

Synthesis and Characterization of *N*-Methyl-2,6-dinitrodiphenylamine-4-diazonium Salt and Its Diazo-resin

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ABSTRACT: A new photosensitive agent, dinitro derivatives of diphenylamine diazonium salt (*N*-methyl-2,6-dinitrodiphenylamine-4-diazonium salt, MDNDDS), and its diazo-resin were synthesized. Their photoreactivities and thermostabilities were investigated. Our results revealed that MDNDDS and MDNDDS-resin exhibited greatly improved thermostability both in solid state and in coating film comparing with the conventional unsubstituted and mononitro substituted diphenylamine diazonium salts (DDS and MNDDS, respectively) and their diazo-resins. The photosensitivity of MDNDDS was found to be slightly lower than DDS but still comparable with MNDDS. As a result of its improved thermostability, both MDNDDS-resin as a photosensitive agent and lithographic printing plate prepared by MDNDDS-resin will have a long shelf-life, which is very important to reduce waste and factory running-cost. MDNDDS also has a maximum absorption wavelength (λ_{max}) at 425 nm, which means that an iodine gallium lamp (main emission wavelength $\lambda_{\text{em}} = 420$ nm), is better than conventional mercury lamp ($\lambda_{\text{em}} = 360$ nm), to be used as the irradiation source in the photoimaging process. Compared with the mercury lamp, iodine gallium lamp is cheaper and greener. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: substituted diphenylamine diazonium salt; synthesis; imaging; photochemistry; thermostability

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INTRODUCTION

Diazo-resin (DDS-resin), the polymerization product of diphenylamine-4-diazonium salt (DDS) and paraformaldehyde, is a very important photosensitive material for presensitized (PS) or computer-to-plate (CTP) lithographic printing, waterless lithographic printing, and screen printing. A lot of patents on its application have also been documented.^{1–8} One of the main disadvantages of conventional DDS and DDS-resin is that their thermostabilities are usually poor,^{9,10} which makes these photosensitive materials based lithographic plate or coatings have a rather short shelf life (a few more months depending on environmental humidity and temperature). So how to improve the thermal stability of diazo-resin is one of the key issues to reduce waste and plant operating cost. At present, to improve the thermal stability of the diazo-resin, the researches have mainly focused their efforts on the design and synthesis of substituted diphenylamine diazonium salt. It has been demonstrated that introduction of a substituent group on the diazobenzene moiety of DDS can greatly improve its thermal stability. For example, 3-methoxy-diphenylamine-4-diazonium salt (MDDS) developed by Hoechst Company has a very good thermostability,^{1,6,11} but unfortunately its preparation process is complex and its price is still high.¹¹ 2-Sulphonic diphenylamine-4-diazonium salt has a

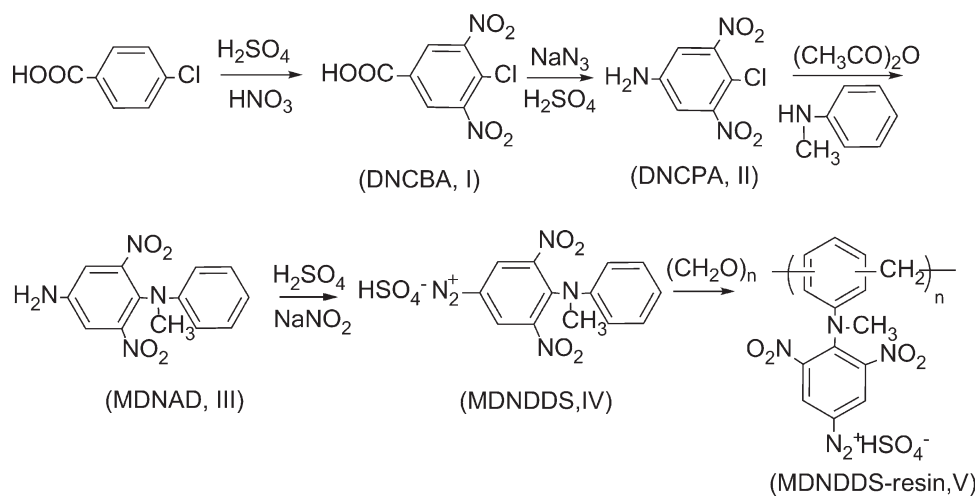
thermostability similar to that of MDDS but its intramolecular salt structure makes it difficult to be dissolved in aqueous solution and most organic solvents,⁹ which greatly reduce its feasibility in practical applications. Cao's group prepared *N*-methyl-2-nitro-diphenylamine diazonium salt (MNDDS) and reported that the stability of MNDDS was better than DDS and the authors proposed that introduction of a nitro group into diazobenzene moiety of DDS might account for the observed stability improvement via hydrophobic effects.^{10,12} Inspired by their work, we rationalize that introduction of the second nitro substituent to the diazobenzene may further improve the thermostability. However, synthesis of multisubstituted diphenylamine diazonium is challenging, and what effects will be brought to the performance of the resulting photosensitive agent. To our best knowledge, there is no published work addressing these issues.

Herein, we report the synthesis and characterization of MDNDDS and its diazo-resin and detailed investigations of their photoreactivities and thermostabilities.

EXPERIMENTAL

Materials

4-Chlorobenzoic acid, *N*-methylaniline were purchased from Alfa Aesar (Tianjin, China). Sulfuric acid, 20% oleum, acetic



Scheme 1. The synthetic scheme of MDNDDS and its diazo resin.

anhydride, sodium carbonate, 36% hydrochloric acid, ethanol, sodium nitrite, paraformaldehyde, Na_2SiO_3 were obtained from Beijing Chemical Reagents Company (Beijing, China). 98% Nitric acid, sodium azide, 1,2-dichloroethane, ZnCl_2 , dimethyl formamide (DMF), benzyl alcohol, sodium dodecyl sulfate were purchased from Beijing Ouhe Technology. (Beijing, China). DDS was obtained from TCI (Shanghai, China) Development. DDS-resin was synthesized according to Ref. 13. (MNDDS), its diazo resin and the binder resin were synthesized according to Ref. 10. The electrolytic grained and anodized aluminum plate was obtained from Taixing city East Industrial Corporation (Taixing, China). All commercially available reagent-grade chemicals were used without further purification unless noted otherwise.

