Synthesis and Characterization of *N*-Methyl-2-nitrodiphenylamine-4-diazonium Salt and Its Diazoresin

RENXIAN WANG, JINYU CHEN, WEIXIAO CAO

College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Received 13 October 1998; accepted 31 January 1999

ABSTRACT: A new substituted diphenylamine diazonium salt, *N*-methyl-2-nitrodiphenylamine-4-diazonium salt (MNDDS) and its diazoresin (MNDDS-resin) were synthesized and their thermostability as well as photosensitivity were investigated. The results show that MNDDS and resin exhibit much higher thermostability than that of the parent compound, diphenylamine-4-diazonium salt (DDS) and resin (DDS resin) in solid state or in coating but the photosensitivities of them are confirmed to be in same level. The excellent thermostability of MNDDS and its diazoresin is very important because the storage life of a negative presensitized plate is mainly dependent on it. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 189–193, 1999

Key words: substituted diphenylamine diazonium salt; diazoresin; photosensitivity; thermostability

INTRODUCTION

Diazoresin, a polycondensation product of diphenylamine-4-diazonium salt (DDS) with formaldehyde, is the most important photosensitive material for the manufacture of negative presensitized (PS) plates and many patents have been published.¹⁻¹¹ The disadvantage of diazoresin from DDS is that its thermal stability does not fully satisfy the demand of negative PS plates which require a storage life of more than 1 year. The efforts to improve the thermal stability of the resin mainly focus on two aspects. One is preparing the diazoresin with 2-hydroxy-4-methoxy diphenyl ketone-5-sulfonic anion as counter ion to bind with the cationic diazonium group,^{10,12,13} but the improvement is limited. Another effort is utilizing the substituted diphenylamine diazonium salt, such as 3-methoxy-diphenylamine-4diazonium salt (MDDS) developed by Hoechst Company as photosensitive material^{1-3,11}; however, the company has not revealed the synthetic method of MDDS so far and the price of MDDS is rather higher. Recently in our laboratory we developed a new substituted diphenylamine diazonium salt—*N*-methyl-2-nitrodiphenylamine-4-diazonium salt (MNDDS) and its diazoresin (MNDDS resin), which have a shorter synthetic route and a lower price than MDDS and higher thermal stability than DDS. In this article we report the synthesis and characterization of MNDDS and its resin. The photochemical and thermal properties of the salt and resin are also reported.

EXPERIMENTAL

Materials

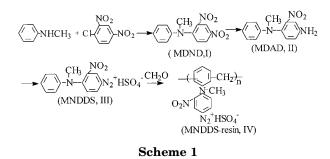
N-Methylaniline was distilled before use. 2,4-Dinitrochlorobenzene, m.p. 52–54°C, was used as received. Diphenylamine-4-diazonium salt (DDS) was reprecipitated from its ethanol solution by ether. MDDS was prepared according to the pro-

Correspondence to: W. Cao.

Contract grant sponsor: NSFC; contract grant numbers: 59633110 and 29874001.

Journal of Applied Polymer Science, Vol. 74, 189-193 (1999)

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cedure described elsewhere.¹⁴ 2-Hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), acrylonitrile (AN), and acrylic acid (AA) were distilled under reduced pressure before use. The other reagents are chemical grade and were used as received.

Preparation of MNDDS and Its Diazoresin

The synthetic route of MNDDS was designed as shown in Scheme 1.

N-Methyl 2,4-Dinitrodiphenylamine (MDND, I)

2,4-Dinitro-chlorobenzene (40.4 g, 0.2 mol), sodium carbonate (23.3 g, 0.22 mol), and absolute ethanol (200 ml) were charged in a 500 mL three necked bottom flask; *N*-methylaniline (23.5 g, 0.22 mol) was added dropwise into the reaction mixture under stirring at reflux temperature. The reaction was continued for 6 h then filtered. I as precipitate with an orange color was obtained; the yield was 49 g, 90%. ¹HNMR (400 MHz, CDCl₃), δ (ppm): 3.46, 3H (--CH₃), 7.09–8.62, 8H (aromatic).

