride and toluene, stirred for 1 h, filtered, and then dried at 90 °C for 1 h prior to use. Other reagents and solvents were used as received. 2,3,4-Tris[2-diazo-1-(2*H*)-naphthalenone-4-sulfonyloxy]benzophenone (**D4SB**) was kindly donated by Toyo Gosei Kogyo Co., Ltd., and used without further purification.

Synthesis of 5-*tert*-Butyldimethylsilylamino-*N*-*tert*-butyldimethylsilyl-1,3,3-trimethylcyclohexanemethylamine (1). Into a three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, a 100-mL pressure-equalizing funnel, and a no-air stopper, 5-amino-1,3,3-trimethylcyclohexanemethylamine (3.54 g, 20.8 mmol) and toluene (40 mL) were placed under a N_2 stream. *tert*-Butyldimethylchlorosilane (8.36 g, 55.5 mmol) was added at 0 °C and stirred for 30 min. TEA (6.31 g, 62.4 mmol) was dropwise added to this solution through the funnel to precipitate white HCl·TEA salt immediately. The reaction was kept for another 2 h at 5 °C and then 24 h at 60 °C. The resulting solution was filtered and concentrated under vacuum. The residue was distilled under reduced pressure to give **1** as a clear oil. The yield was 7.38 g (89%): bp 120−123 °C (0.15 Torr); IR (NaCl) $\nu = 3405$ (N−H), 1253 (Si−*tert*-butyl), 829 (Si−*tert*-butyl) cm^{-1}. Anal. Calcd for ($C_{22}H_{50}N_2Si_2$): C, 66.26%; H, 12.64%; N, 7.02%. Found: C, 66.07%; H, 12.32%; N, 7.26%.

Synthesis of Poly(amic acid *tert*-butyldimethylsilyl ester) (3). Into a flame-dried flask charged with dry N_2, **1** (0.877 g, 2.19 mmol), DMAc (0.20 g), and toluene (0.40 g) were placed. Dianhydride **2** (0.550 g, 2.19 mmol) was added to this solution. The mixture was stirred for 1 h at 25 °C and diluted with DMAc (0.510 g) and toluene (1.02 g), which was then stirred for 3 h at room temperature to form a clear solution. The solution of polymer **3** was poured into diethyl ether. The precipitate was collected by filtration (90.0%). IR (NaCl) $\nu =$ 1708 (C=O, silylester), 1658 (C=O, amide) cm^{-1}.

Polymer **3** was converted into the corresponding poly(amic acid) by hydrolysis. IR (KBr) $\nu = 1720$ (C=O, carboxylic acid), 1650 (C=O, amide) cm^{-1}. Anal. Calcd for $(C_{22}H_{32}N_2O_6 \cdot 1.0H_2O)_n$: C, 60.26%; H, 7.36%; N, 6.39%. Found: C, 60.26%; H, 7.56%; N, 6.24%.

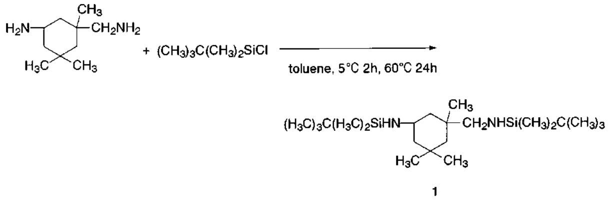
Dissolution Rate. D4SB was added to a polymeric solution (10−30 wt % of the total solid) to construct a photosensitive polymer. The polymer film spin-cast on a silicon wafer was prebaked at 80 °C for 5 min and then exposed to a filtered super-high-pressure mercury lamp (365 nm). The exposed film was developed with a 2.38 wt % aqueous tetramethylammonium hydroxide (TMAH) solution at 25 °C for 95 s. The changes in the film thickness against the **D4SB** contents were measured with a Dectak3 surface profiler (Vecco Instrument Inc.).

Photosensitivity. A 2.3-μm-thick binary resist film on a silicon wafer was exposed to radiation at a wavelength of 365 nm through the filtered super-high-pressure mercury lamp, developed with the 2.38 wt % aqueous TMAH solution at 25 °C and rinsed with water. A characteristic curve was obtained by plotting a normalized film thickness against exposure energy.

