Positive-type Alkaline Developable Photosensitive Branched Polyamides with Low Degree of Branching and Diazonaphthoquinone as a Photosensitive Compound

Jijun XIAO,¹ Yosuke INAI,² Li LI,² Teruaki HAYAKAWA,² and Masa-aki KAKIMOTO^{2,†}

¹*Department of Polymer Material, Hebei University of Science and Technology,
No. 186 Yuhua East Street, Shijiazhuang, Hebei 050018, China*

²*Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo 152-8552-S8-26, Japan*

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ABSTRACT: A positive-type photosensitive polyamide based on the branched polyamides with low degree of branching and 1-[1,1-bis[4-(2-diazo-1-(2H)naphthalenone-5-sulfonyloxy)phenyl]ethyl]-4-[1-[4-(2-diazo-1-(2H)naphthalenone-5-sulfonyloxy)phenyl]methyl]ethyl]benzene (S-DNQ) as a photosensitive compound has been developed. The branched polyamides with low degree of branching having amino end groups (**2a** and **2b**) were prepared from a ABB' type monomer, 4-(2,4-diaminophenoxy) benzoic acid **1** in the presence of diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP) and triphenylphosphite/pyridine (TPP/Py) as a condensing agent, of which the degrees of branching (DB) were 0.10 and 0.36, respectively. Followed by end-capping with 4-hydroxy benzoic acid, end-modified polymers with phenolic hydroxy groups (**4a** and **4b**) were successfully prepared. The polymer properties were characterized by ¹H and ¹³C NMR, GPC, TG/DTA and DSC, respectively. The photosensitive polymer based on polymer **4a** and 30 wt % S-DNQ showed a sensitivity of 140 mJ cm⁻² and a contrast of 2.1 when it was pre-baked at 80 °C for 5 min, subsequently exposed to a 436 nm light (g-line) and developed with a developer of 5 wt % aqueous tetramethylammonium hydroxide (TMAH) solution: 2-propanol (4:1 by weight ratio) at 25 °C. A fine positive image of 6 μm line-and-space pattern was obtained when the film was exposed to 300 mJ cm⁻² by contact-printing mode.

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KEY WORDS Positive-type Photosensitive Polymer / Branched Polyamide / Alkaline Developable / Low Degree of Branching /

Aromatic polyamide is well known as an important class of high-performance polymeric materials due to their high thermal stability and excellent mechanical property. The applications, however, are restricted by their poor processability due to their insolubility and high softening temperature. The key reasons for insolubility and non-melting character in aromatic polyamides are the lack of chain flexibility and strong intermolecular interactions due to high symmetry, highly polar groups and extensive hydrogen bonding. To remedy this, a great deal of efforts have been expended by introducing bulky pendant groups or flexible segment along the polymer backbone, incorporating a crank and twisted non-coplanar into the polymer backbone, and replacing symmetrical aromatic rings by unsymmetrical ones and so on.^{1–5} On the other hand, a strategy to utilize the abilities in dendritic macromolecules to avoid the strong chain entanglement and to introduce a variety of functional end groups is particular recent interests. Dendritic aromatic polyamides consists of dendrimer, dendron, or hyperbranched type structures possess a variety of unique properties such as good solubility, low viscos-

ity, multivalence, and encapsulation effects, which mainly are caused by the branching and spherical architecture. In particular, hyperbranched polyamides are of great interest from a synthetic point of view because of relatively easier for rapid and large-scale synthesis compared with the dendrimers. However, producing the film with good physical properties still remains a challenge for conventional hyperbranched polymers due to the lack of chain entanglement.^{6–15}

We recently reported that the branched polyamides with low degree of branching (low DB) approximately 0.2 prepared by the polycondensation of a ABB' type monomer, 4-(2,4-diaminophenoxy) benzoic acid.¹⁶ The polycondensation of ABB' type monomer, in which A is a carboxyl group and B and B' are amino groups with different circumstance, provides the polyamides with relatively lower degree of branching. The advantage of the branched polyamides with low degree of branching is not only good solubility for aprotic polar solvents such as dimethylformamide (DMF), *N,N*-dimethyl acetamide (DMAc) and 1-methyl-2-pyrrolidone (NMP), but also high tensile strength of the casting films. This is due to the adequate chain

[†]To whom correspondence should be addressed (Tel: +81-3-5734-2429, Fax: +81-3-5734-2875, E-mail: mkakimot@o.cc.titech.ac.jp).

entanglement and the hydrogen bonding of the amino substituents with the main chain. The films of polyamide with low degree of branching, thus, are expected to a variety of technological applications that require an excellent thermal and chemical stability.