N-Methyl 2-Nitro-4-aminodiphenylamine (MNAD, II)

I (27.3 g, 0.1 mol), sodium carbonate (10.6 g, 0.1 mol), and 95% ethanol (80 mL) were added in a 500 mL three neck round bottom flask. Na₂S · 9 H₂O (48 g, 0.2 mol in 80 mL water) was added dropwise to the mixture (about 1 h), then continued for another 1 h. The liquid was poured, while hot, into a 500 mL beaker and cooled. II, with an orange color, was precipitated and filtered. The filtrate was then poured into the water to receive the other part of II remaining in the filtrate. The yield was 16.9 g, 70%. Fifteen g of II was dissolved in 50% H₂SO₄ (200 mL hot), then was added to 1.5 L boiling water. The bisulfate of II was precipitated from the solution after cooling and filtered; the yield was 18.2 g, 86%. ¹HNMR (CDCl₃), δ

(ppm): 3.26,3H (—CH₃); 4.13, 3H (—NH₃⁺); 6.58/ 2H, 6.76/1H, 6.94/1H, 7.13–7.25/4H (aromatic).

N-Methyl-2-nitrodiphenylamine-4-diazonim Salt (HSO₄⁻ as anion) (MNDDS, III)

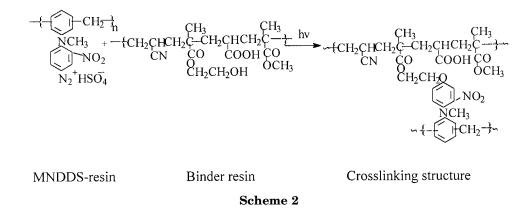
Bisulfate of II (34.6 g, 0.1 mol) was added to the mixture composed of 130 mL 5% H_2SO_4 and 240 g crashed ice under stirring in a 500 mL beaker which was cooled by an ice water bath. NaNO₂ (8.3 g, 0.12 mol in 40 mL water) was added dropwise under stirring at 0–5°C, then the reaction was continued for 1 h and the product was filtered. 54.4 g of ZnCl₂ (0.4 mol in 100 mL water) was added into the filtrate, the diazonium salt III as 1/2 ZnCl₂ complex with yellow color, was precipitated. The yield was 31.2 g, 74 %. ¹HNMR (D₂O), δ (ppm): 3.68, 3H (—CH₃); 7.30–7.55/6H, 8.30/1H, 8.88/1H (aromatic).

MNDDS-Resin (IV)

Concentrated sulfuric acid (135 mL) was added to a 250 ml three necked bottom flask, MNDDS (0.1 mol) was added in batches to the H₂SO₄ under stirring, then paraformaldehyde (grounded carefully, 0.12 mol) was added at 0–5°C. The reaction was continued for 4 h. Six hundred milliliters of H₂O was added to the bottle to dissolve the diazoresin, then filtered. ZnCl₂ (66g, 0.5 mol) was added to the filtrate, the diazoresin as 1/2 ZnCl₂ complex with yellow color was precipitated. The yield was 38.9 g, 90%. $\eta_{sp}/C = 0.15$ dLg⁻¹.

Preparation of Binder Resin

The photosensitive coating of the negative PS plate is comprised of diazoresin as the photosensitive agent and a binder resin is used as the film-forming material. The most extensively used binder resin is a copolymer composed of HEMA, MMA, AN, and AA^{10,11} in which the HEMA unit is used to form crosslinkage through the reaction between the hydroxy and diazonium groups under UV irradiation; the MMA and AN are used for ink-affinity and the AA is used for alkali solubility. The binder resin [in N,N-dimethylformamide (DMF)solution] was prepared as follows: HEMA/8 g, AA/2 g, AN/6 g, MMA/4 g, isopropyl alcohol 2 ml and benzoyl peroxide (BPO) 0.04 g were added into 140 ml of DMF. The mixture was deaerated with N₂ then heated at 75°C for 6 h. A viscous solution containing about 14% polymer can be used directly as binder resin (DMF solution). $\eta_{sp}/C = 0.41 \text{ dLg}^{-1}$.



Determination of T_d and D %

The decomposition temperature T_d of the diazonium salt and resin were measured by differential scanning calorimetry (DSC, on Schimadzu-50) with the temperature rising rate of 10°C/min. The photochemical decomposition percent (D^p %) was obtained from the decreasing absorbance of the sample solution at 372 nm which is the characteristic absorption of diazonium group of MNDDS and its resin. The absorbance of the solution is proportional to the concentration of diazonium compound (Beer-Lambert Law), therefore the D^p % of the MNDDS or its resin can be calculated from the eq. (1):

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

where A_0 and A_t represent the absorbance of the solution before and after irradiation, respectively.