Measurement

The ^1H and ^{13}C NMR spectra of the synthesized compounds were recorded on a Bruker Avame PRX400 spectrometer. Elemental analysis was performed by Vario EL. The molecular weight of the diazo resin was determined by gel permeation chromatography (GPC) (YL9100, Young In Scientific, Korea Republic) with the column (WAT011535 Ultrahydrogel 1000, Waters), water as the mobile phase and polyethylene glycol as the standard. The decomposition temperature (T_d) of samples was detected by TG-DSC [thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) 1/1100 SF, METTLER-TOLEDO, Switzerland] at a heating rate of 10 K/min under a nitrogen gas flow. Real-time infrared spectroscopy (RTIR) was recorded on Nicolet 5700 spectrometer (Nicolet Instrument, Thermo Company). The irradiation was performed with the UV spot light source (Rolence-100 UV, Taiwan, China) and the light intensity at 365 nm and 420 nm was detected by radiometry (UV-A, Beijing Normal University, China). UV-VIS spectra were recorded with a Cintra10e spectrophotometer. The solution of sample was exposed to irradiation source of a high pressure mercury lamp (GY-13, Tuopu Tianjin Instrument, China). The plate maker machine is SBK-III from Qufu Normal University (China).

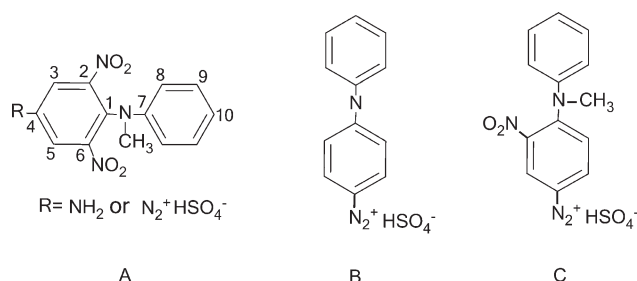
Synthesis of MDNDDS and its Diazo resin

The synthetic route of MDNDDS and its diazo resin was shown in Scheme 1.

3,5-Dinitro-4-chlorobenzoic Acid (DNCBA, I)¹⁴. 4-Chlorobenzoic acid (60 g, 0.38 mol) was added in batches to concentrated sulfuric acid (98%) 240 g in a 500 mL four neck round-bottom flask. Concentrated nitric acid (98%; 60 g, 0.95 mol) was added dropwise into the mixture and the temperature was kept below 110°C , then the reaction mixture was stirred at 125°C for 4 hours. Then the mixture was cooled and poured into ice, I (83 g, yield 90%) as precipitate with off-white color was obtained by filtration. ^1H NMR (400 Hz, acetone- d_6 , δ): 8.65 (s, 2H, Ar H); IR (KBr): $\nu = 2660\text{ cm}^{-1}$, 2524 cm^{-1} (w, COOH); 1708 cm^{-1} (vs; C=O), 1613 cm^{-1} , 1572 cm^{-1} , 1546 cm^{-1} (vs, Ar); 1352 cm^{-1} , 1300 cm^{-1} , 1272 cm^{-1} (s, Ar- NO_2); mp: $129\text{--}131^\circ\text{C}$.

3,5-Dinitro-4-chlorophenylamine (DNCPA, II). I (61 g, 0.25 mol) was added to a mixture of 20% oleum 150 mL and 1,2-dichloroethane 200 mL. Then sodium azide (18.5 g, 0.28 mol) was added in batches to the mixture in 15 min under stirring with the temperature below 25°C . The reaction mixture was heated carefully to reflux under stirring for 2 h and cooled to room temperature, then the 1,2-dichloroethane layer was removed. The rest solution was poured into ice, and the precipitate was collected by filtration and washing with water to give II (43 g, yield 80%) as yellow-orange powder crystals.¹⁵ ^1H NMR [400 Hz, dimethyl sulfoxide (DMSO)- d_6 , δ): 7.38 (s, 2H, Ar H), 6.57 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO- d_6 , δ): 149.49 (C- NO_2), 149.26 (C- NH_2), 111.80 (C-Cl), 100.61 (C-H); IR (KBr): $\nu = 3474\text{ cm}^{-1}$, 3382 cm^{-1} (m, N-H); 1637 cm^{-1} (s, N-H), 1532 cm^{-1} (vs, Ar); 1359 cm^{-1} (s, Ar- NH_2); mp: $176\text{--}177^\circ\text{C}$.

N-Methyl-2,6-dinitro-4-aminodiphenylamine (MDNAD, III). II (70 g, 0.32 mol) was added into acetic anhydride (84 mL, 0.89 mol), and heated to reflux at 135°C for 1 h. After cooled to room temperature, the mixture was poured into water. The acetylate of II (83 g, yield 99%) as white color powder precipitate was collected by filtration and washed with water.¹⁶ The acetylate of II (83 g, 0.32 mol) and grounded sodium carbonate (19.6 g, 0.18 mol) were added into *N*-methylaniline (244 mL, 2.18 mol) under stirring. The reaction mixture was heated to 150°C for 5 h and cooled over night.¹⁷ The obtained precipitate



Scheme 2. The chemical structures of A (MDNAD/ MDNDDS), B (DDS) and C (MNDDS).

was collected by filtration and washed with water, then added into mixed solution of concentrated hydrochloric acid (200 mL) and ethanol (300 mL), heated to reflux for 3 h and cooled.^{18,19} The hydrochloride of **III** (74.3 g, yield 72%) as red brown lamellar crystals was obtained by filtration and washing with little water. ¹H NMR (400 MHz, DMSO-*d*₆, δ): 7.38 (s, 2H, Ar H), 7.11 (t, *J* = 8 Hz, 2H; Ar H), 6.69 (t, *J* = 7 Hz, 1H; Ar H), 6.43 (d, *J* = 8 Hz, 2H; Ar H), 3.10 (s, 3H, CH₃); ¹³C NMR

(100 MHz, DMSO-*d*₆, δ) (carbon atoms were labeled as shown in Scheme 2, structure A): 150.57 (C7), 149.18 (C-NH₂), 147.37 (C-NO₂), 128.93 (C9), 119.11 (C1), 117.82 (C10), 112.00 (C3), 111.86 (C8), 40.06 (H₃C-N); IR (KBr): ν = 3449 cm⁻¹, 3372 cm⁻¹ (m, N-H), 2825 cm⁻¹ (w, H₂C-H), 1599 cm⁻¹ (m, N-H), 1542 cm⁻¹, 1495 cm⁻¹ (vs, Ar), 1352 cm⁻¹ (s, Ar-NH₂).

