

A Novel Water-Soluble Photoinitiator for the Acrylic Photopolymerization Type Resist System

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A novel water-soluble photoinitiator, sodium 4-[2-(4-morpholino)benzoyl-2-dimethylamino]butylbenzenesulfonate (MBS), was synthesized by sulfonation of 2-benzyl-2-(dimethylamino)-1-(4-morpholinophenyl)-1-butanone (BDMB) for “environmentally friendly” and “completely water-soluble” resist systems. MBS showed sufficient solubility in water and the same high sensitivity as BDMB. Novel water-soluble photopolymerization resist systems, composed of MBS, polyfunctional acrylate monomers, and water-soluble polymers, were also evaluated. Among the commercially available polyfunctional acrylate monomers, a trifunctional epoxy acrylate monomer from glycerol (DA-314) showed good solubility in water. The sensitivity of this resist system to irradiation of 365-nm UV light was 1.5 mJ/cm² at 2- μ m film thickness. Advantages of the resist are no need for any organic solvent or any alkaline developer. The chemistry of MBS was investigated by IR and photolysis. It was proved that the radical generation mechanism of MBS was the same as for BDMB.

1. Introduction

The history of water-soluble photoinitiation materials goes back to the 19th century.¹ Chromium compounds are efficient initiators as photo-cross-linkers to poly-(vinyl alcohol) (PVA) and are still widely used in the stencil and phosphor screening process for cathode ray tube production.² However, these materials have led to short shelf life, due to dark reactions, and have created environmental problems. Recently, chromium-free water-soluble photoinitiator systems have gained increasing attention. Several water-soluble photoinitiators such as benzophenone derivatives^{3,4,5} and thioxanthone derivatives⁶ are known, but their performance is far from complete. Consequently, conventional “water-soluble photoresists” actually means water-developable; usually these photoresists are coated using organic solvents or used as dry films. Considering their potential as fire hazards and the need for environmentally friendly systems, completely water-soluble resist systems, meaning supplied as aqueous solutions, are strongly desirable with the increased attention to environmental concerns.⁷

On the other hand, hundreds of organic photoinitiators, almost all of them insoluble in water, have been developed.⁸ Among the already-known photoinitiators, 2-benzyl-2-(dimethylamino)-1-(4-morpholinophenyl)-1-

butanone (BDMB) is one of the best. It shows high sensitivity at the i-line (365 nm).⁸ The easiest way to obtain a water-soluble photoinitiator of high efficiency beyond those already-known is to add polar substituents to BDMB. This paper describes the results of synthesis of a novel water-soluble photoinitiator, sodium 4-[2-(4-morpholino)benzoyl-2-dimethylamino]butylbenzenesulfonate (MBS), from BDMB, and the characteristics of “completely” water-soluble photoresists using MBS.

2. Experimental Section

2.1. Materials. BDMB and 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propan-1-one (I-2959) were obtained from Ciba-Geigy. [3-(3,4-Dimethyl-9-oxo-9H-thioxanthene-2-yl)-2-hydroxypropyl]trimethylammonium chloride (QTX) and *p*-benzoylbenzyltrimethylammonium bromide (BTC) were obtained from Nihon Kayaku Co. The trifunctional monomer epoxy acrylate from glycerol (DA-314) was obtained from Nagase Kasei Co. 2,2,6,6-Tetramethylpiperidinoxyl (TEMPO) was purchased from Aldrich Chemical Co. Inc. *N*-Methyldiethanolamine (MDEA) was purchased from Tokyo Kasei Kogyo Co. Ltd. Poly(vinyl alcohol) (PVA) was obtained from Kuraray Co. Ltd. Polyvinylpyrrolidone (PVP) was obtained from ISP Inc.; the molecular weight (MW) of the PVP used was 2 700 000. Poly(acrylamide-*co*-diacetoneacrylamide) (PAD) was synthesized in our laboratory,⁹ and its MW was 2 000 000. These reagents were used without any further purification.