In our continuing investigation of the versatility of the branched polyamides with low DB, herein, we report the synthesis of branched polyamides with low DB containing phenol hydroxy groups and its application for a positive working alkaline developable photosensitive polyamide system, which consists of these polyamides and 1-{1,1-bis[4-(2-diazo-1-(2H)naphthalenone-5-sulfonyloxy)phenyl]ethyl}-4-{1-[4-(2-diazo-1-(2H)naphthalenone-5-sulfonyloxy)phenyl]methyl-ethyl}benzene (S-DNQ) as a polymer matrix and a photosensitive dissolution inhibitor to alkaline developer, respectively.

EXPERIMENTAL

Materials

N-methyl-2-pyrrolidinone (NMP) was dried over calcium hydride and distilled under reduced pressure. 1-{1,1-bis[4-(2-diazo-1-(2H)naphthalenone-5-sulfonyloxy)phenyl]ethyl}-4-{1-[4-(2-diazo-1-(2H)naphthalenone-5-sulfonyloxy)phenyl]methyl-ethyl}benzene (S-DNQ) was kindly donated by Ueda's laboratory and was used without further purification (Scheme 1). The other reagents and solvents were obtained commercially and used as received.

Measurement

^1H NMR and ^{13}C NMR spectra were recorded on a JNM-AL 300 instrument using tetramethylsilane as an internal reference. Infrared (IR) spectra were obtained with a FT-IR 460 plus spectrometer. Differential scanning calorimetry (DSC) was performed with a Seiko DSC 6200 instrument at a heating rate of $10^\circ\text{C min}^{-1}$, in nitrogen. Thermal stability, as measured by 5% weight loss of the polymer samples, was determined on a Seiko TG/DTA 6200 analyzer at a heating rate of $10^\circ\text{C min}^{-1}$, in nitrogen. The molecular weights of the polymers were determined by gel permeation

chromatography (GPC) relative to polystyrene standards, using dimethylformamide (DMF) at 50°C at a flow rate of 1.0 mL min^{-1} . The inherent viscosity of polymers was measured with an Ostwald viscometer at 30°C from the solution of 0.5 g dL^{-1} (DMF). The photochemical properties of the polymers were studied by illuminating thin films obtained by spin-coating of the solution in NMP, before and after irradiation, absorbance or transmittance spectra were recorded on a Hitachi U-3400 UV-VIS-IR spectrometer. The film thickness was measured with a Veeco Instrument Dektak surface profiler. Irradiation was conducted by a UV exposure apparatus, and the dose was measured at the g-line with wavelengths of 436 nm. The resulting pattern surface was coated with a thin layer of Au using an ion-sputtering apparatus, and the microstructure was observed with a scanning electron microscope (SEM, HITACHI S-800), the accelerating power was 15 kV.

Monomer Synthesis

The asymmetry monomer 4-(2,4-diaminophenoxy) benzoic acid **1** was prepared according to our previous report.¹⁶

Synthesis of Branched Polyamides with Low Degree of Branching: Method A with DBOP (2a). To a solution of **1** (2.928 g, 0.013 mol) in the 60 mL of NMP, DBOP (5.140 g, 0.0134 mol) and TEA (1.83 mL) were added. The mixture was stirred at room temperature for 3 h. Then the homogeneous mixture was poured into 750 mL of methanol containing 0.1% lithium chloride. The precipitated solid was filtered, washed with methanol and dried at 50°C *in vacuo* for overnight. The polymer **2a** was collected as a light gray solid and the yield was 95%. IR (KBr, cm^{-1}): 1652 ($\text{C}=\text{O}$ of amide).

