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Photosensitive poly(benzoxazole) based on precursor from diphenyl isophthalate and bis(*o*-aminophenol)

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Abstract

A new synthetic method for the preparation of poly(benzoxazole) (PBO) precursor, poly(*o*-hydroxyamide) (**7**) from bis(*o*-aminophenol) (**5**) and diphenyl isophthalate (**6**) has been developed. Polymer **7** was prepared by the polycondensation of **5** and **6** in 1-methyl-2-pyrrolidinone (NMP) at 185–205 °C. Model reactions were carried out in detail to elucidate appropriate conditions for the formation of 2-hydroxybenzanilide (**3**) from *o*-aminophenol (**1**) and phenyl benzoate (**2**). The photosensitive (PBO) precursor based on polymer **7** containing a 22% of benzoxazole unit and 30 wt% 1-{1,1-bis[4-(2-diazo-1-(2*H*)naphthalenone-5-sulfonyloxy)phenyl]ethyl}-4-{1-[4-(2-diazo-1(2*H*)naphthalenone-5-sulfonyloxy)phenyl]methylethyl}benzene (S-DNQ) showed a sensitivity of 110 mJ cm^{-2} and a contrast of 5.0 when it was exposed to 436 nm light followed by developing with a 2.38 wt% aqueous tetramethylammonium hydroxide solution at room temperature. A fine positive image featuring 8 μm line and space patterns was observed on the film of the photoresist exposed to 200 mJ cm^{-2} of UV-light at 436 nm by the contact mode.

Keywords: Thermally stable polymer; Photosensitive poly(benzoxazole); Poly(*o*-hydroxyamide)

1. Introduction

The continuous evolution toward portable, high-frequency microelectronic system places high demands on material properties, notably low dielectric constant (e), low dissipation factor, low moisture uptake, and good thermal stability. Photopatternable insulating polymers with these properties are required for protective chip over coatings for mega-bit memories and logic components, and planarizing low ε interlayer dielectrics in complex multi-layer electronic devices to achieve high switching speeds in thin-film multi-chip modules [1].

Recently, photosensitive poly(benzoxazole)s (PBO)s are attracting great attention as photosensitive and thermally stable polymers because of their high mechanical strength, thermal stability, and low dielectric constants. The most promising system is a formation composed of a PBO precursor, poly(*o*-hydroxyamide) and a diazonaphthoquinone sensitizer [2,3]. The hydroxyl side groups of the precursor are desirable as base-soluble functional groups for aqueous alkaline developable photosensitive resists just like novolac-based resists. Furthermore, the hydroxyl groups which increase dielectric constants completely disappears after thermal cyclization of poly(*o*-hydroxyamide).

A chlorine-free synthetic method is generally applied to prepare poly(*o*-hydroxyamide) as a PBO precursor from an aromatic dicarboxylic active diester and bis(*o*-aminophenol) [4]. The reported active ester such as a 1-hydroxybenztriazolyl ester is prepared from an aromatic dicarboxylic acid and 1-hydroxybenztriazole in the presence of condensing agents. Furthermore, the PBO precursor should be isolated to remove by-products and again dissolved in solvents for the resist formulation. To remedy these tedious procedures, we reported the direct resist formulation method for photosensitive PBO, where the polymerization solution from an active diamide and bis(*o*-aminophenol) was used without isolation of poly(*o*-hydroxyamide) [5]. In this procedure, the leaving group of active diamide was removed during thermal treatment of the positive image.

It is of interest to develop a more simple procedure. One of the most important route to PBOs is a solid-state

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polycondensation of aromatic bis(*o*-aminophenol)s with aromatic dicarboxylic diphenylesters [5], which are commercially available. Polycondensation of bis(*o*-aminophenol) with diphenyl isophthalate would be expected to produce poly(*o*-hydroxyamide) by controlling the polymerization conditions.