2.2. Synthesis of Sodium 4-[2-(4-Morpholino)benzoyl-2-dimethylamino]butylbenzenesulfonate (MBS). A chloroform (10 mL) solution of BDMB (7.0 g, 19.1 mmol) was slowly added to fuming sulfuric acid (24.4 g) with stirring at room temperature. Sulfonation immediately proceeded exothermically. The reaction mixture was kept stirring for 1 h and then poured slowly into water (300 mL). Calcium hydroxide (22.0

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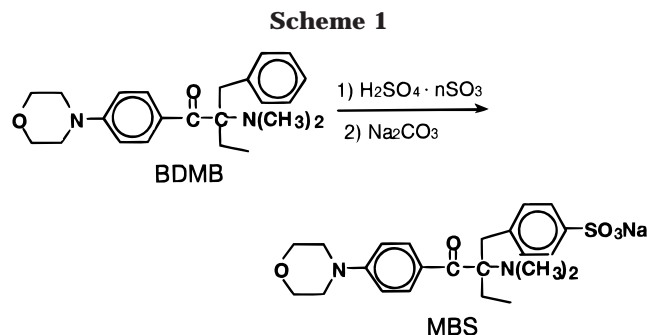
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g, 297 mmol) was added to the solution until it was completely neutralized, and the precipitated calcium sulfate was filtered off. Sodium carbonate (0.764 g, 9.20 mmol) was added to the filtrate and the precipitated calcium carbonate was filtered off. The filtrate was concentrated and chromatographed on activated magnesium silicate using ethyl acetate and ethanol, producing the water-soluble product MBS as a pale yellow powder (6.63 g, 71.4% yield).

2.3. Resist Processing and Characterization. The resists were composed of polymers, a trifunctional monomer, and an initiator. The quantity of the monomer was varied from 70% to 100% on the basis of the weight of the polymer. The quantity of the initiator was varied from 5% to 10% on the basis of the weight of the polymer. Resist solutions were prepared by dissolving the components in water. The resists were spin-coated onto silicon substrates or glass substrates, and the resist films were prebaked at 80 °C for 2 min. Then they were exposed to 365-nm light with a super-high-pressure mercury lamp or a Xe-Hg lamp (USHIO Inc.), and developed in water until the unexposed area disappeared. The film thickness was measured with a profilometer, Alpha-Step 200 (Tencor Instrument Co.).

The infrared spectra were measured with a Perkin-Elmer FT-IR 1720X. The ^1H NMR spectrum was measured with a Varian Mercury 200 or Bruker AMX-500 spectrometer. The UV-vis spectra were measured with a Hitachi U-3410 UV spectrophotometer.

2.4. Photolysis. A 1,4-dioxane (6.0 g) solution containing an excess of TEMPO (150 mg, 0.960 mmol) to MBS was added to an aqueous (1.5 g) solution of MBS (150 mg, 0.409 mmol). The solution was irradiated with a super-high-pressure mercury lamp for 7 h until the MBS disappeared. After the evaporation of 1,4-dioxane, water was added and the mixture was extracted with ethyl acetate. Both the ethyl acetate layer and the aqueous layer were concentrated and the residues were chromatographed on silica gel, respectively. The decomposed products were identified by UV-vis absorption spectra, IR, and NMR.

2.5. Reaction Mechanism Analysis. The photopolymerization reaction was monitored by measuring the difference between IR spectrum in air. Conversion of the acrylic group of the monomer (DA-314) versus exposure dose was estimated by the change of absorbance at 811 cm^{-1} due to $\text{CH}_2=\text{CH}$ twisting.