Method B with Triphenyl Phosphite (TPP)/Pyridine (Py) (2b). Into a flask were placed lithium chloride (1.200 g) and dried with heat gun, then were added **1** (2.928 g, 0.013 mol), freshly distilled NMP (120 mL), TPP (9.60 mL) and Py (6.75 mL). The mixture was heated to 100°C and stirred at this temperature for 3 h. After cooling to room temperature, the mixture was precipitated from 750 mL of methanol containing 0.1% lithium chloride. The precipitated solid was collected and washed with methanol, and dried *in vacuo* at 65°C for overnight. The polymer **2b** was obtained with a light brown powder and the yield was 96%. IR (KBr, cm^{-1}): 1655 ($\text{C}=\text{O}$, amide).

Synthesis of Model Compound: 4-Hydroxy-*N*-phenyl Benzamide (3). To a mixture of 0.552 g (4.0 mmol) of 4-hydroxybenzoic acid, 8 mL of NMP and 0.36 mL (4.0 mmol) of aniline were added 0.9 mL (8.0 mmol) of TPP and 0.65 mL of pyridine. The mixture was heated to 100°C and stirred at this temperature for

Scheme 1. Chemical structure of S-DNQ.

Positive-type Photosensitive Branched Polyamide

Scheme 2. Synthesis of branched polyamides **2a** and **2b**.

24 h. After cooling to room temperature, the mixture was poured into 1 wt % aqueous sodium hydrogen carbonate. The precipitate solid was filtered and washed with water, and then dried *in vacuo* at 50 °C. The product **3** was obtained with a white powder and the yield was 96%. ¹H NMR (DMSO-*d*₆) δ (ppm): 6.88 (d, Ar, 2H), 7.05 (t, Ar, 1H), 7.31 (t, Ar, 2H), 7.77 (d, Ar, 2H), 7.87 (d, Ar, 2H), 10.02 (s, OH, 1H), 10.15 (s, amide, 1H). ¹³C NMR (DMSO-*d*₆) δ (ppm): 115.0, 120.4, 123.4, 125.5, 128.6, 129.8, 139.6, 160.7, 165.2. IR (KBr, cm⁻¹): 3450, 3343 (OH, NH), 1655 (C=O of amide I), 1599, 1534 and 1510 (C=O of amide II).

End Modification of Polymer 2a (4a). To a solution of 2.4 g of **2a**, 3.12 g (26.0 mmol) of 4-hydroxybenzoic acid, 165 mL of NMP and 5 mL of triethylamine, were added 5.08 mL (45.0 mmol) of TPP and 3.67 mL of pyridine. The solution was heated to 100 °C and stirred for 8 h at this temperature. After cooling to room temperature, the solution was poured into 300 mL of methanol. The precipitate solid was filtered and washed with methanol, and then dried *in vacuo* at 50 °C for overnight. The polymer **4a** was obtained with a light grey powder and the yield was 95%.

End Modification of Polymer 2b (4b). The same procedure as for polymer **4b** was used for the preparation of polymer **4b**. The polymer **4b** was obtained with a light grey powder and the yield was 96%.

Dissolution Rate. The photosensitive polyamides

(PSPAs) were formulated by the polymer **4a** as a polymer matrix and S-DNQ compound (30 wt % of polymer) as a photosensitive agent dissolved in DMF. The PSPAs were spin-coated onto a silicon wafer, and the films formed were about 1.5 μm in thickness after prebaking at 80 °C for 5 min. The resulting films were exposed with a super high-pressure-mercury lamp with a filter at a 436 nm light (g-line) and developed with a developer of 5 wt % aqueous tetramethylammonium hydroxide (TMAH) solution: 2-propanol (4:1 by weight ratio) at 25 °C and rinsed with non-ion water to determine a dissolution rate (Å/s).

Photosensitivity. A 1.5 μm-thick polymer film on a silicon wafer was exposed to a 436 nm light (g-line) and developed with a developer of 5 wt % aqueous tetramethylammonium hydroxide (TMAH) solution: 2-propanol (4:1 by weight ratio) at 25 °C and rinsed with water. A characteristic curve was obtained by a normalized film thickness against the exposure energy.