N-Methyl-2,6-dinitrodiphenylamine-4-diazonium Salt (MDNDDS, IV). Hydrochloride salt of **III** (32.5 g, 0.1 mol) was added to the mixture of 240 g crashed ice and 588 mL 10% sulfuric acid, and the suspension was kept at 0–5°C in an ice water bath. Then sodium nitrite (13.8 g, 0.2 mol) in 65.7 mL water was added dropwise under stirring and the reaction was continued at this temperature for 2 h. The raw product of **IV** precipitated out from the solution and was collected by filtration, then it was dissolved in 2 L water and insoluble impurities were removed by filtration. ZnCl₂ (108 g in 200 mL water) was added into the filtrate, and 1/2 ZnCl₂ complex of MDNDDS **IV** (32.2 g, yield 65%) as red precipitate was obtained by filtration. ¹H NMR (400 MHz, D₂O, δ) [¹H NMR spectra is shown in Figure 1(a)]: 9.08 (s, 2H, Ar H), 7.33–7.22 (m, 5H, Ar H), 3.38

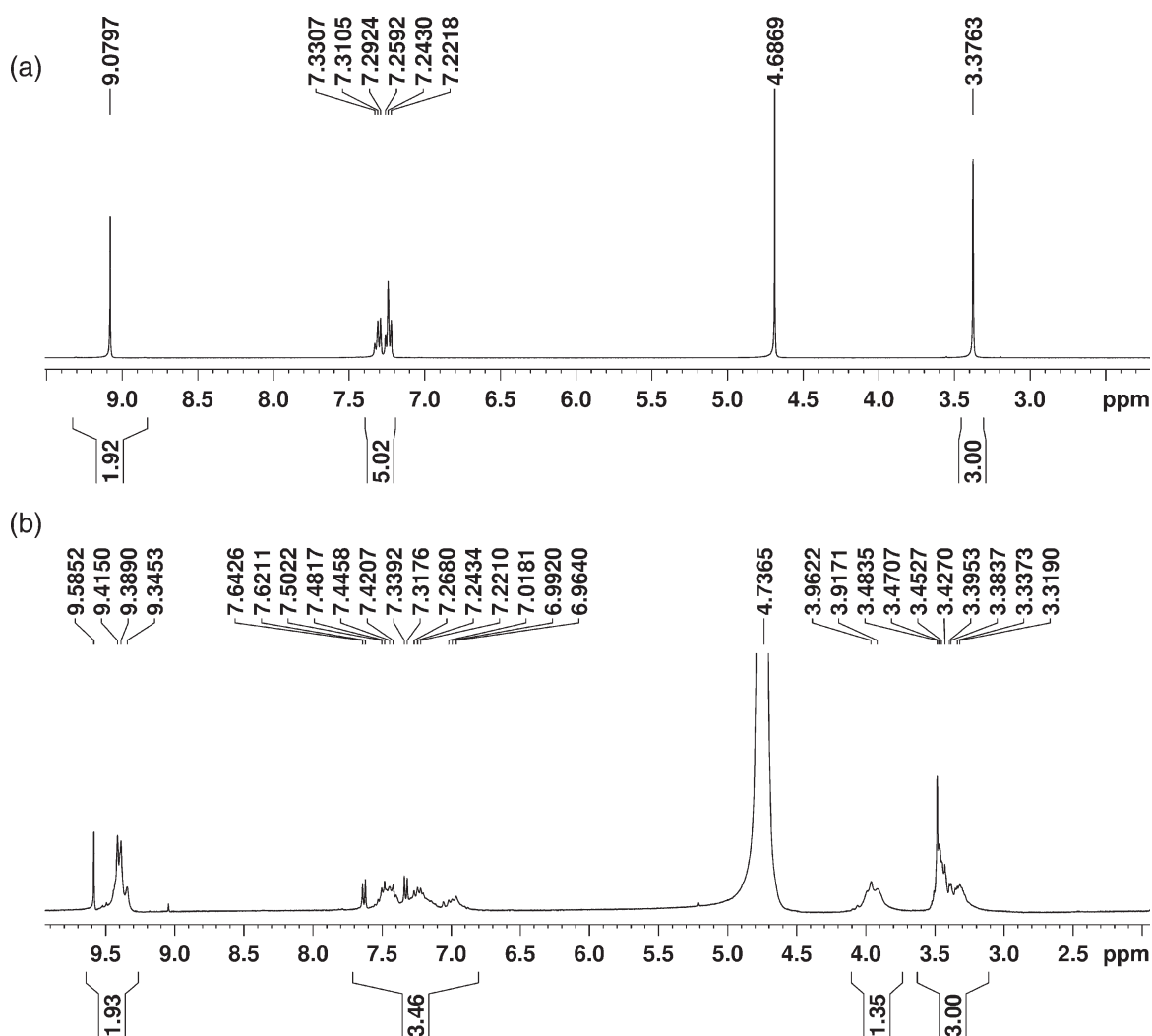


Figure 1. (a) ¹H NMR spectra of MDNDDS. (b) ¹H NMR spectra of MDNDDS-resin.