This paper describes a new synthetic method for the preparation of poly(*o*-hydroxyamide) and development of a positive working photosensitive PBO based on poly(*o*-hydroxyamide) and 1-{1,1-bis[4-(2-diazo-1-(2*H*)naphthalenone-5-sulfonyloxy)phenyl]ethyl}-4-{1-[4-(2-diazo-1(2*H*)naphthalenone-5-sulfonyloxy)phenyl]methylethyl}-benzene (S-DNQ) as a photosensitive compound.

2. Experimental

2.1. Materials

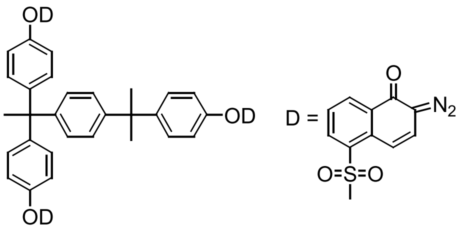
4,4′-(Hexafluoroisopropylidene)bis(*o*-aminophenol) (**5**) and diphenyl isophthalate (**6**) were recrystallized from hexane/tetrahydrofuran (THF) and toluene, respectively. 1-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation from calcium hydride and stored over 4 Å molecular sieves. 1-{1,1-Bis[4-(2-diazo-1-(2*H*)naphthalenone-5-sulfonyloxy)phenyl]ethyl}-4-{1-[4-(2-diazo-1(2*H*)naphthalenone-5-sulfonyloxy)phenyl]methylethyl}-benzene (S-DNQ) was kindly donated by Shipley Japan and used without further purification (Scheme 1). Other reagents and solvents were used as received.

2.2. Model compounds

The model compounds 2-hydroxybenzanilide (**3**) and 2-phenylbenzoxazole (**4**) were prepared to determine their yields and to verify the structure of polymers.

2.2.1. 2-Hydroxybenzanilide (*3*)

The title compound **3** was prepared from **1** and benzoyl chloride in NMP at 25 °C for 1 h. The yield was 95%, mp 170–171 °C (recrystallization from methanol) (lit. [6], 170–171 °C) IR (KBr): ν (cm^{-1}) 3300 (O–H), 1654 (C═O), 1607 (Ar), ^{1}H NMR (DMSO-d_6): δ (ppm) 9.64 (brs, 1H), 9.44 (brs, 1H), 7.98–7.95 (m, 2H), 7.68 (dd, $J = 7.8$ and 1.4 Hz, 1H), 7.60–7.50 (m, 3H), 7.07–7.01 (m, 1H), 6.92 (dd, $J = 8.1$ and 1.5 Hz, 1H), 6.85–6.82 (m, 2H).



Scheme 1.

2.2.2. 2-Phenylbenzoxazole (*4*)

The title compound was prepared from **1** and benzoic acid in polyphosphoric acid at 160 °C for 2 h. The yield was 94%, mp 102–103 °C (lit. [7], 102–104 °C). IR (KBr): ν (cm^{-1}) 1615 (C═N), 1552 (oxazole). ^{1}H NMR (DMSO-d_6): δ (ppm) 8.23–8.20 (m, 2H), 7.83–7.77 (m, 2H), 7.66–7.60 (m, 3H), 7.49–7.39 (m, 2H).

2.3. Model reactions of o-aminophenol (*1*) and phenyl benzoate (*2*)

A solution of **1** (0.109 g, 1.0 mmol) and **2** (0.198 g, 1.0 mmol) in NMP (2 ml) was stirred at 185 °C for 6 h under N$_2$ and then cooled to room temperature. To this solution was added 1,1-bis(3,4-dimethylphenyl)ethane (0.238 g 1.0 mmol) as an internal standard compound. The yields of **3** and **4** were determined by ^{1}H NMR spectroscopy.

2.4. N,N′-Bis(2-hydroxyphenyl)isophthalamide

The title compound was prepared from **1** and isophthaloyl chloride in NMP at 25 °C for 1 h. The yield was 95%, mp 241–243 °C (recrystallization from methanol). IR (KBr): ν (cm^{-1}) 3300 (OH), 1631 (C═O), and 1608 (Ar). ^{1}H NMR (DMSO-d_6): δ (ppm) 9.60 (brs, 4H), 8.51 (s, 1H), 8.12 (d, $J = 8.0$ Hz, 2H), 7.73–7.67(m, 3H), 7.10–7.04 (m, 2H), 6.97–6.95 (m, 2H), 6.90–6.84 (m, 2H). Anal. Calcd for $C_{20}H_{16}N_2O_4$: C, 68.96%; H, 4.63%; N, 8.04%. Found: C, 68.90%; H, 4.74%; N, 7.83%.