3. Results and Discussion

3.1. Synthesis of MBS. In general, the simple way to obtain water-soluble photoinitiators is to introduce highly polar groups such as quaternary ammonium salt,

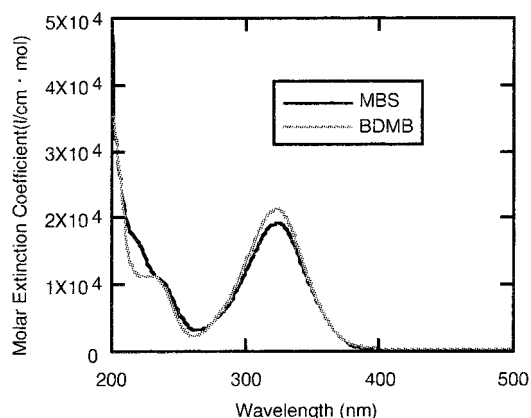


Figure 1. UV and VIS absorption spectra of MBS and BDMB.

carboxylic acid, or sulfonic acid to already-known photoinitiators which are not soluble in water. If the photoinitiator is stable under strongly acidic conditions, sulfonation is a very suitable choice. As BDMB is one of the best UV photoinitiators for organic solvent systems,⁸ sulfonation of BDMB was performed. BDMB was immediately sulfonated in fuming sulfuric acid at room temperature (Scheme 1), without losing the property of radical generation, as described later.

3.2. Identification of MBS. Upon comparing the UV-vis absorption spectra of MBS ($\lambda_{\text{max}} = 324$ nm) to that of BDMB ($\lambda_{\text{max}} = 323$ nm) in methanol (Figure 1), one sees that there are no drastic structural differences between the two. IR and NMR data of MBS are shown in Table 1. The IR absorption peaks at 1014 and 1046 cm^{-1} are assigned to the sulfonic acid group. On the basis of the four doublet absorption peaks in the aromatic region of the ^1H NMR spectrum (Figure 2), it is presumed that MBS has two pairs of para-substituted benzene rings. And this result means that the para position of the benzyl group of BDMB is sulfonated and determines the structure as MBS, as shown in Scheme 1.

3.3. Formulations for Photoresists. The water-soluble photopolymerization type resists were designed as compositions of water-soluble polymers, photoinitiators, and monomers. Poly(vinyl alcohol) (PVA), poly(vinylpyrrolidone) (PVP), and poly(acrylamide-co-diacetoneacrylamide) (PAD) were chosen as the water-soluble polymers. Although the choice of water-soluble monomers was also limited, a trifunctional epoxy acrylate monomer from glycerol (DA-314, Scheme 2) was used. In water, PVP showed the best compatibility with DA-314 as the water-soluble monomer, and PAD followed. On the other hand, PVA was incompatible with DA-314, presumably owing to the too strong hydrophobicity. Accordingly, PVP and PAD are suitable for the photoresist. Resists using PVA showed rough profiles after development, due to phase separation.

Table 1. Analytical Data of MBS

IR, ν (cm^{-1})	^1H NMR, δ (CD_3OD , TMS, ppm)	^{13}C NMR, δ (CD_3OD , ppm)
2968, 2861, 1659, 1596, 1512, 1451, 1382, 1227, 1187, 1128, 1046, 1014, 929, 832	0.63 (3H, ethyl CH_3), 1.97 (2H, ethyl CH_2), 2.37 (6H, $\text{N}(\text{CH}_3)_2$), 3.21 (2H, PhCH_2), 3.31 (4H, morpholino NCH_2), 3.81 (4H, morpholino OCH_2), 6.90 (2H, d, Ar), 7.33 (2H, d, Ar), 7.67 (2H, d, Ar), 8.30 (2H, d, Ar)	10.04 (ethyl CH_3), 28.76 (ethyl CH_2), 36.58 (PhCH_2), 39.38 ($\text{N}(\text{CH}_3)_2$), 48.76 (morpholino NCH_2), 67.77 (morpholino OCH_2), 75.29 (Me_2NC), 114.07, 126.53, 128.98, 132.10, 133.04, 141.41, 143.26 and 155.42 (Ar), 203.26 ($\text{C}=\text{O}$)