(s, 3H, CH₃); ¹³C NMR (100 MHz, D₂O, δ; carbon atoms were labeled as shown in Scheme 2, structure A): 144.79 (C7), 144.00 (C1), 143.47 (C-NO₂), 134.70 (C9), 130.28 (C3), 128.62 (C10), 122.64 (C8), 99.33 (C-N₂⁺), 43.43 (H₃C-N); IR (KBr): ν = 2967 cm⁻¹ (w, H₂C-H), 2272 cm⁻¹ (s, C-N₂⁺), 1604 cm⁻¹, 1585 cm⁻¹, 1542 cm⁻¹ (vs, Ar); Anal. calcd for C₁₃H₁₁N₅O₈SClZn_{0.5} (%): C 33.54, H 2.38, N 15.05; found (%): C 32.40, H 2.34, N 14.71; T_d: 165°C.

MDNDDS-Resin (V). MDNDDS **IV** (18.1 g, 0.039 mol) was added in batches to 98% sulfuric acid 52.5 mL under stirring, then grounded paraformaldehyde (1.4 g, 0.047 mol) was added in batches to the mixture at 0–5°C. The reaction mixture was stirred at this temperature for 5 h and slowly poured into 230 mL ice-cold ethanol under stirring. MDNDDS-Resin **V** (14.4 g, yield 91%) as red-orange color precipitate was obtained by filtration. M_w (by GPC) = 1326. ¹H NMR (400 MHz, D₂O, δ) [spectra is shown in Figure 1(b)]: 9.58–9.34(m, 2H, Ar H), 7.64–6.96(m, ≈3.5H, Ar H), 3.96–3.91(m, ≈1.3H, CH₂), 3.48–3.31(m, 3H, CH₃). IR (KBr): ν = 2225 cm⁻¹ (s, C-N₂⁺), 1592 cm⁻¹, 1540 cm⁻¹ (vs, Ar); T_d: 170°C.

Determination of Decomposition Percent (D%)

The photoreactivity was determined by the photo decomposition (D_p %) of diazonium compound under irradiation. The D_p % of MDNDDS was obtained by measuring absorbance changes at 425 nm (characteristic absorption of diazonium group) in solution. According to the Beer-Lambert Law, the absorbance of the solution is proportional to the concentration of diazonium compound; therefore, the D_p % of MDNDDS can be calculated from eq (1):

$$D\% = (A_0 - A_t)/A_0 \times 100\% \quad (1)$$

where, A_0 is the absorbance of the solution before irradiation and A_t is the absorbance after exposed to irradiation in a certain period of time (t , second).

The diazonium group is also sensitive toward heat. The thermal decomposition (D_t %) can also be studied by UV-VIS. In the solid state, samples were grounded carefully into fine powder, divided into several parts with the same weight, and heated in the oven at 80°C for a given time. Then the absorbance of the solution from the heated sample was determined. In the case of coating film that was coated in the inside of wall of a quartz cuvette, its UV absorbance was measured before and after heating. The thermal decomposition D_t % was also calculated according to eq (1).

Kinetics of Photoreactivity by RTIR

RTIR spectroscopy has become an important method for obtaining kinetics data of photoreactivity in thin film. Therefore, we use RTIR to characterize the photoreactivities of diazonium salts and their diazoresins in the coating film. First, diazonium salts or their diazoresins were dissolved in DMF with the same concentration of the diazonium groups. A drop of the resulting solution was coated on NaCl crystal, dried and exposed to UV radiation using a spot light source. The intensity of UV radiation on the surface of the samples was 1730 μW cm⁻² (at 365 nm) and 1240 μW cm⁻² (at 420 nm). A series of

RTIR measurements were carried out to determine the conversion rate of the diazonium compounds. The degree of the conversion of the diazonium compounds could be determined by measuring the peak area of diazonium group at each time of the irradiation and calculated by using eq (2):

$$\text{Conversion\%} = [1 - (A_t/A_0)] \times 100\% \quad (2)$$

where, conversion is the conversion of diazonium group at time t . A_0 and A_t are the peak areas of the functional group before and after irradiation, respectively. The conversion rate could be calculated from the differential of the curve of conversion versus irradiation time.²⁰

Photoimaging Test of PS Lithographic Plate

1.0 part (in weight) of MDNDDS-resin (or diazoresins of DDS, MNDDS) and 4.0 parts of binder resin [obtained from Ref. 10, a copolymer composed of hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), acrylic nitrile (AN), and acrylic acid (AA)] were dissolved in 69.2 parts DMF containing 0.1 part of background dye and spin coated on the electrolytic grained and anodized aluminum plate. The thickness of aluminum plate was 0.3 mm and the anodic film was 3 g m⁻², the arithmetic mean of the absolute departures of the roughness profile from the mean line (Ra) was about 0.6 μm. The coating thickness was controlled at about 2 g m⁻² (The coating thickness was measured as follows. A coated aluminum plate was cut into 10 × 10 cm² and weighed W_1 g and the coating on the plate was washed with acetone and then water. The plate was dried and weighed W_2 g. The value of the coating thickness was calculated by the formula $(W_1 - W_2) \times 100$ g m⁻²). Then it was dried for 5 min at 90°C in an oven, exposed under a 2 kW iodine gallium lamp at a distance of 1 m for 1–2 min and developed 1–2 min at 25°C. The developer is composed of 3 g Na₂SiO₃, 8 mL benzyl alcohol, 5 g sodium dodecyl sulfate (surfactant) in 100 mL water. A clear image was obtained after the unexposed area was dissolved by developer but the exposed area remained on plate.

RESULTS AND DISCUSSION

Synthesis of MDNDDS and MDNDDS-Resin

It was reported that the 4-nitro group of 2,4,6-trinitrotoluene could be selectively reduced to an amino group.²¹ Both sodium sulfide or hydrogen sulfide was used as the reductive reagent, but lots of experiments carried out by us proved that the selectivity of reduction was not effective to obtain MDNAD **III** with reasonable yield, instead, only a mixture of 2-amino, 4-amino, or 2,4-diamino compounds were observed. Therefore, we first synthesized 3,5-dinitro-4-chlorophenylamine **II**, and then the chlorine was substituted with *N*-methyl-aniline group.

Under the basic condition, the amino group of **II** also participated in the substitution reaction with chlorine atom of **II** itself, so no target product **III** had been obtained. While the amino of **II** was protected by acetylation, **III** was synthesized smoothly by this route.