2.5. 2,2′-m-Phenylene-bis(benzoxazole)

The title compound was prepared from **1** and isophthalic acid in polyphosphoric acid at 160 °C for 2 h. The yield was 95%, mp 227–228 °C (lit. [7], 227–228 °C). IR (KBr): ν (cm^{-1}) 1635 (C═N), 1542 (oxazole), 798 (Ar). ^{1}H NMR (DMSO-d_6): δ (ppm) 8.99 (brs, 1H), 8.43 (d, $J = 7.9$ Hz, 2H), 7.98–7.78 (m, 5H), 7.52–7.43 (m, 4H).

2.6. 2,2′-Hexafluoroisopropylidene-bis(3-N-benzoylamino-4-hydroxybenzene)

This compound was prepared from **5** and benzoyl chloride in NMP at 25 °C for 1 h. The yield was 98%, mp > 300 °C. IR (KBr): ν (cm^{-1}) 3414 (NH), 3150 (OH), 1647 (C═O), 1600 (Ar), 1252 (CF$_3$). ^{1}H NMR (DMSO-d_6): δ (ppm) 10.29 (s, 2H), 9.51 (s, 2H), 7.98–7.96 (m, 6H), 7.64 (m, 6H), 7.03 (brs, 4H). Anal. Calcd for $C_{29}H_{20}F_6N_2O_4$: C, 60.63%; H, 3.51%; N, 4.88%. Found: C, 60.23%; H, 3.79%; N, 4.81%.

2.7. 2,2′-Hexafluoroisopropylidene-bis(benzoxazole)

This compound was prepared from **5** and benzoic acid in polyphosphoric acid at 160 °C for 2 h. The yield was 93%, mp 185–186 °C (recrystallization from DMF/H_2O). IR (KBr): ν (cm^{-1}) 1628 (C=N), 1615 (Ar), 1556 (oxazole), 1252 (CF_3). ^{1}H NMR (DMSO-d_6): δ (ppm) 8.24–8.20 (m, 4H), 7.92 (d, $J = 8.9$ Hz, 2H), 7.81 (s, 2H), 7.69–7.61 (m, 6H), 7.41 (d, $J = 8.9$ Hz, 2H). Anal. Calcd for $C_{29}H_{16}F_6N_2O_2$: C, 64.69%; H, 3.00%; N, 5.20 %. Found: C, 64.83%; H, 3.09%; N, 5.25%.

2.8. Synthesis of poly(o-hydroxyamide)

Monomers **5** (0.636 g, 2.0 mmol), **6** (0.732 g, 2.0 mmol), and NMP (5.6 ml) were placed in a 10 ml round-bottomed flask under N_2. The solution was heated at 205 °C for 12 h, and poured into an aqueous methanol solution (9:1 in volume ratio 200 ml) to precipitate the polymer. The obtained polymer was washed with water and dried in vacuo over P_2O_5. The yield was 99%. IR (KBr): ν (cm^{-1}) 3300 (OH), 1654 (C=O), 1608 (Ar), and 1253 (CF_3). ^{1}H NMR (DMSO-d_6): δ (ppm) 10.0 (brs, 2H), 9.62 (s, 2H), 8.51 (s, 1H), 8.12 (d, $J = 8.0$ Hz, 2H), 7.85 (s, 1H), 7.64 (t, $J = 8.0$ Hz, 1H), 7.01 (brs, 4H).

2.9. Dissolution rate

S-DNQ was added to a polymerization solution (30 wt%, of the total solid) to construct a photosensitive polymer. The polymer film spin-cast on a silicon wafer was pre-baked at 110 °C for 3 min, and then exposed to a filtered super-high pressure mercury lamp. The exposed film was developed with a 2.38 wt% aqueous tetramethylammonium hydroxide (TMAH) solution at 25 °C. The changes in the film thickness against the exposure energy were measured with a Dectak^3 surface profiler.