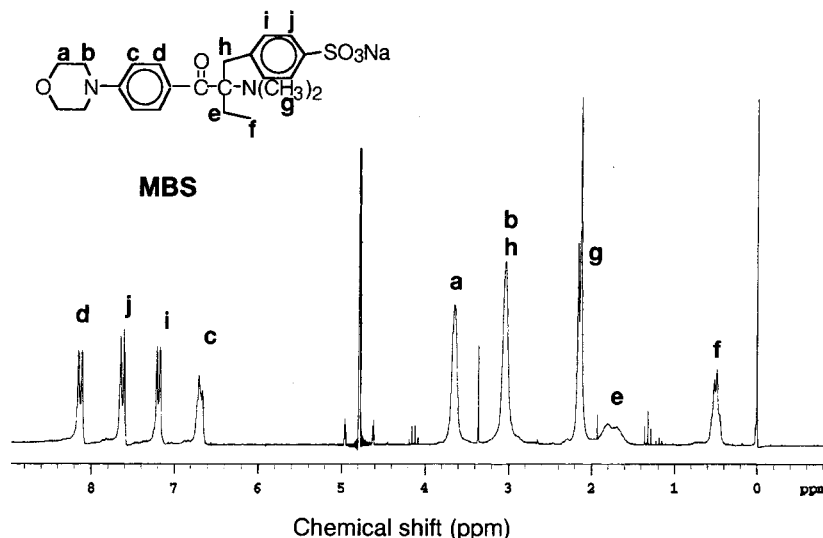


Figure 2. ^1H NMR spectra of MBS in D_2O .

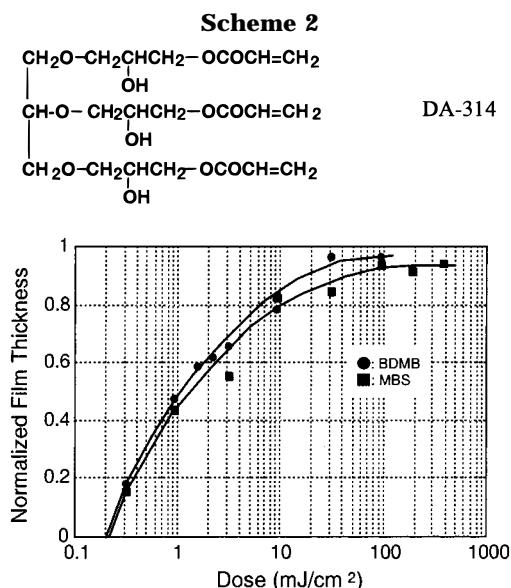


Figure 3. Exposure characteristic curves for resists using MBS and BDMB. PVP/DA-314/initiator = 100/100/5; film thickness, 2000 nm.

3.4. Sensitivity of Photopolymerization Resists.

The sensitivity of resists to MBS as a photoinitiator was compared to that of resists containing BDMB using PVP as a base polymer and 2-methoxyethanol as a casting solvent. As shown in Figure 3, the dose for obtaining the insolubilized film thickness of 50% of the initial resist film thickness (E_{50} , mJ/cm^2) is 1.5 mJ/cm^2 for the MBS resist and 1.1 mJ/cm^2 for the BDMB resist. The MBS resist shows slightly lower sensitivity than the BDMB resist. On the other hand, concerning the contrasts of the resists, they are almost identical. Therefore, it is clear that MBS, as well as BDMB, is a photoinitiator with excellent sensitivity.

Next, MBS was evaluated in a water system and compared to the other already-known water-soluble initiators, BTC, QTX, I-2959, and MDEA, a sensitizer for QTX. The results are shown in Figure 4. BTC and I-2959 are very inefficient as initiators for the resists due to their low absorbance at 365 nm. On the other hand, QTX has a longer absorption band extending to

over 400 nm. In the case of the QTX resist, the addition of MDEA improved the sensitivity (E_{50}) from 800 to 200 mJ/cm^2 . Even after such sensitization,¹⁰ the MBS resist is the best of all.