Measurement. Infrared spectra were recorded on a Horiba FT-210 spectrophotometer. ^1H NMR spectra were recorded on a Bruker GPX300 (300 MHz) spectrometer. UV spectra were obtained on a Jasco V-650 spectrophotometer. Thermal analyses were performed on a Seiko thermal analyzer at a heating rate of 10 °C/min for thermogravimetry (TG). Molecular weights were determined by a gel permeation chromatograph (GPC) with polystyrene calibration using Tosoh HPLC equipped with a TSK gel column at 40 °C in DMF. The film thickness was measured by a Dektak^3 surface profiler (Vecco Instrument Inc). Refractive indices of polyimide films formed on quartz substrates were measured at a wavelength of 1.320 μm at room temperature with a Metricon model PC-2000 prism coupler. Using linearly polarized laser light with parallel (TE: transverse electric) and perpendicular (TM: transverse magnetic) polarization to the film plane, the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices and the film thickness of the samples were determined.

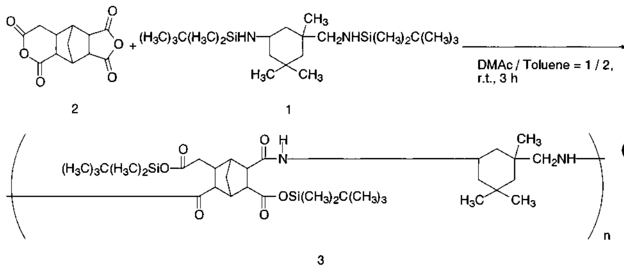
Results and Discussion

Synthesis of 5-*tert*-Butyldimethylsilylamino-*N*-*tert*-butyldimethylsilyl-1,3,3-trimethylcyclohexanemethylamine (1). Monomer **1** was prepared by the reaction of 5-amino-1,3,3-trimethylcyclohexanemethylamine with *tert*-butyldimethylchlorosilane in the presence of TEA as an acid acceptor in toluene for 2 h at 5 °C and then 24 h at 60 °C. The structure of **1** was identified as the corresponding *N*-silylated alicyclic diamine by IR spectroscopy and elemental analysis (eq 1).



(1)

Synthesis of Poly(amic acid *tert*-butyldimethylsilylester). The ring-opening polyaddition of **1** with alicyclic dianhydride, bicyclo[2.2.1]heptane-2-methanecarboxylic-3,5,6-tricarboxylic-2,3:5,6-dianhydride **2** was carried out in DMAc and toluene at room temperature. Polymerization proceeded smoothly to give a desired poly(amic acid *tert*-butyldimethylsilylester) (**3**) with a number-average molecular weight of 19000 and a polydispersity of 2.1. The structure of the polymer was identified as the corresponding poly(amic acid silylester) by IR spectroscopy. The IR spectrum showed characteristic amide and silylester absorptions at 1658 and 1708 cm^{-1} (eq 2).



(2)

Polymer **3** was readily converted to the corresponding PI by thermal treatment. The traces of TG for polymer **3** and the corresponding PI are shown in Figure 1. A rapid weight loss was observed at 200−350 °C for polymer **3**. In this range, the weight loss of 37% is in good agreement with the value (40.8%) calculated from the elimination of *tert*-butyldimethylsilanol due to the imidization. A 10% weight loss temperature of PI is 420 °C. The IR spectrum of the thermally treated PI exhibited characteristic imide absorptions at 1778 and 1704 cm^{-1}.

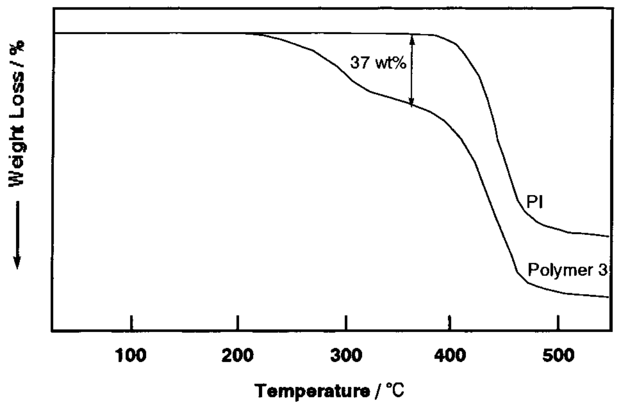


Figure 1. TG curves of polymer **3** and the corresponding PI.