2.10. Photosensitivity

A 1.3 μm-thick polymer film on a silicon wafer was exposed to radiation at a wavelength of 436 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 a normalized film thickness against exposure energy. Image-wise exposure through a mask was carried out in a contact-printing mode.

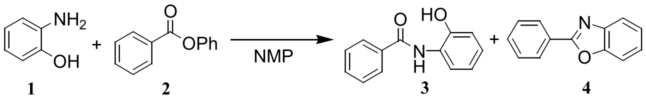
2.11. Measurement

The infrared spectra were recorded on a Horiba FT-210 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker GPX300 (300 MHz) spectrometer. UV spectra were obtained on a Jasco V-650 spectrophotometer. Thermogravimetry were performed on a Seiko thermal analyzer at a heating rate of 10 °C/min. Molecular weights were determined by a gel permeation chromatograph (GPC) with polystyrene calibration using a Hitachi HPLC D-7100-G equipped with TSK gel column at 40 °C in *N*,*N*-dimethylformamide containing 0.01 mol/l lithium bromide. The film thickness was measured by a Dektak surface profiler (Veeco Instrument Inc).

3. Results and discussion

3.1. Model reaction

Prior to polymer synthesis, the reaction of **1** with **2** was performed to determine whether compound **3** was formed in quantitative yield to constitute a polymer forming reaction. The reaction was carried out in NMP (Eq. (1))



(1)

The results are summarized in Table 1. Condensation proceeded at 165 °C for 6 h, giving **3** in 75% yield. A quantitative yield of **3** was obtained at 185 °C for 6 h, and the prolonged reaction time for 24 h at this temperature produced thermally cyclized compound **4** in 35% yield. The yields of **3** and **4** were determined by ^{1}H NMR spectra of the reaction solution using 1,1-bis(3,4-dimethylphenyl)ethane as an internal standard. Ortho protons of benzoylamino group for **3** and phenyl group for **4** were appeared at around 8.20 and 7.94 ppm, respectively. The yields of **3** and **4** were calculated with the integration ratios of those signals to the dimethyl protons (1.5 ppm) of the internal standard compound.

3.2. Polymer synthesis

Based on the results of the model reactions, the synthesis of poly(*o*-hydroxyamide) **7** was carried out with **5** and **6** in

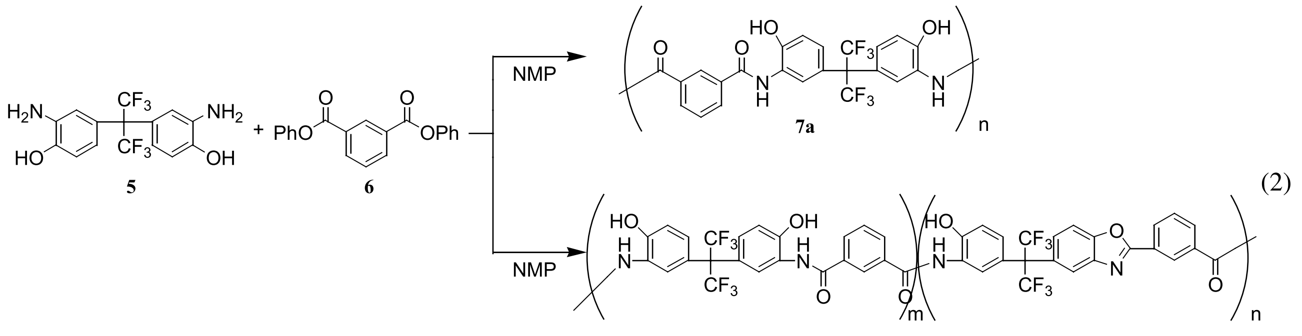
Table 1
Model reaction of **1** and **2**

Reaction temperature (°C)	Time (h)	Yield (%)[a]	
		3	**4**
165	6	75	0
185	2	73	0
185	4	89	0
185	6	97	0
185	24	64	35

Model reaction was carried out with each compound (1 mmol) in NMP (2 ml) under nitrogen.