3.5. Photolysis of Photoinitiator. The preparative photochemistry of BDMB has already been investigated.¹¹ The results of CIDNP (chemically induced dynamic nuclear polarization) spectral analysis and photolysis confirmed that the α -cleavage reaction was the dominant pathway of decomposition of BDMB.

In a similar way as BDMB, photodecomposition of MBS was investigated using TEMPO as a trapping agent. Three compounds, labeled A, B, and C, were isolated after photodecomposition. Compounds A and B were soluble in ethyl acetate but insoluble in water, and C was water-soluble. Their structures were determined as shown in Figure 5. During the irradiation, α -cleavage of MBS occurred and produced a benzoyl radical and an α -aminoalkyl radical. The benzoyl radical was trapped by TEMPO, resulting in compound A. The α -aminoalkyl radical was also trapped by TEMPO, followed by hydrolysis, resulting in compound C. The hydrolysis produced a hydroxylamine, which decomposed to an amino radical and hydroxyl radical, as a result of photoexcitation, then the amino radical combined with the benzoyl radicals, resulting in compound B.

Consequently, it is proved that MBS decomposes to a benzoyl radical and an α -aminoalkyl radical due to the α -cleavage reaction with exposure, as for BDMB.

3.6. Reaction Mechanism Analysis. 1. *Insolubilization Reaction.* To elucidate the nature of the photopolymerization reaction of the resist, the IR spectrum of the resist was measured. Figure 6 shows the spectral difference, owing to photopolymerization, before and after exposure. The differences that appear in Figure 6 are due entirely to the polymerization of DA-314 initiated by the radicals generated from MBS. PAD does not participate in the insolubilization of the resist at all. The decreased bands at 1721 and 1196 cm^{-1} are

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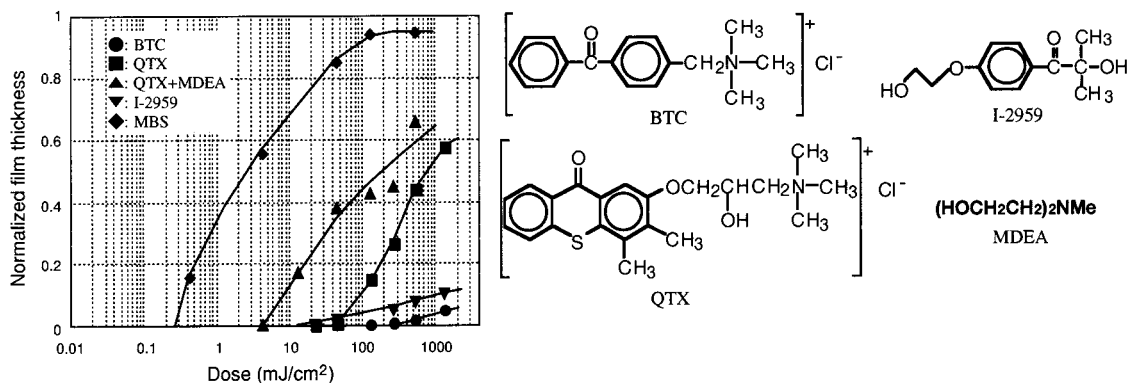


Figure 4. Exposure characteristic curves for resists using water-soluble photoinitiators. PAD/DA-314/Initiator = 100/80/7; film thickness, 2000 nm.