The chemical structures of DDS and MNDDS are shown in Scheme 2 (structure B and C respectively). As is shown in Figure 2 and Table I, introduction of the mononitro group to

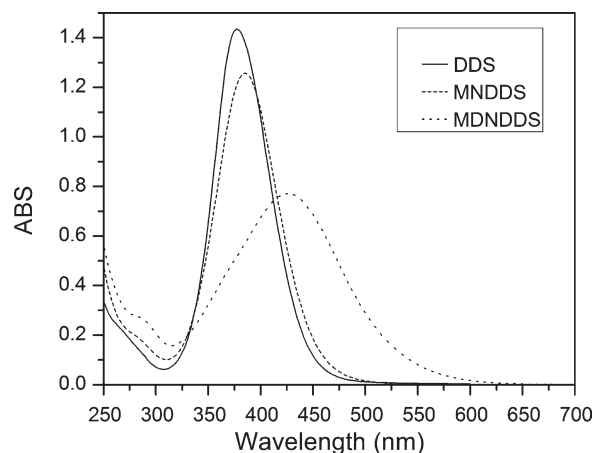


Figure 2. The UV-VIS spectra of MDNDDS, MNDDS and DDS in water. The concentration was $5 \times 10^{-5} \text{ mol L}^{-1}$ for all samples.

diazobenzene moiety of DDS produces a red shift in λ_{max} of 11 nm with slightly lower ϵ . Introduction of the second nitro substituent to the diazobenzene produce a larger red shift in λ_{max} of 50 nm with an even lower ϵ . But for the diazonium based sensitizers, $1.61 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ is still a reasonable value of ϵ .

High pressure mercury lamp with a λ_{em} of 310–360 nm is widely used as the irradiation source in the photo-patterning of PS plate, waterless lithographic plate, and screen printing plate. But the mercury vapor leaked and the residual mercury from scraped lamp are harmful to humans and will pollute the environment. Iodine gallium lamp is a new type of metal halide lamp (filled with iodide of cobalt and gallium) with a λ_{em} of 400–450 nm. MDNDDS has a λ_{max} of 425 nm, so an iodine gallium lamp could be better than a mercury lamp to be used as the irradiation source for MDNDDS-based photoimaging materials. What is more, compared with mercury lamp, iodine gallium lamp has a longer service life, lower power consumption, more stable intensity of UV radiation, more environmental friendly, and cheaper. As a result, the use of iodine gallium lamp can make the proceeding of making printing plate more costs effective and greener. The photosensitive determination of MDNDDS was discussed in detail below.

The Photoreactivities Behavior

The UV-VIS spectra of an aqueous solution of MDNDDS with various irradiation time are shown in Figure 3. The results demonstrate that the photo decomposition of the MDNDDS is very rapid, and it decomposes almost completely within 2 min under the experiment conditions. In addition, the result in Figure 3

Table I. The λ_{max} and ϵ (molar absorption coefficient) of the MDNDDS, MNDDS, and DDS in Aqueous Solution

Diazonium salt (HSO ₄ ⁻ as counterion)	λ_{max} (nm)	ϵ ($10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$)
MDNDDS	425	1.61
MNDDS	386	2.61
DDS	375	2.85

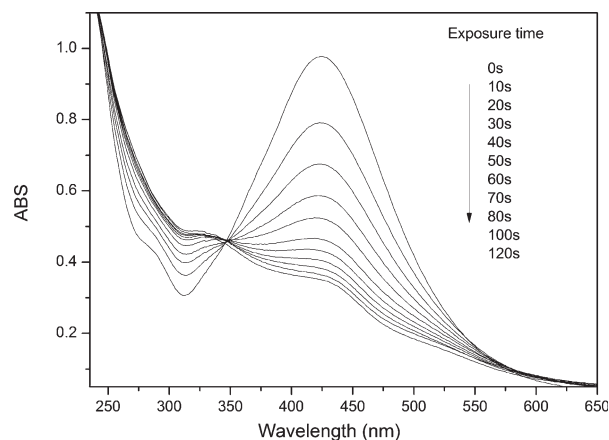


Figure 3. The UV-VIS spectra of MDNDDS in water exposed to the high pressure mercury lamp with various irradiation time. [MDNDDS] = $6 \times 10^{-5} \text{ mol L}^{-1}$; the intensity of UV light from high pressure mercury lamp is $474 \mu\text{W cm}^{-2}$ (365 nm) and $310 \mu\text{W cm}^{-2}$ (420 nm); irradiation time (top to bottom, s): 0, 10, 20, 30, 40, 50, 60, 70, 80, 100, 120.

also demonstrates that the photo decomposition of MDNDDS in aqueous solution follows the kinetics of first-order reaction. According to Beer-Lambert law, the absorbance of the solution is proportional to the concentration of diazonium salt. Therefore, the k_p of photo decomposition can be obtained from the slope of plot of $\ln(A_0/A_t) - t$ in Figure 4, where, A_0 and A_t represent the absorbance of the sample solution before and after irradiation, respectively. The half-life period $t_{1/2}$, can be calculated from the equation of $t_{1/2} = \ln 2/k_p$. For comparison, the k_p and $t_{1/2}$ of DDS and MNDDS in the same condition are also listed in Table II.

As is shown in Table II, the introduction of one *meta* nitro group to diazobenzene moiety of DDS can reduce the photosensitivity of diazoresin by half. Furthermore, after introduction of the second nitro substituent to the diazobenzene, the k_p of MDNDDS is nearly a half of that of MNDDS. But for MDNDDS, the low k_p is also caused by mismatching of its λ_{max} (425 nm) and main λ_{em} (360 nm) of high pressure mercury

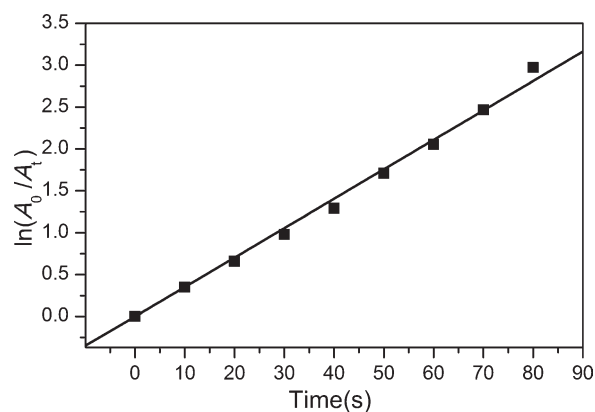


Figure 4. Plot of $\ln(A_0/A_t)$ versus time in photo decomposition of MDNDDS in aqueous solution. The intensity of UV light from high pressure mercury lamp is $474 \mu\text{W cm}^{-2}$ (at 365 nm) and $310 \mu\text{W cm}^{-2}$ (at 420 nm).