[a] Determined by ^{1}H NMR.

NMP at 185 and 205 °C (Eq. (2))



5 6 7a 7b, c (2)

Polycondensation at 185 °C for 6 h proceeded smoothly, producing polymer **7a** with a number average-molecular weight of 4500. On the other hand, polymers **7b** and **7c** containing partly benzoxazole units were produced at 185 °C for 24 h and at 205 °C for 12 h, respectively (Table 2).

Polymer **7a** was defined as poly(*o*-hydroxyamide) by IR and ^{1}H NMR spectroscopy. The IR spectrum of **7a** exhibited characteristic absorptions at 3300, 1654, 1253 cm^{-1} due to the O–H, C=O (amide), and C–F stretchings, respectively.

To clarify the structure of the polymer, model compounds were prepared from isophthalic acid and *o*-aminophenol, or **5** with benzoic acid. The data in Scheme 2 show the chemical shifts of aromatic protons in ^{1}H NMR spectra.

The ^{1}H NMR spectrum of **7a** is presented in Fig. 1. The inset of Fig. 1 shows the assignment of each resonance. All peaks were well assigned to the expected polymer structure. Several peaks were observed at 6.6–7.5 ppm (peaks 8, 9 and 11) that would be derived from the end phenyl groups.

Fig. 2 shows the ^{1}H NMR spectrum of **7c** with the assignment of each resonance. The assignment of these

Table 2
Polymerization of **5** and **6**

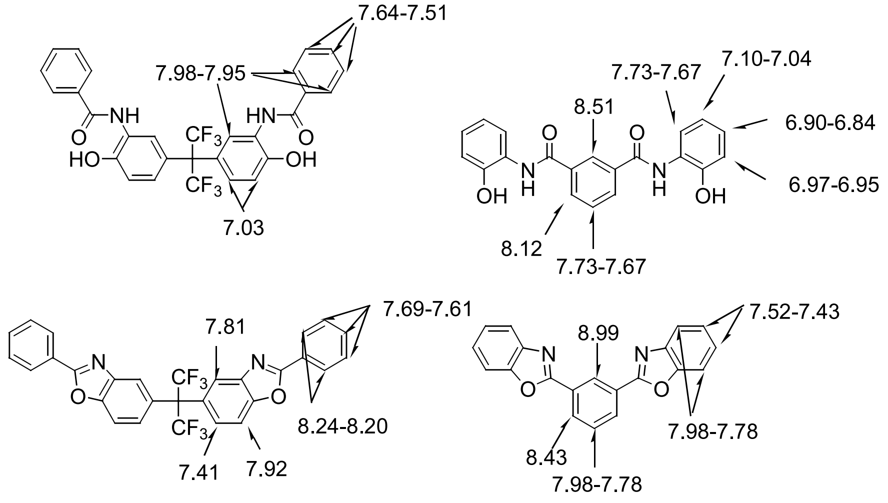
Polymer	Reaction conditions		Yield (%)[a]	M_n[b]	M_w/M_n[b]	Polymer composition[c], $m:n$
	Temperature (°C)	Time (h)				
7a	185	6	99	4500	1.4	100:0
7b	185	24	99	7600	1.5	82:18
7c	205	12	99	8000	1.5	78:22

Polymerization was carried out with each monomer (2 mmol) in NMP (5.3 ml) under nitrogen.

[a] Precipitated by MeOHaq (MeOH/H_2O = 9:1).

[b] Estimated by GPC based on PSt in DMF.

[c] Determined by ^{1}H NMR.



Scheme 2.

