Synthesis and Characterization of 3-Methoxydiphenylamine-4-diazonium Salt and Its Diazoresin

WEIXIAO CAO, CHAO ZHAO, JIAWEI CAO

College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

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ABSTRACT: 3-Methoxydiphenylamine-4-diazonium salt (MDDS) and its diazoresin were synthesized. The photo- and thermal decomposition of salt and the resins were investigated. The results show that MDDS exhibits excellent thermostability as well as high photosensitivity. A series of diazoresins with different organic counteranions, which dissolve in common solvents and usually were chosen to manufacture the negative presensitized plate, were also synthesized The kinetics of the photo- and thermal decomposition of MDDS in ethanol is reported. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1975–1982, 1998

Key words: diazonium salt; diazoresin; photosensitivity; thermostability; presensitized plate

INTRODUCTION

The diazoresins from the polycondensation of 3-methoxydiphenylamine-4-diazonium salt (MDDS) with formaldehyde or 4,4′-dimethoxymethylene diphenyl ether have been used in the manufacturing of negative presensitized plates (negative PS plates), and a series of patents, mainly by Hoechst Co., was published.[1–5] However, as we know, the companies have not revealed the synthetic method of MDDS and its properties, especially the photo- and thermal decomposition behaviors. This article presents a synthetic method for preparing MDDS and its photo- and thermal decomposition properties. The corresponding behaviors of its diazoresin are also reported.

EXPERIMENTAL

Preparation of MDDS

A synthetic route with six steps was designed to prepare MDDS:

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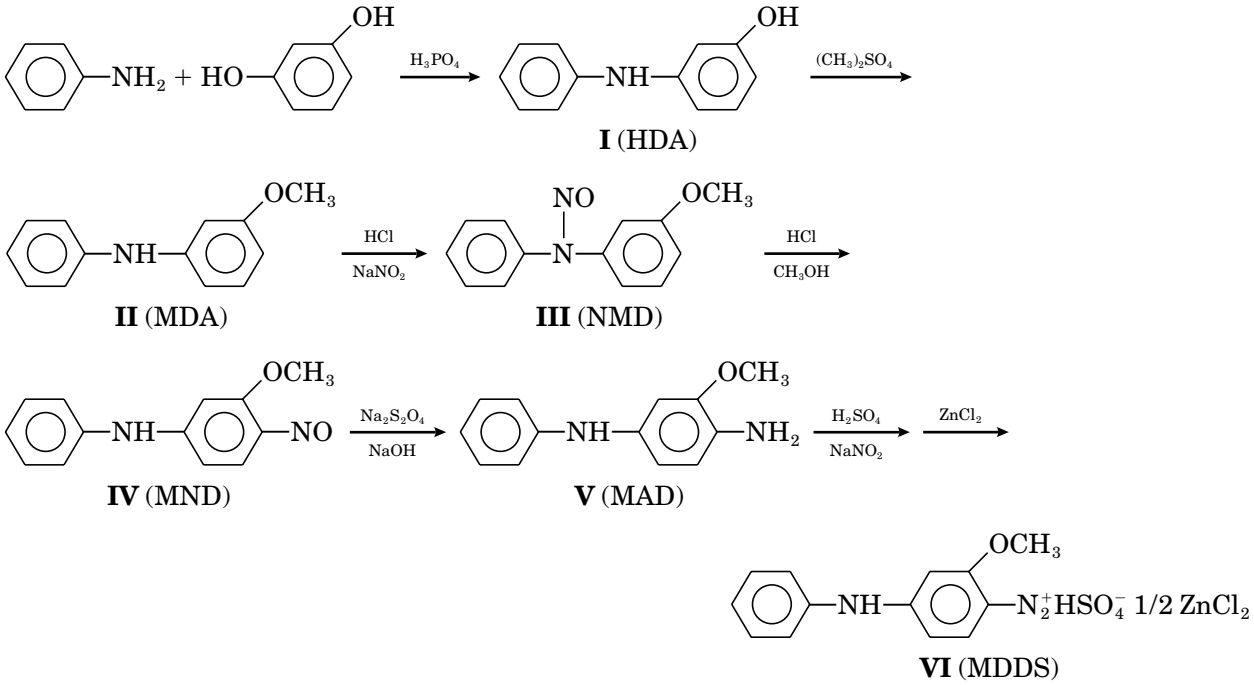


3-Hydroxydiphenylamine I (HDA)

Referring to Ref. 6 with some modification, HDA was prepared: Aniline (300 mL, 3.3 mol), phosphoric acid (55.6 mL, 1.04 mol), H_2O (700 mL), and resorcinol (220 g, 2.0 mol) were added into an autoclave (2 L) with stirring. The mixture was heated at 180°C for 12 h. After cooling, the resultant was filtered and washed twice with water and dried (300 g, 81%). The rough product with an orange color was used directly in the next step. The purification can be carried out by recrystallization in water (2 g/1000 mL H_2O) twice; a white crystal was obtained (70%; mp: 80–81°C).