Table II. The k_p and $t_{1/2}$ of the MDNDDS, MNDDS, and DDS in Aqueous Solution Exposed to High Pressure Mercury Lamp^a

Diazonium salt (HSO ₄ ⁻ as counterion)	k_p (s ⁻¹)	$t_{1/2}$ (s)
MDNDDS	3.51×10^{-2}	19.7
MNDDS	6.86×10^{-2}	10.1
DDS	1.60×10^{-1}	4.3

^a[MDNDDS] = [MNDDS] = [DDS] = 5×10^{-5} mol L⁻¹. The intensity of UV light from high pressure mercury lamp is $474 \mu\text{W cm}^{-2}$ (365 nm) and $310 \mu\text{W cm}^{-2}$ (420 nm).

lamp. So we used an iodine gallium lamp (lamp power 2 kW, exposure distance 1 m), instead of mercury lamp, to irradiate the aqueous solution of MDNDDS. The UV-VIS spectra of the aqueous solution of MDNDDS exposed to the iodine gallium lamp with various irradiation time are shown in Figure 5. The corresponding photo decomposition rate (k_p 1.37×10^{-1} s⁻¹, $t_{1/2}$ 5.1 s) is four times faster than that exposed to the mercury lamp. Hence, iodine gallium lamp could be used as a better irradiation source for MDNDDS.

Diazo-resin with high molecular weight has poor solubility in solvents such as DMF, ethylene glycol monomethyl ether, so diazo-resin with low average degree of polymerization is desirable, usually 3–6.^{10,13} As a result, the photoreactivity of diazo-resin is almost the same as that of its diazonium salt and no data of photoreactivity about diazo-resin was needed to be listed separately.

Kinetics of Photo Decomposition with RTIR

As a photo imaging material, diazonium salt and diazo-resin are mainly used for coating film, so its photosensitivity in film form is very important. However, to our knowledge, there is no published work addressing this issue so far. Nowadays, RTIR spectroscopy has become an important method for obtaining kinetics data of photo decomposition in coating film. In this

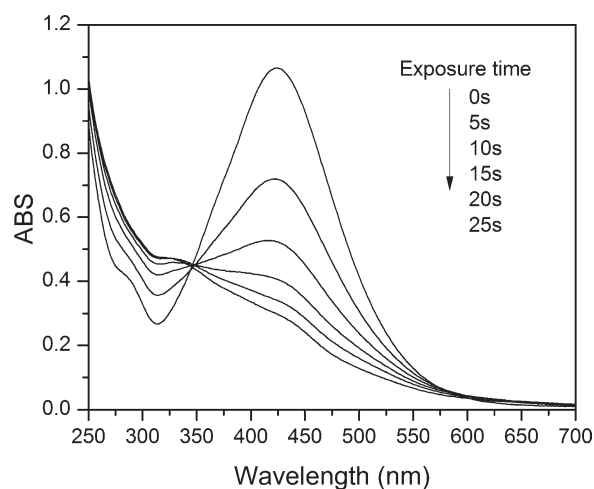


Figure 5. The UV-VIS spectra of MDNDDS in water exposed to the iodine gallium lamp with various irradiation time. [MDNDDS] = 6.6×10^{-5} mol L⁻¹. The intensity of UV light from the iodine gallium lamp is $4400 \mu\text{W cm}^{-2}$ (420 nm).

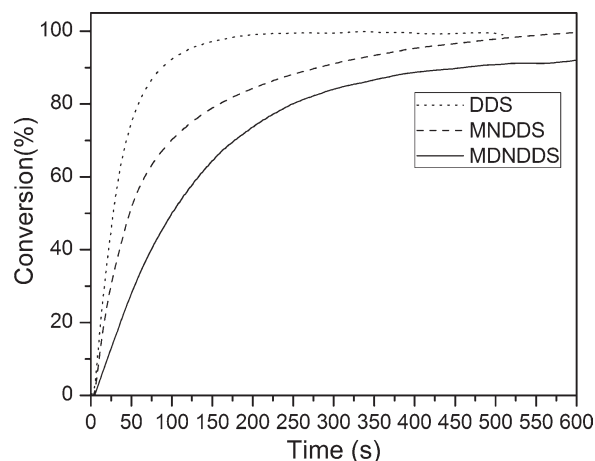


Figure 6. The time dependent conversion of the diazonium group of MDNDDS, MNDDS and DDS.

study, we characterized the real-time photoreactivity of diazonium film by RTIR. The photo decomposition rate of the photosensitive compound was monitored by the intensity changes of absorption of the diazonium group around 2240 cm^{-1} with OMNIC 7.0 software. Under irradiation, the decrease rate of the absorption area changes of the diazonium group reflected the photo decomposition rate of the photosensitive compound.^{20,22}

Under the UV irradiation with a mercury lamp, the conversion and conversion rate of the diazonium group of MDNDDS, MNDDS, and DDS films were shown in Figures 6 and 7, which were calculated from RTIR data. The intensity of UV radiation