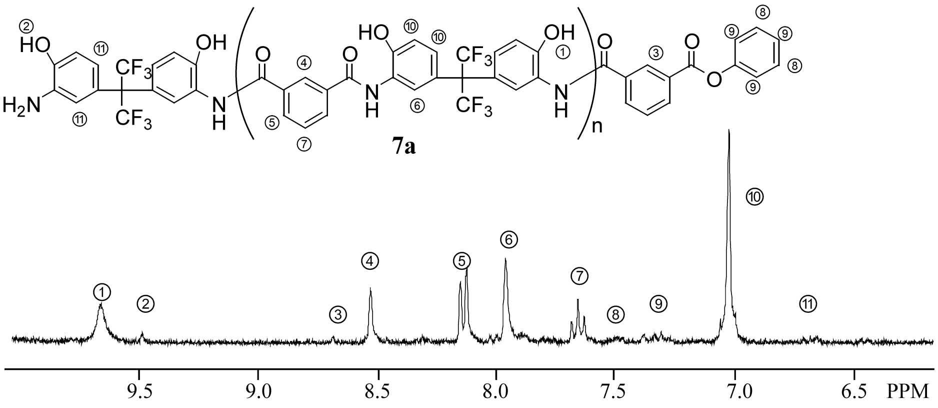


Fig. 1. ^{1}H NMR spectrum of polymer **7a** in DMSO-d_6.

resonances was performed with the aid of model compounds along with the use of spectral simulation software. New peaks due to the partial formation of benzoxazole appeared at 9.83 (peak 2, hydroxyl protons) and 8.77 ppm (peak 4, phenyl protons). The contents of benzoxazole units were calculated with the integration ratios of these signals to hydroxyl groups (peak 3) of **7c**.

3.3. Lithographic evaluation

A photosensitive PBO precursor solution was prepared by adding a photoactive compound S-DNQ to the polymerization solution. To clarify the effect of S-DNQ on the solubility of the films obtained from several polymers **7**, the solubility of spin-cast polymer **7** films and those containing 30 wt% S-DNQ in the developer (2.38 wt% TMAH) was estimated by measuring the film thickness after development. The film spin-cast on silicon wafers were pre-baked at 110 °C for 3 min, and then exposed to a filtered super pressure mercury lamp (436 nm, 200 mJ cm^{-2}). The effect of the dissolution inhibition of S-DNQ was not observed for polymer **7a**. This behavior may be attributed to the low molecular weights of polymer **7a** that indicates the presence of many *o*-aminophenol end-groups. On the other hand, polymer **7b** and **7c** films were easily soluble in the developer and the addition of S-DNQ apparently suppressed the solubility of the polymer films. Decreasing the content of hydroxyamide moieties by the formation of benzoxazole units in the main chains allowed for better control of the dissolution rate (Fig. 3). Polymer **7c** compared to polymer **7b** gave the better dissolution contrast. These results indicated that polymer **7c** would be the suitable matrix polymer.