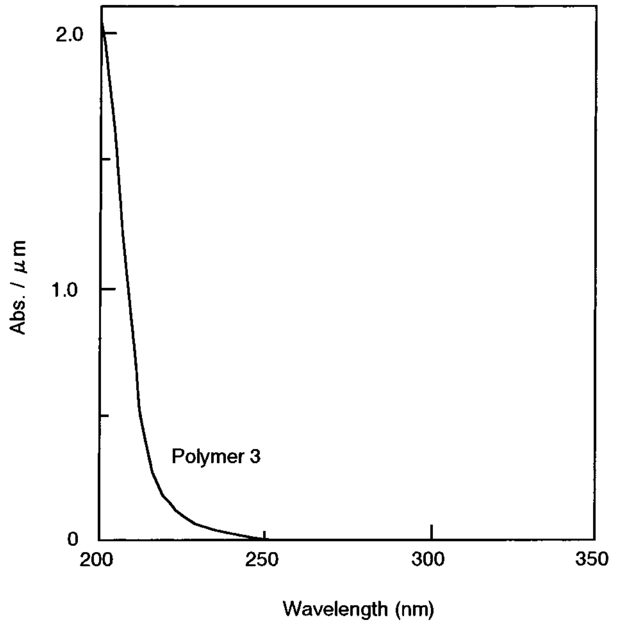
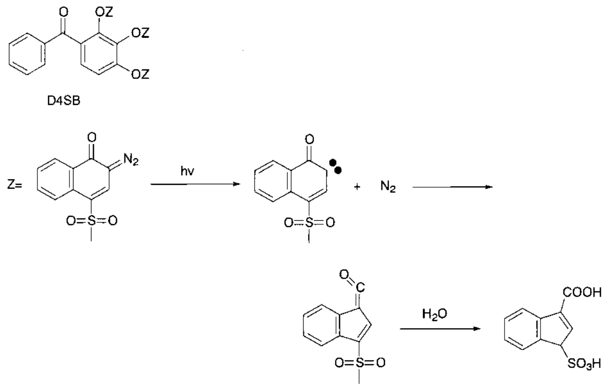


Figure 2. UV−visible spectra of polymer **3** film.

Lithographic Evaluation. The UV−visible spectrum of polymer **3** film with 2.8-μm thickness (Figure 2) shows an excellent transparency in the region above 250 nm. This means that 2,3,4-tris[2-diazo-1-(2H)-naphthalenone-4-sulfonyloxy]benzophenone (**D4SB**), which has a strong absorption in the range of 350−420 nm, can be used as a photoactive compound. **D4SB** is photochemically transformed to 3-sulfoindenecarboxylic acid[15] (eq 3).

Figure 3 shows the changes in the UV−visible spectra of a polymer **3** film containing 30 wt % **D4SB** upon 365-nm UV (i-line) irradiation. The intensity of the characteristic absorption band in the range of about 350−420 nm gradually decreased, and this absorption band disappeared completely at 200 mJ/cm^2. Therefore, the resist-consisting polymer **3** as a matrix and **D4SB** as a photoactive compound would be expected to work as an i-line sensitive **PSPI** system.

To clarify the difference of dissolution behavior between the exposed and unexposed areas, the effect of **D4SB** loading on the dissolution rate in the developer (2.38 wt % TMAH) was studied, and the results are shown in Figure 4. The films spin-cast on silicon wafers were prebaked at 80 °C for 5 min, and then exposed to a filtered super-high-pressure mercury lamp (365 nm, 300 mJ/cm^2). The dissolution rate was estimated by measuring the film thickness after development. The unexposed areas were not dissolved in the TMAH solution. On the other hand, the solubility of the exposed areas increased gradually with increasing **D4SB** contents. The difference of the dissolution rates between the exposed and unexposed areas reached almost 800 times at the 30 wt % **D4SB** loading.



(3)

The most widely used positive resists are two-component materials consisting of an alkaline soluble matrix resin that is rendered insoluble in an aqueous alkaline solution through addition of hydrophobic radiation-sensitive materials.[16,17] In our case, hydrolysis of polymer **3** might occur in the exposed areas by aqueous alkaline solution because the developer can penetrate easily into polymer film **3** due to the existence of hydrophilic groups such as carboxylic acid and sulfonic acid groups.