The diazonium group is also sensitive toward heat, so the thermal decomposition $(D^t \%)$ also can be determined spectrophotometrically. In the case of solid state, the samples were grounded at first carefully into fine powder and heated in an oven, usually at 80°C, for a given time, then the absorbance of the solution from the heated sample was determined and the D^t % was calculated. In the case of coating, the D^t % of the samples was calculated directly by the weight of the coating, which was coated on a substrate such as hydrophilic PET film or printing Al plate. The diazonium salt and diazoresin dissolve in water but the thermal decomposition product of them is insoluble; therefore, from the weight W_1 remaining on the substrate after heating and washing with water, the D^t % can be calculated according to eq. (2):

$$D^t \% = W_1 / W_0 \times 100 \%$$
 (2)

where W_0 represents the weight of coating before heating.

Photoimaging Test

MNDDS-diazoresin or DDS-diazoresin, 1.0 part (in weight), was dissolved in 90.0 parts DMF containing 10 parts of binder resin and was coated on a printing Al plate, dried in the dark, and exposed with a 300 W medium pressure Hg lamp at a distance of 40 cm for 2 min then developed 2–4 min at room temperature. The developer is composed of Na₂SO₃ 5 g, benzyl alcohol 10 mL, OP-10 (nonionic surfactant) 5 g, sodium dodecyl sulfate (cationic surfactant) 5 g in 250 mL water. The unexposed area was dissolved by developer but the exposed area remained due to photocrosslinking and a clear image was obtained.

RESULTS AND DISCUSSION

MNDDS and MNDDS-Resin

The reaction between *N*-methylaniline and 2,4dinitro-chlorobenzene to form *N*-methyl-2,4-dinitrodiphenylamine (MDND) was performed in ethanol using sodium carbonate as neutralizer. The quality and yield (90%) are satisfactory. In reduction of a nitro group to an amino group, Na₂S was selected as reductant. It was confirmed that in the experimental condition used, only the para-nitro group was reduced. The evidence is that the λ_{max} (372 nm in water) of the compound is close to the λ_{max} of diphenylamine-4-diazonium salt (375 m) rather than the absorption of diphenylamine-2diazonium salt which has λ_{max} at 430 nm.¹⁵

The MNDDS-resin was prepared from polycondensation between MNDDS and paraformalde-

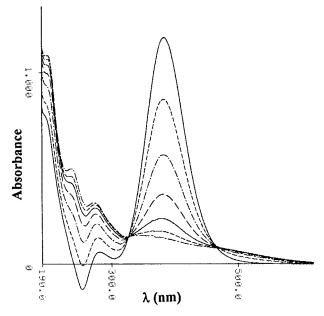


Figure 1 The UV-VIS spectra of MNDDS in water with various irradiation times [MNDDS] = 5×10^{-5} mol/L; intensity of irradiation (at 360 nm): $655 \,\mu$ m/cm² irradiation time (top to bottom, s): 0, 20, 40, 60, 80, 100, 120.

hyde in concentrated acid. The dissociation of paraformaldehyde to its monomer is not complete at the experimental condition (4–5 h/0–5°C) used, so it is necessary to control the molar ratio of CH₂O/–N₂⁺ at about 1.2 to obtain the diazoresin with specific viscosity $\eta_{sp}/C \approx 0.15 \text{ g}^{-1} \text{ dL}$ corresponding to $2 \times 10^3 \text{ M}_n$. Too high molecular weight will decrease the solubility of diazoresin in water or in polar organic solvents such as in DMF, 2-hydroxyethanol but too low molecular weight will weaken the strength of the film.