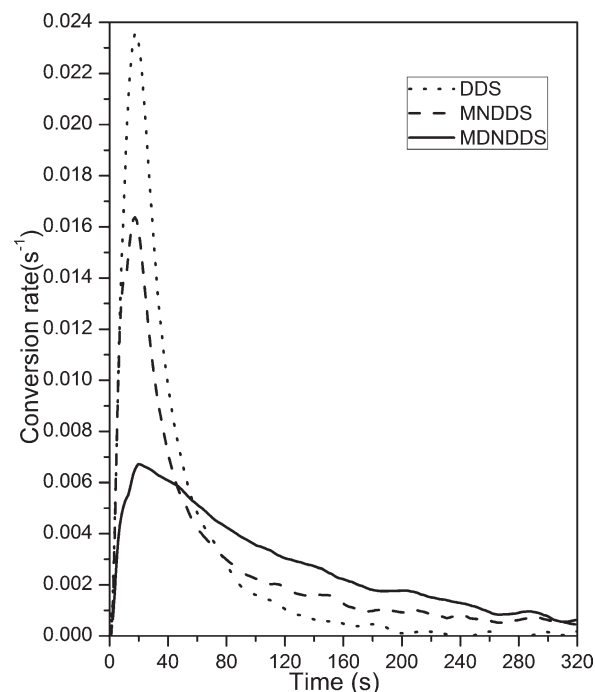
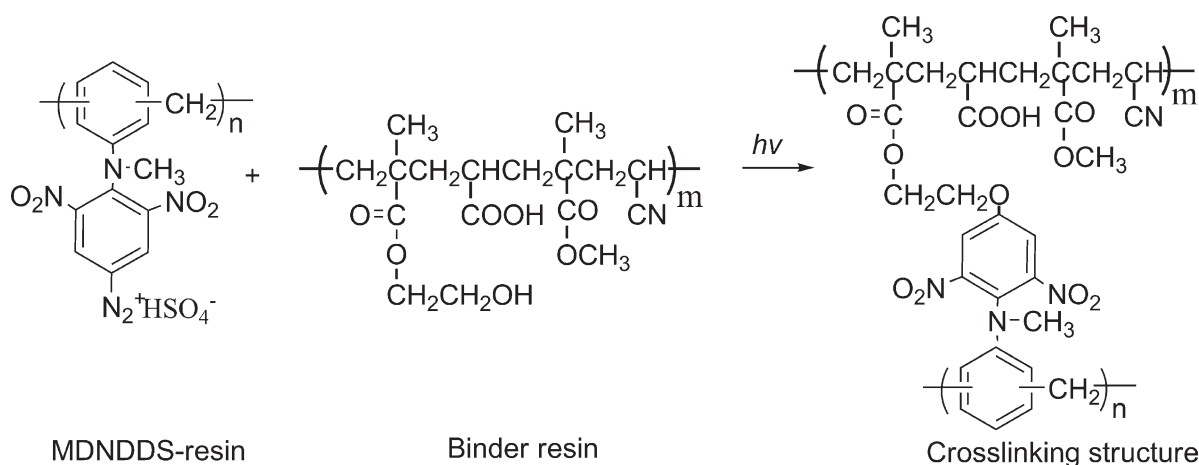


Figure 7. The time dependent conversion rate of the diazonium group of MDNDDS, MNDDS and DDS.



Scheme 3. The mechanism of the photoreaction of MDNDDS-resin and binder resin.

on the surface of the samples was $1730 \mu\text{W cm}^{-2}$ at 365 nm and $1240 \mu\text{W cm}^{-2}$ at 420 nm. The results reveal that their photosensitivities in the coating film is the same as that in aqueous solution, with the same order as $\text{DDS} > \text{MNDDS} > \text{MDNDDS}$, and the conversion of DDS, MNDDS, and MDNDDS are 90%, 70%, and 50% at 100 s, respectively. After 250 s, the conversion of 80% for MDNDDS has been achieved. The results also reveal that all of their conversion rates increase very fast at the beginning, and almost simultaneously reach the maximum in 25 s, then decline rapidly.

As mentioned before, iodine gallium lamp could be used as the irradiation source for MDNDDS. When a 2 kW iodine gallium lamp (the intensity of UV light is $4400 \mu\text{W cm}^{-2}$ at 420 nm) was used to irradiate the coating film of MDNDDS, the conversion rate in the film should be as fast as that in the aqueous solution to fully satisfy the demand of practical photo imaging process in factory.

The Photoreaction Between Diazo-resin and Binder Resin

The photoimaging of diazo-resin and binder resin in the coating is believed to involve the photocrosslinking reactions between the hydroxyl group of the binder resin and the diazonium group of diazo-resin,^{10,13} so we proposed the mechanism of the photoreaction of MDNDDS-resin and binder resin in Scheme 3. Upon UV irradiation, MDNDDS-resins of exposed area react with hydroxyl groups of binder resin to form a crosslinked structure which is insoluble in developer and remain on plate.

Table III. The Thermal Decomposition of MDNDDS, MNDDS, DDS, and their Diazo-resins in Solid State at 80°C

Heating time (h)	$D_t\%$ (mol %)			
	9	18	24	34
MDNDDS	3.9	16.9	26.2	36.6
MNDDS	16.2	48.2	75.4	85.8
DDS	~ 100			
MDNDDS-resin	3.3	12.1	37.2	50.1
MNDDS-resin	17.8	80.0	89.1	~ 100
DDS-resin	~ 100			

Thermal Decomposition of MDNDDS and its Diazo-resin

The thermal decomposition of diazonium salt and its diazo-resin in the solid state is a major determining effect for the storage life of photosensitive agent in solid powder, while that in a coating film state is related to the storage life of printing plates.^{10–12}

The thermal decomposition mol percent ($D_t\%$) was measured by a spectrophotometric method and calculated from the decreasing absorbance of solution from sample after heating. The $D_t\%$ for MDNDDS and its diazo-resin in solid state at 80°C are listed in Table III. For comparison, the data of MNDDS, DDS, and their diazo-resins in the same condition are also listed in Table III. The result reveals that the thermal stabilities of MNDDS, MDNDDS, and their diazo-resins are much better than that of DDS and its diazo-resin. In addition, the improvement of the thermal stability of MDNDDS and its diazo-resin in solid state is greater comparing with that of MNDDS and its diazo-resin. At 80°C, the $D_t\%$ for MNDDS and its diazo-resin is 85.8% and 99% at 34 h, but under the same condition the $D_t\%$ of MDNDDS and its diazo-resin is only 37% and 50%, respectively. Thus, the shelf-life of diazo-resin based photoimaging agent would be extended by using MDNDDS-resin as the photosensitizer, in comparison with diazo-resin of DDS and MNDDS.