RESULTS AND DISCUSSION

Polymer Synthesis

For the synthesis of the branched polyamides with low DB, we examined two different condensing agents, diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP) and triphenyl phosphite/pyridine (TPP/Py) (Scheme 2). In case of DBOP, the polymerization of monomer **1** was carried out at

Table I. Degree of branching, inherent viscosities and average molecular weights of polyamides and end-modified polyamides

Polymer	DB ^a	M_w/M_n ^b	M_w^b ($\times 10^4$)	α^b	η_{inh}^c (dl g ⁻¹)
2a	0.10	3.8	14.0	0.60	1.07
2b	0.36	1.9	7.5	0.61	0.40
4a	—	3.8	19.9	0.41	1.25
4b	—	3.6	14.9	0.45	0.66

^aDetermined by ¹H NMR spectra. ^bDetermined by GPC in DMF containing lithium bromide (0.01 mol l⁻¹); polystyrene was used as the standard. ^cMeasured in NMP at a concentration of 0.5 g dl⁻¹ at 30 °C.

Scheme 3. Synthesis of model compound **3**.

room temperature through a “one step” procedure to form polymer **2a**.¹⁷ Otherwise, when TPP/Py was used, the polymer **2b** was prepared by high temperature direct polymerization of **1**. Both polymerizations proceeded homogeneously and resulted in light brown powder with a yield of 95% and 96%, respectively.

As summarized in Table I, the inherent viscosities (η_{inh}) of polymer **2a** and **2b** were 1.07 and 0.4 dl g⁻¹, respectively. The weight-average of molecular (M_w) weights of polymer **2a** and **2b** obtained by GPC were 14.0×10^4 and 7.49×10^4 , respectively. The polydispersities (PD) were 3.79 and 1.88, respectively.

The structures of polymers were identified by IR, ¹H and ¹³C NMR spectroscopies. In the IR spectra, a new carbonyl absorption corresponding to an amide bond was observed at 1652 or 1655 cm⁻¹ while an absorption corresponding to carbonyl absorption at 1688 cm⁻¹ observed in the monomer disappeared. The absorption at 3361 cm⁻¹ attributable to amino groups was observed, verified the formation of polyamide. Moreover, all signals of ¹H NMR spectra were assigned clearly to the terminal, linear and dendritic units in the polymer **2a** and **2b** (Figure 1). The ¹H NMR spectra of polymer **2a** and **2b** showed that a major amide peak at 9.97 ppm was assigned to amide proton of para-reacted amide of linear unit (L_p) and three minor peaks at 10.29, 9.80 ppm and 9.43 ppm were assigned to amide protons of para-amine reacted dendritic unit (D_p) and ortho-amine reacted dendritic unit (D_o), and ortho-amine reacted linear unit (L_o), respectively. According to Frey definition, which introduced a general expression for DB without molecular weight limitation based on hyperbranched polymers from AB_n monomers, *e.g.*,

Figure 1. ¹H NMR spectra of (a) polymer **2a** and (b) polymer **2b** in DMSO-*d*₆.

$DB = 2D/(2D + L)$.¹⁸ In this case, the DB of Frey definition needs to modify to be $DB = (2D)/(2D + L_p + L_o) = (D_p + D_o)/(D_p + D_o + L_p + L_o)$. By integrated intensity of the peaks (D_p , D_o , L_p and L_o), the estimated DBs of polymer **2a** and **2b** were calculated as 0.10 and 0.36, respectively. It was found that polymer **2a** obtained *via* polymerization of ABB' monomer in the presence of DBOP indicates lower dendritic content than polymer **2b**.

End Modification of Branched Polyamides with Low Degree of Branching

Most standard resist materials used in semiconductor manufacturing are positive-type resists based on novolac resists with diazonaphthoquinone (DNQ), where DNQ acts as a dissolution inhibitor for aqueous base development of novolac resin.¹⁹ Similar to the novolac resin used in the commercial g-line or i-line photoresists, the polymer matrix bearing phenolic hydroxy groups can be inhibited by the addition of DNQ photoactive compound.^{20–28}

In order to introduce phenolic hydroxy groups into the branched polyamides obtained, the end-modification of the amino groups was carried out by using 4-hydroxy benzoic acid. Prior to the end-modification of polymers, we initially studied the reaction of aniline and 4-hydroxy benzoic acid in the presence of TPP/Py to determine whether the desired model compound **3** was formed in quantitative yield to constitute a polymer-forming reaction and to confirm the structure of polymers (Scheme 3).