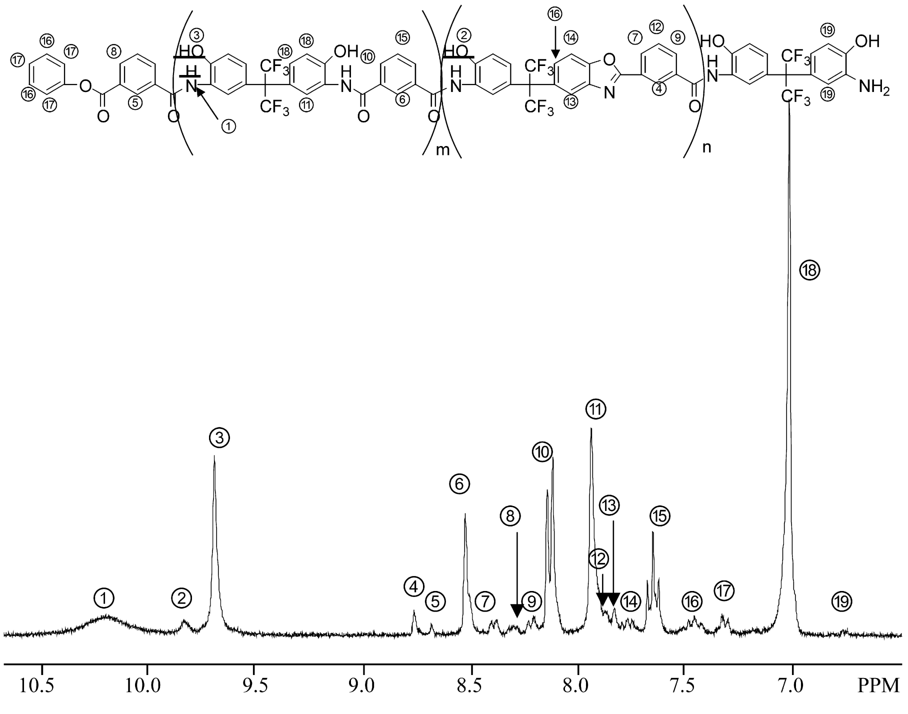


Fig. 2. ^{1}H NMR spectrum of polymer **7c** in DMSO-d_6.

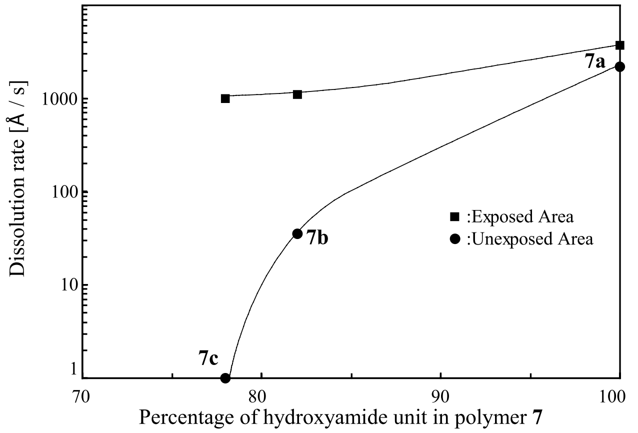


Fig. 3. Dissolution rate of polymer **7** with 30 wt% S-DNQ using 2.38 wt% aqueous TMAH solution as a developer. Exposure dose: 200 mJ cm^{-2}.

Then, the dissolution behavior of the exposed (200 mJ cm^{-2}) and unexposed areas using polymer **7c** was investigated. The effect of S-DNQ loading on the dissolution rate in the developer at room temperature is shown in Fig. 4. The dissolution rate of the unexposed area decreased gradually with increasing S-DNQ contents. On the other hand, the solubility of the exposed area remained almost unchanged. The difference of the dissolution rates between the exposed and unexposed areas reached almost 10^3 times with 30 wt% S-DNQ loading.

Then, a resist system consisting of polymer **7c** and S-DNQ (30 wt%) was formulated as described above. The sensitivity curve for a 1.3 μm-thick polymer film **7c** shown in Fig. 5 was consistent with the dissolution behavior studied above, showing a sensitivity (D^0) and contrast (γ^0) were 110 mJ cm^{-2} and 5.0, respectively.

Fig. 6 shows a scanning electron micrograph of the contact printed positive image after exposure of 200 mJ cm^{-2} light. The resist was capable of resolving a 8 μm feature when a 2.2 μm thick film was used.

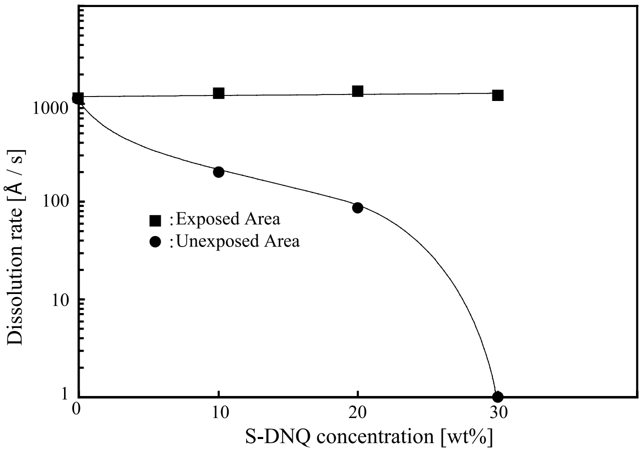


Fig. 4. Dissolution rate of polymer **7c** with different S-DNQ content and using 2.38 wt% aqueous TMAH solution. Exposure dose: 200 mJ cm^{-2}.