The decomposition behavior of MDNDDS and its diazo-resin in coating film (coated in the inside of wall of a quartz cuvette) at

Table IV. The Thermal Decomposition of MDNDDS, MNDDS, DDS and their Diazo-resins in Solid Coating Film at 80°C

Heating time (h)	$D_t\%$ (mol %)				
	6	12	22	35	57
MDNDDS	2.6	5.6	10.2	12.4	18.1
MNDDS	4.0	6.8	12.7	16.2	33.9
DDS	36.6	50.1	-	~ 100	
MDNDDS-resin	1.1	2.5	3.8	5.1	7.4
MNDDS-resin	2.0	4.3	6.0	11.5	14.7
DDS-resin	15.1	25.0	41.1	53.3	61.6

80°C were also determined by a spectrophotometric method and calculated from the absorbance decrease of the coating film after heating. The $D_t\%$ for MDNDDS and its diazo resin in solid coating film at 80°C are listed in Table IV. For comparison, the data of DDS, MNDDS, and their diazo resins in the same condition are also listed. The result also reveals that the thermal stability of MDNDDS and its diazo resin in coating film still show an obvious improvement compared with that of MNDDS and its diazo resin, which is consistent with the thermal decomposition in solid state.

Our study shows that MDNDDS and its diazo resin exhibited greatly improved thermostability both in solid state and in coating film comparing with that of DDS, MNDDS, and their diazo resins. Using MDNDDS and its diazo resin as the photosensitive agent might provide a possible solution to the problem of short shelf-life of printing plate.

CONCLUSIONS

MDNDDS and its diazo resin were designed, synthesized for the first time by only four steps and characterized. Their photoreactivities and thermostabilities were also investigated. The results revealed that MDNDDS and MDNDDS-resin exhibited greatly improved thermostability both in solid state and in coating film than that of DDS, MNDDS, and their diazo resins. As a result of the improved thermostability, lithographic plate prepared by MDNDDS and its diazo resin will have a long shelf-life. For the photosensitivities, MDNDDS was found to be slightly lower than DDS but still comparable with MNDDS. So using MDNDDS and its diazo resin as the photosensitive agent might provide a solution to the problem of short shelf-life of printing plate, which is very important for reducing waste and plant running-cost. Furthermore, MDNDDS has a λ_{\max} at 425 nm and iodine gallium lamp could be used as a better irradiation source for MDNDDS. Compared with mercury lamp, the use of iodine gallium lamp can make the proceeding of making printing plate more costs effective and greener. Consequently, the MDNDDS and its diazo resin could be applied in practical as new photosensitive diazonium salt and diazo resin, especially in manufacture of diazo resin based plates of PS or CTP lithographic printing, waterless lithographic printing, and screen printing.

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REFERENCES AND NOTES

- Walls, J. E.; Dhillon, M. S. (*Hoechst Co.*). *U. S. Pat.* 4,448,873, May 15, 1984.
- Schlosser, H. J. (*Hoechst Co.*). *U. S. Pat.* 4,775,607, October 4, 1988.
- Ohta, K.; Otawa, S.; Kasukawa, S. (*Tokyo Ohka Kogyo Co., Ltd.*). *GB Pat.* 2057704A, Jun 13, 1980.
- Schlosser, H. J.; Gersdorf, J. (*Hoechst Co.*). *U. S. Pat.* 4,956,262, September 11, 1990.
- Shiraishi, Y.; Aoshima, K.; Aono, S. (*Fuji Photo Film Co., Ltd.*). *Eur. Pat.* 679950, November 2, 1995.
- Otani, Y.; Saito, A. (*Tokyo Ohka Kogyo Co., Ltd.*). *Jpn. Pat.* 9553777A, February 28, 1995.
- Zou, Y. Q.; Wang, J. G. (*Beijing Normal University*). *CN Pat.* 102096323A, June 15, 2011.
- Zou, Y. Q.; Wang, J. G. (*Beijing Normal University*). *CN Pat.* 102173181A, January 24, 2011.
- Zhao, C.; Lu, Y. X.; Cao, W. X. *Polym. Int.* 1999, 48, 150.
- Wang, R. X.; Chen, J. Y.; Cao, W. X. *J. Appl. Polym. Sci.* 1999, 74, 189.
- Cao, W. X.; Zhao, C.; Cao, J. W. *J. Appl. Polym. Sci.* 1998, 69, 1975.
- Sun, F.; Yang, B. X.; Wang, R. Y.; Cao, W. X. *Photogr. Sci. Photochem.* 2001, 19, 193.
- Cao, S. G.; Zhao, C.; Cao, W. X. *Polym. Int.* 1998, 45, 142.
- Yang, C. G.; Xie, K. Z.; Wen, C. X. (*Dongfang Chemical Industry Co.*). *CN Pat.* 1415598A, November 7, 2002.
- Nielsen, A. T.; Chafin, A. P.; Christian, S. L. *J. Org. Chem.* 1984, 49, 4575.
- Bofill Augé, J. A.; Espinos Taya, J. M. *ES Pat.* 371070 August 13, 1969.
- Milos, S. B. (*Bristol Myers Co.*). *GB Pat.* 1405222A, October 30, 1972.
- Bagolini, C.; Witt, P. D.; Pacifici, L.; Ramacci, M. T. *J. Med. Chem.* 1978, 21, 476.
- Shilova, E. A.; Perevalov, V. P.; Samata, A.; Moustrou, C. *Tetrahedron Lett.* 2007, 48, 4127.
- He, Y.; Xiao, M.; Wu, F. P.; Nie, J. *Polym. Int.* 2007, 56, 1292–1297.
- Arnold, T. N.; Ronald, A. H.; William, P. N.; Ronald, L. A.; Donald, W. M.; Albert, H. L. *J. Org. Chem.* 1979, 44, 2499.
- Liu, L.; Zou, Y. Q. *J. Appl. Polym. Sci.* 2012, 123, 554.