The IR spectrum of **3** showed characteristic hydroxy, amide N-H, amide I, and amide II bands at 3450, 3343, 1655, and 1534 cm⁻¹, respectively. The

^1H NMR and ^{13}C NMR spectra of **3** are shown in Figure 2 with the assignments of each resonance. The peaks due to the hydroxy and amide protons

Figure 2. ^1H and ^{13}C NMR spectra of model compound **3** in $\text{DMSO}-d_6$.

can be clearly observed at 10.02 and 10.15 ppm, respectively. In the ^{13}C NMR spectrum, the signal of the carbon nuclei of the amide carbonyl and quaternary carbons connected to the hydroxy groups for model compound **3** appeared at 165.2 and 160.7 ppm, respectively. The results show that the reaction of hydroxy group with carbonyl group does not take place.

Based on the reaction conditions of model compound above described, the end-modification reaction of polymer **2a** and **2b** was carried out as shown in Scheme 4, respectively. The results show that the complete substitution reaction had not finished until reaction time was prolonged to 8 h. Figure 3 shows the ^1H NMR spectra of polymer **4b** obtained at different reaction time. The assignments of these resonances were performed with the aid of chemical shift of model compound. As an example, it is clear from Figure 4(a) to 4(d) that the peaks at 9.97 (L_p), 9.43 (L_o) and 5.03 ppm for free amine end group in the ^1H NMR of polymer **2b** gradually disappeared due to the end modification, but the peaks at 10.29 and 9.80 ppm for dendritic structure (D_p and D_o) remained. It should be mentioned that the dendritic peak at 10.29 ppm was overlapped by the amide proton peak attributed to end-modified hydroxy benzamide. Four new major amide peaks were observed at 10.59, 10.30, 10.09 and 9.65 ppm, respectively. The peaks at 10.30, 9.65 and 10.09 ppm were assigned to the amide peak of para- and ortho- end-modification and proton

Scheme 4. Synthesis of branched polyamides with phenolic hydroxy groups **4a** and **4b**.

Figure 3. ^1H NMR spectra of end-modified polymer **4b** obtained at various reaction times in $\text{DMSO}-d_6$.

Figure 4. ^1H NMR spectra of (a) polymer **4a** and (b) polymer **4b** in $\text{DMSO}-d_6$.

of hydroxy group, respectively. The peaks at 10.59 and 10.15 ppm were assigned to the amide derived from self-polycondensation and were shifted from 9.97 and 9.43 ppm due to the end-modification. Of them, the amide peak at 10.15 ppm was overlapped. The inherent viscosities, M_w , M_n , and polydispersity index of end-modified polymer **4a** and **4b** are shown in Table I. Their ^1H NMR spectra are presented in Figure 4. IR spectra of polymer **4a** and **4b** showed characteristic absorption of carbonyl groups of the amides at 1655 cm^{-1} . The absorption peak at about 3360 cm^{-1} resulting from N-H asymmetrical stretching vibrations changed into a broader absorption band, which clarifies the existence of hydroxy group. These findings confirm that end-modification reactions have performed.

Polymer Properties

The thermal properties of resulting polymers are

Table II. Thermal properties of polyamides and end-modified polyamides

Polymer	T_{d5}^a ($^{\circ}\text{C}$)	T_{d10} ($^{\circ}\text{C}$)
2a	385	408
2b	360	411
4a	300	361
4b	306	375

^aThe temperature at which 5 wt % (T_{d5}) and 10 wt % of weight loss (T_{d10}) were determined by TGA in nitrogen at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

tabulated in Table II. The glass-transition temperature (T_g) of polymers, determined by means of differential scanning calorimetry (DSC) was not detected from 30 to $300\text{ }^{\circ}\text{C}$. The thermogravimetric analysis (TGA) revealed that the temperatures of 5% weight loss (T_{d5}) for polymer **2a** and **2b** were in the range of 360 to $385\text{ }^{\circ}\text{C}$, whereas that of end-modified polymer **4a** and **4b** were found to be about $300\text{ }^{\circ}\text{C}$, indicating that T_d of polymers depended on the structure of end groups, but were little affected by the DB of polymers.

All of the polymers were readily soluble in aprotic polar solvents including NMP, DMAc, DMF, and DMSO at room temperature, but insoluble in THF, chloroform, methanol, and acetone. The good solubility of these polymers may be due to the existence of flexible ether linkage and branching chain, which reduced the polymer interchain interaction and entanglement.