Therefore, this dissolution-accelerating behavior in the exposed film is considered to be the polarity change of polymer **3** due to the photochemical reaction of **D4SB** and the hydrolysis of polymer **3** in the developing process.

A photosensitive polymer system consisting of polymer **3** and 30 wt % **D4SB** in DMAc and toluene was formulated. The sensitivity curve for a 2.8-μm-thick polymer film **3** shown in Figure 5 was consistent with the dissolution behavior studied above, indicating that the sensitivity (D^0) and contrast (γ^0) were 60 mJ/cm^2 and 1.7, respectively.

Figure 6 presents a scanning electron micrograph of the contact-printed image after exposure of 300 mJ/cm^2 light, followed by development with the 2.38 wt % aqueous TMAH solution. Clear positive patterns with 10-μm resolution were obtained. Furthermore, this positive image in polymer film **3** was converted to a positive image of PI film by high-temperature treatment without any deformation.

Refractive Indices and Estimated Dielectric Constants. The average refractive index (n_{AV}) was calculated using the equation $n_{AV} = (2n_{TE} + n_{TM})/3$, and in-plane/out-of-plane birefringence (Δn) is given as

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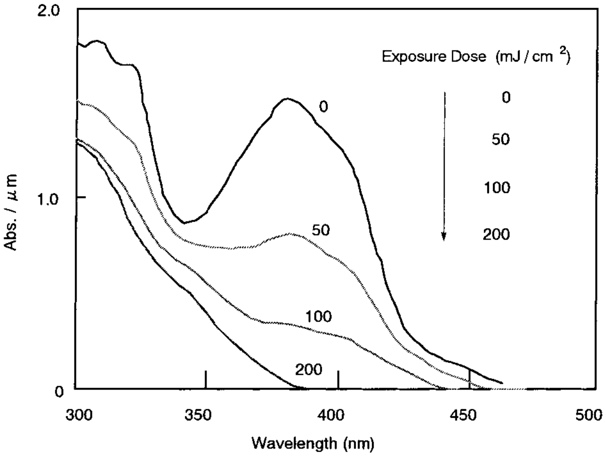

Figure 3. Photoreaction of **D4SB**.

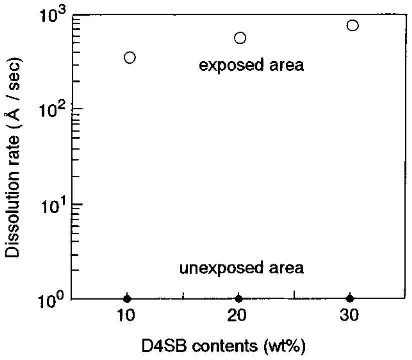

Figure 4. Relationship between dissolution rate and **D4SB** content of polymer film.

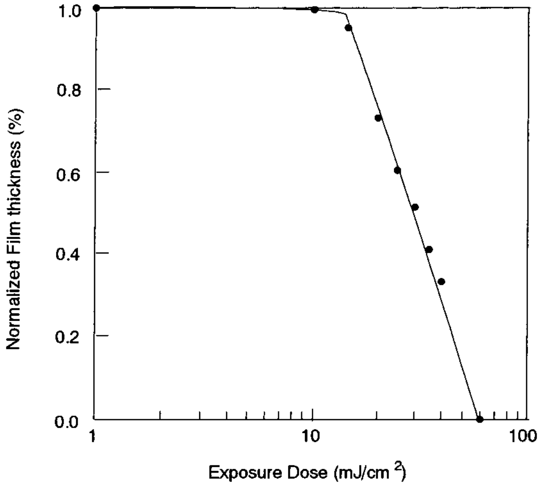

Figure 5. Exposure characteristic curve for the system of polymer **3** and 30 wt % **D4SB**.