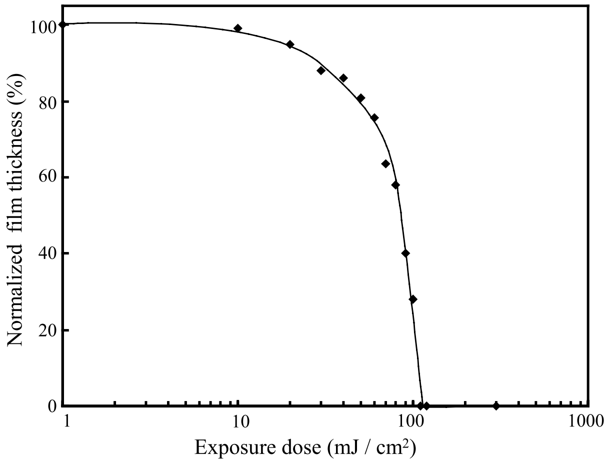


Fig. 5. Exposure characteristic curve for the system of polymer **7c** and 30 wt% S-DNQ.

The printed film was converted to the PBO film by heating at 150 °C for 20 min, 250 °C for 30 min, and 350 °C for 30 min. The formation of the PBO was confirmed by the IR spectrum, where the characteristic oxazole ring absorption at 1635 cm^{-1} appeared and the absorptions due to the hydroxyl and amide carbonyl groups at 3300 and 1654 cm^{-1}, respectively, in polymer **7c** disappeared. A strong film was obtained by this thermal treatment because of further solid-state polycondensation.

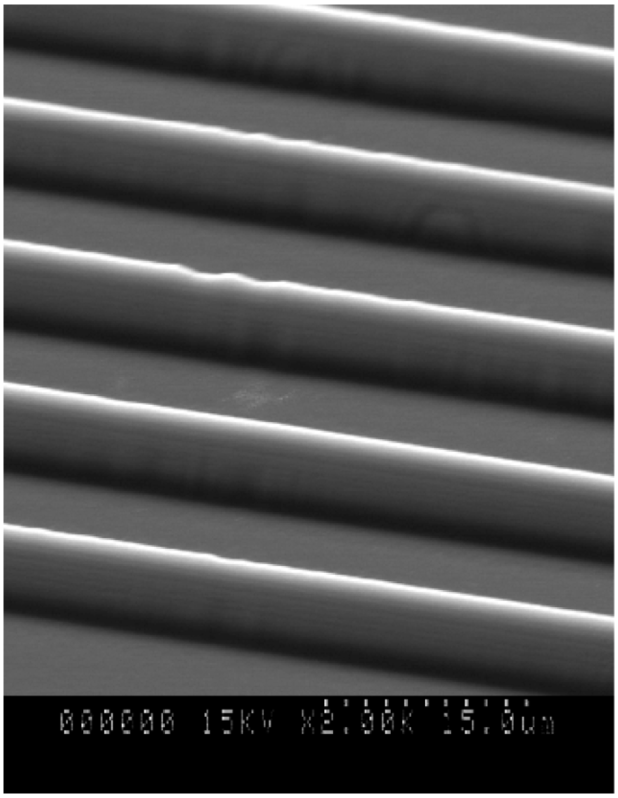


Fig. 6. Scanning electron micrograph of positive pattern from polymer **7c** containing 30 wt% S-DNQ (contact-printed).

4. Conclusion

Polymer **7c** with a number average-molecular weight of around 8000 was easily prepared by the high-temperature solution condensation of bis (*o*-aminophenol) **5** with commercially available diphenyl isophthalate **6** in NMP. The resist system simply prepared by adding S-DNQ to the polymerization solution functioned as a positive type photosensitive resist. Its sensitivity and contrast were 110 mJ cm^{-2} and 5.0 with 436 nm light, respectively. This direct resist formulation method from the polymerization solution is very simple and advantageous compared to the conventional multi-step procedure for PBO resist.

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