The polymer films were prepared by casting from the polymer solution in DMF onto glass plates upon heating. All of the polymers formed continuous films, but the film formed from polymer **4b** could not be peeled up continuously.

Lithographic Evaluation

We initially attempt to examine lithographic evaluation of the polymer **4a** because the film-forming ability of polymer **4a** was relatively higher than that of polymer **4b** for a polymer matrix of positive-type photoresists system with DNQ. In general, DNQ compounds have a strong absorption around the g-line and convert from a carbene intermediate to ketene, which rapidly reacts with water to give a more polar carboxylic acid derivative. The UV spectrum of the matrix of polymer **4a** illustrates that no absorption was observed above 360 nm as shown in Figure 5. Therefore S-DNQ with a strong absorption at 436 nm , which produce carboxyl groups after irradiation, can be used as a photosensitive compound in the resist formulation.

To clarify the dissolution behaviors of the exposed and unexposed areas toward a mixture of 5 wt % aqueous solution of tetramethylammonium hydroxide

Figure 5. UV-vis spectrum of polymer **4a**.

(TMAH): 2-propanol (4/1 by weight) at room temperature, the dissolution rate was estimated from the change of the film thickness before and after the development. The values for dissolution rate at both exposed and unexposed areas are 2.89 Å/s and 520 Å/s, respectively. The dissolution rate ratio between the unexposed and exposed areas reaches up to 180 times, which seems to be sufficient for use as a polymer matrix for photoresist. The adhesion of polymers on silicon wafers was examined and judged by bar eyes after being developed. On the other hand, in case of the polymer **4b**, the dissolution rate was not able to estimate since the film was swollen during the development with the developer. This could be due to the excess number of the phenolic hydroxy groups in the polymer **4b** with higher degree of branching compared with that of the polymer **4a**.

After a series of optimization studies, a photosensitive polymer system consisting of polymer **4a** and S-DNQ (30 wt % of polymer) was investigated by irradiation of g-line 436 nm sources. The irradiated films were developed with a mixture of 5 wt % aqueous solution of tetramethylammonium hydroxide (TMAH) and 2-propanol (4/1 by weight) at room temperature. The characteristic curve of the film with a thickness of 1.5 µm is shown in Figure 6, indicating that the sensitivity ($D_{0.5}$) and contrast ($\gamma_{0.5}$) are 140 mJ cm⁻² and 2.1, respectively.

Figure 7 shows a scanning electron micrograph of positive patterns printed in 1.5 µm thick film. The photopolymer film composed of polymer **4a** and 30 wt % S-DNQ of polymer was pre-baked at 80 °C for 5 min and exposed at 300 mJ cm⁻², subsequently, developed in a developer of 5 wt % TMAH aqueous solution and 2-propanol (4:1 by weight ratio) at 25 °C for 30 s, and then rinsed in non-ion water for 2 min. Fine patterns of the photoresist at a 6 µm dimension were observed without any swelling and distortion.

Figure 6. Exposure characteristic curve for the system of polymer **4a** and 30 wt % S-DNQ. The film was pre-baked at 100 °C for 5 min, and developed with a developer of 5 wt % aqueous tetramethylammonium hydroxide (TMAH) solution:2-propanol = 4:1 by weight ratio at 25 °C.

Figure 7. Scanning electron micrograph of the pattern from polymer **4a** containing 30 wt % S-DNQ on a silicon wafer.

CONCLUSIONS

Two branched polyamides with low DB **2a** and **2b** were prepared by self-polycondensation from an asymmetric ABB' monomer, 4-(2,4-diaminophenoxy)-benzoic acid **1**, in the presence of DBOP or TPP/Py as a condensing agent. The DBs of polymer **2a** and **2b** calculated from ¹H NMR measurement were 0.1 and 0.36, respectively. The end-modifications of **2a** and **2b** were achieved by end-capping reactions with 4-hydroxy benzoic acid to introduce the phenolic hydroxy groups at the termini. The polymers were soluble in polar aprotic solvents, such as DMF, NMP and DMSO. Polymer **4a** containing 30 wt % S-DNQ functioned as a positive-type photosensitive polymer, and its sensitivity and contrast were 140 mJ cm⁻² and 2.1 with 436 nm light in a 1.5 µm film, respectively. A clearly positive pattern with a resolution of 6 µm was obtained.

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