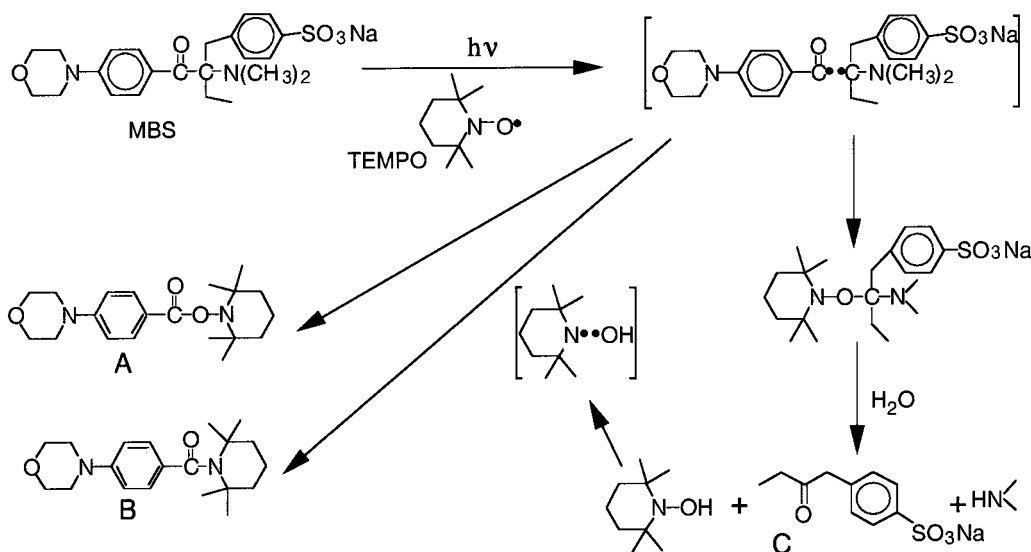


Figure 5. Photolysis of MBS trapping with TEMPO.

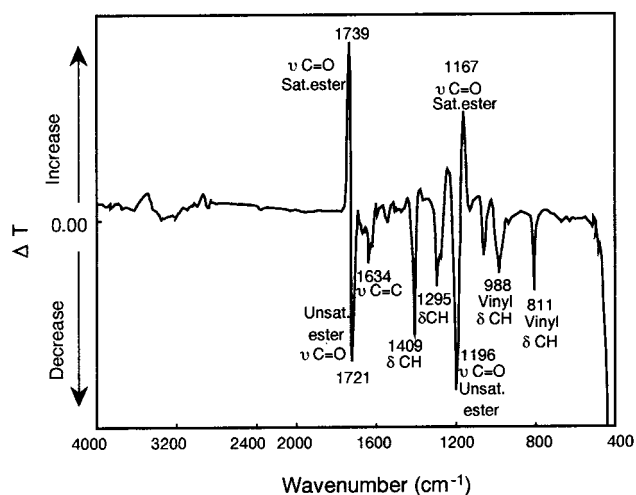


Figure 6. IR difference spectrum of the photopolymerization resist before and after exposure. PAD/MBS/DA-314 = 100/8/80.

assigned to vibration of C=O of the unsaturated ester of DA-314 and the decreased band at 1295 cm^{-1} is assigned to C-H of the unsaturated ester. The decreased bands at 1408, 987, and 811 cm^{-1} are assigned to C=C. The increased bands at 1739 and 1167 cm^{-1} are caused by the polymerization of DA-314. This leads us to believe that resist insolubilization is caused by the formation of a three-dimensional interpenetrating poly-

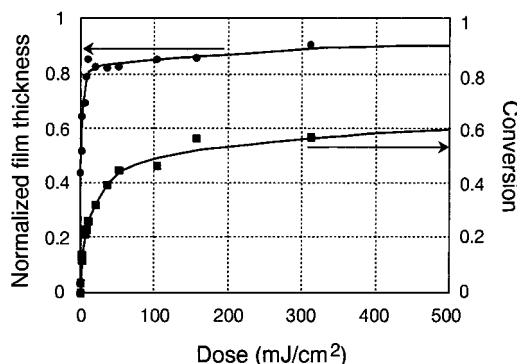


Figure 7. Correlation between resist sensitivity and conversion of monomer.

mer network structures entwining the base polymer chain.