The Photoreaction Between Diazoresin and Binder Resin

The photoimaging function of MNDDS resinbinder resin in the coating is based on the photocroslinking reaction between the hydroxy group of the binder resin and the diazonium group of the diazoresin (see Scheme 2). Under irradiation of UV light, the diazoresin reacts only with hydroxy group of binder resin to form a crosslinking structure.¹⁶

The Photosensitive Behavior

Figure 1 shows the UV-VIS spectra of an aqueous solution of MNDDS. It was shown that the pho-

Table I The k_d^p and $t_{1/2}^p$ of MNDDS, DDS, and MDDS

Diazonium Salt			MDDS	
$k_d^p \; (\mathrm{s}^{-1}) \ t_{1/2}^p \; (\mathrm{s})^\mathrm{a}$	$rac{1.8 imes 10^{-2}}{46.6}$	$4.2 \ imes \ 10^{-2} \ 34.8$	$1.2 \ imes \ 10^{-2} \ 62.7$	

[MNDDS] = [DDS] = 4.0×10^{-5} mol/L (in ethanol). ^a The intensity of UV light (360 nm): 655 μ W/cm₂.

tochemical decomposition of the MNDDS is very rapid, the diazonium group decomposes almost completely within 2 min under the experimental condition. The concentration of diazonium salt in photochemical decomposition in aqueous solution follows first order reaction and the absorbance of the solution is proportional to the concentration of diazonium salt (Beer-Lambert law). Therefore, the rate constant k_d^p of photodecomposition can be obtained from the plot of $\ln A_0/A_t - t$, where A_0 and A_t represent the absorbance of the solution before and after irradiation (for t time). The halflife period $t_{1/2}^{p}$, can be calculated from the equation of $t_{1/2}^{p} = \ln 2/k_d^p$. The k_d^p and $t_{1/2}^{p}$ of MNDDS were calculated and listed in Table I (the corresponding data of DDS and MDDS are also listed).

From the data of Table I the rate of photochemical decomposition of MNDDS, MDDS, and DDS does not differ considerably as compared with the thermal decomposition (Table II).

The Thermal Decomposition of MNDDS

The thermal decomposition of diazonium salt and diazoresin in the solid state or in a coating are related closely to the storage life of a negative PS plate, when they were used as photosensitive materials in the manufacture of them. The thermal decomposition percent $(D^t \%)$ for MNDDS and its

Table II	The Thermal Decomposition of
MNDDS,	DDS, and Their Diazoresin
in Solid S	State at 80°C

	$D^t \% \pmod{\%}$			
Heating Time (h)	9	18	24	34
MNDDS	16	45.7	74.5	85
DDS	~ 100	—	—	—
MNDDS-resin	17.2	79.3	88.1	99
DDS-resin	~ 100	_	_	

Heating Time (h)		$D^t \% \pmod{\%}$				
	0.5	1.0	1.5	2.0	2.5	4.0
MNDDS	1.48	3.54	6.32	11.4	_	_
DDS	8.26	9.28	21.9	35.3	52.7	_
MNDDS-resin	2.22	_	3.54	4.50		6.90
DDS-resin	—	6.67	_	8.69	_	27.4

Table III The D^t % of MNDDS, DDS, and Their Diazoresins at 80°C in Coatings

diazoresin in solid state at 80°C are listed in Table II (the data of DDS are also listed).

From Table II we can see that in the solid state the thermal stability of MNDDS and its resin is much better than that of DDS and resin. The decomposition of DDS and its resin is almost complete within 9 h at 80°C but under the same condition the $D^t \%$ of MNDDS and its resin is only 16.0 and 17.2%, respectively.

As a kind of photosensitive material, the diazonium salts and diazoresins are mainly used in coating. The thermal decomposition data of MNDDS and its resin in coatings at 80°C are listed in Table III (the correspondent data of DDS and its resin are also listed).

The data of Table III show that both MNDDS and MNDDS-resin are more stable than DDS and its resin in coatings. This property is very important because the problem of the short storage life of the negative PS plate may be resolved by using MNDDS-resin instead of DDS-resin as a photosensitive agent in a negative PS plate.

CONCLUSION

MNDDS and its diazoresin were synthesized for the first time through only three steps with the total yields of $\approx 50\%$ and characterized. The thermal and photochemical decompositions of them were investigated and compared with that of DDS and its resin. The results show that the photosensitivity of MNDDS and its resin are similar to that of DDS and DDS-resin but the thermostability of MNDDS and its diazoresin are much superior to that of DDS and DDS-resin in the solid state or in a coating. The MNDDS and its resin may be available in practice because of its short synthetic route and the excellent thermostability in a coating, as a new diazonium salt and diazoresin, especially in manufacture of negative PS plates.

The authors are grateful to NSFC for financial support of this work (Numbers 59633110 and 29874001).

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