$n_{TE} - n_{TM}$. The results are listed in Table 1 along with those of a **D4SB**-containing polyimide. The n_{AV} of the PI (from polymer **3**) film is almost the same as that of PI (from polymer **3** + **D4SB**). The dielectric constants (ϵ) of the material at optical frequencies can be estimated from the refractive index n according to the Maxwell's equation, $\epsilon \doteqdot n^2$. The value of ϵ around 1 MHz has been evaluated as $\epsilon \doteqdot 1.1 n_{AV}^2$, including an additional contribution of ≈10% from the infrared absorption.[4,18] The refractive indices of 1.4908 and 1.4913

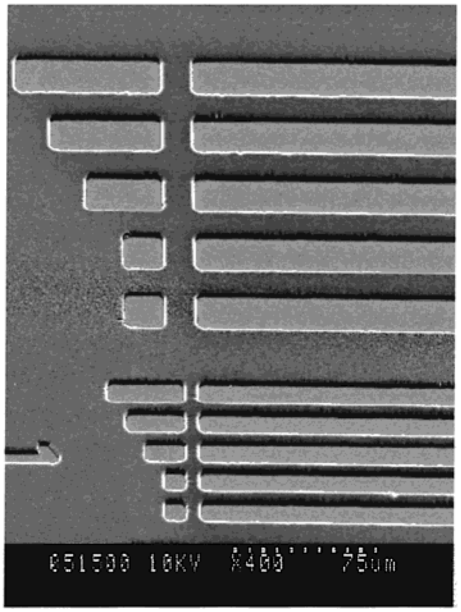

Figure 6. Scanning electron micrograph of the pattern from polymer **3** containing **D4SB**.

Table 1. Refractive Indices and Estimated Dielectric Constants of Polyimide Films

polyimide	d (μm)[a]	n_{TE}[b]	n_{TE}[c]	n_{AV}[d]	Δn[e]	ϵ[f]
polymer **3**	3.4	1.4908	1.4909	1.4908	−0.001	2.44
polymer **3** + **D4SB**	5.1	1.4927	1.4885	1.4913	0.0042	2.45

[a] Film thickness. [b] In-plane refractive indices. [c] Out-of plane refractive indices. [d] Average refractive index; $n_{AV} = (2n_{TE} + n_{TM})/3$. [e] Birefringence; $\Delta n = n_{TE} - n_{TM}$. [f] Optically estimated dielectric constant; $\epsilon = 1.10 n_{AV}^2$.

determined for PI (from polymer **3**) and PI (from polymer **3** + **D4SB**) can be translated into dielectric constants of 2.44 and 2.45, respectively. These values are lower than the optically estimated ϵ of an alicyclic polyimide reported by Matsumoto et al. (2.55). The estimated value of ϵ (2.44) is ≈22% smaller than that of a conventional aromatic polyimide (pyromellitic dianhydride + 4,4′-oxydianiline, 3.14). The incorporation of **D4SB** into PI is advantageous because it gives high photosensitivity without an increase in dielectric constant.

Because birefringence is related to inherent anisotropy in molecular polarizability and degree of orientation of refracting units, it provides additional information regarding the orientation of polyimide. It has been reported that aromatic polyimides may exhibit large birefringence, indicating the preferential orientation of polymer chains to the film plane.[19] The Δn of the PI (from polymer **3**) film is nearly equal to zero, while that of PI (from polymer **3** + **D4SB**) exhibits a small positive value of Δn. The negligibly small birefringence of PI (from polymer **3**) implies that this polymer has small polarizability anisotropy, and the polymer chains are randomly oriented. On the other hand, the positive Δn of PI (from polymer **3** + **D4SB**) could be ascribed to the residual aromatic groups oriented in the film plane which were generated from thermally treated **D4SB** molecules.

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Conclusions

Polymer **3** with a high molecular weight was prepared by the ring-opening polyaddition of *N*-silylated alicyclic diamine **1** and alicyclic dianhydride **2**. The photochemical reaction of **D4SB** in polymer **3** film occurred smoothly because of its excellent transparency in the UV region above 250 nm. Polymer **3** containing 30 wt % **D4SB** functioned as a positive-type photosensitive polymer, and its sensitivity and contrast were 60 mJ/cm^2 and 1.7 with 365-nm light, respectively. The positive image of polymer **3** film after development was converted to the corresponding PI image by thermal treatment. A 10% weight loss of the corresponding PI (from polymer **3**) under nitrogen was 420 °C. The optically estimated dielectric constant is 2.44, which is $\approx$22% lower than that of a conventional aromatic polyimide. The incorporation of **D4SB** into PI is advantageous because it gives high photosensitivity without an increase in the dielectric constant.

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