2. Conversion versus Dose. The insolubilization of the resist corresponded to the conversion of the acrylic group of the trifunctional monomer DA-314. The resist composition was PAD/DA-314/MBS = 100/80/7, and the film thickness was 2.2 μm . The result is shown in Figure 7. If 0.8 of normalized film thickness is defined as insolubilized, the required minimum conversion of the acrylate groups for the resist insolubilization is 0.22. On the other hand, the conversion is saturated at 0.64, which means that two acrylic groups of the three of DA-314 can react in the resist film. This might be because the

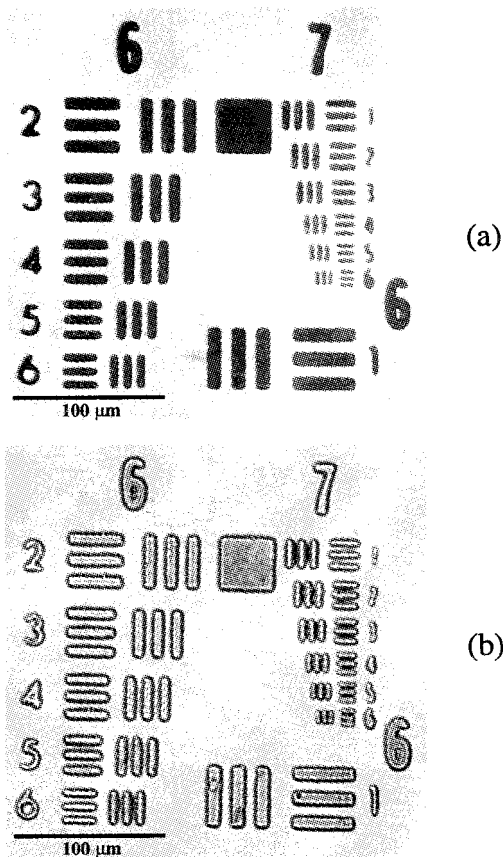


Figure 8. Optical microscope photograph of mask (a) and patterns (b) derived from the photopolymerization resist; thickness, $0.48 \mu\text{m}$; dose, 6.58 mJ/cm^2 ; PAD/PVP/DA-314/MBS = 70/30/80/7.

residual one acrylic group cannot polymerize because the monomer unit loses mobility in the film due to partial polymerization.

3.7. Lithographic Characterization. Patterning of a resist composed of PAD, PVP, MBS, and DA-314 was carried out with a Xe-Hg lamp by contact exposure. PVP was added to the resist to improve the homogeneity of the film. The result is shown in Figure 8. Figure 8a shows the exposure mask and Figure 8b shows the obtained pattern with a dose of 6.58 mJ/cm^2 . The thickness after development is $0.48 \mu\text{m}$. The resolution is limited up to $4 \mu\text{m}$ by swelling of the film during development in water.

4. Conclusion

A novel water-soluble photoinitiator, MBS, was synthesized by sulfonation of BDMB, and the chemical structure of MBS was determined by IR and NMR spectrum. Completely water-soluble photoresists composed of water-soluble polymers, epoxy-acrylate monomer DA-314, and MBS were developed and evaluated. The sensitivity of the photoresists containing MBS was as high ($E_{50} = 1.5 \text{ mJ/cm}^2$) as that of the photoresists containing BDMB and much higher than those using the other water-soluble initiators. It was confirmed that insolubilization of the new resists was caused by photopolymerization of the monomer. Photolysis using TEMPO, a radical trapping reagent, proved that the dominant pathway of MBS decomposition is that of α -cleavage. The resolution of the resist was limited to $4 \mu\text{m}$ at $0.48 \mu\text{m}$ of film thickness because of swelling of PAD in water.

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