^{1}H-NMR ($CDCl_3$, ppm): 5.3–5.6 (2H, NH, and OH), 6.3–7.3 (9H, aromatic nuclear).

3-Methoxydiphenylamine II (MDA)

Referring to ref. 7, the methylation of **I** was carried out as follows: **I** (300 g, 1.62 mol), H_2O (500 mL), and NaOH (150 g, 3.75 mol) were added into a flask (1 L) and heated to near boiling. Dimethyl sulfate (190 mL, 2.01 mol) was added dropwise from a condenser in 1 hour, then refluxed for 5 h. The oil layer was separated during a hot treatment and washed with each 20% NaOH (100 mL) and water (100 mL). After being dried with Na_2SO_4, the oil was distilled under a reduced pressure and the distillate was collected at 162–168°C/0.3 mmHg (white solid, 257 g, 80%). After recrystallization from ethanol–water (2 : 1), a white crystal was obtained; mp: 63–64°C.

^{1}H-NMR ($CDCl_3$, ppm): 3.7(3H, OCH_3), 6.8–8.0 (9H, aromatic nuclear).

3-Methoxy-4-nitrosodiphenylamine IV (MND)

Referring to ref. 8, the nitrosation was performed: Into a 100-mL three-neck flask, **II** (25.3 g, 0.127 mol), 95% ethanol (600 mL), and concentrated hydrochloric acid (40 mL) were added. $NaNO_2$, 10.8 g (0.157 mol), in 20 mL of water was added dropwise with stirring at 0°C in 0.5 h. The resultant was poured into a 2-L beaker containing 500 g of crushed ice and adjusted with 20% NaOH to pH 7.0; then, most of the ethanol and water was evaporated with a rotary evaporator. The remainder was extracted with chloroform twice; after evaporation of the chloroform, *N*-nitroso-3-methoxydiphenylamine **III** as a brown oil was obtained and used directly in the next step.

III (28 g, 0.123 mol) in 30 g toluene was added into 24 g of 32% HCl—CH_3OH (CH_3OH was saturated with dried HCl) and stirred at 20–25°C for

Table I Elementary Analysis Data

Compound	Experimental			Calculated		
	C	H	N	C	H	N
$C_6H_5NHC_6H_4(OH)$ **II**	78.36	6.48	6.63	78.40	6.50	7.00
$C_6H_5NHC_6H_4(OCH_3)$ **IV**	67.73	5.20	11.93	68.40	5.30	12.30
$C_6H_5NHC_6H_3(OCH_3)NH_2$ **V**	72.73	6.47	12.80	72.90	6.50	13.10
$C_6H_5NHC_6H_3(OCH_3)N_2^+HSO_4^-$ **VI**	47.72	3.96	12.70	48.30	4.02	13.00

1 h. The reactant was adjusted with 20% NaOH to pH > 12 and stirred 1 h at room temperature, then let stand overnight. The toluene layer was poured out carefully to retain the solid and water. The remainder was adjusted with 30% H_2SO_4 to pH 9–10. **IV** as a purple crystal was obtained (23 g, 82%) and was used directly in the next step. The purification of **IV** can be carried out by recrystallization in ethanol; a purple crystal with a metallic luster was obtained; mp: 153–154°C.

3-Methoxy-4-aminodiphenylamine V (MAD)

The reduction of **IV** to **V** was carried out by the method of ref. 9: **IV** (12 g, 0.053 mol) was dissolved in 10% NaOH (100 mL), then $Na_2S_2O_4$ (20.6 g, 0.118 mol) was added at 35°C with stirring. The temperature of the reaction mixture increased automatically to around 65°C and was kept for 0.5 h. The mixture color changed from red–orange to yellow. Hydrochloride acid, 3*N* (65 mL), was added to precipitate the product. The MAD with a gray color was filtered, washed with water, and dried under a vacuum (9.65 g, 85%). The MAD was oxidized easily and was used immediately in the next step. The further purification of MAD can be carried out by recrystallization in ethanol–H_2O (mp 86–87°C).

3-Methoxy-diphenylamine-4-diazonium salt VI (MDDS)

Into the mixture of **V** (9.65 g, 0.045 mol), crushed ice (30 g), and 30% H_2SO_4 (20 mL), $NaNO_2$ (3.45 g, 0.050 mol) in 10 mL water was added dropwise at 0–5°C with stirring. The reaction mixture was kept for 2 h at 0–5°C, then filtered, into the filtrate, the $ZnCl_2$ (10 g in a saturated aqueous solution) was added. The MDDS with a yellow color was filtered, washed twice with a saturated $ZnCl_2$ aqueous solution, and dried at room temperature (14 g, 80%). If the concentrated sulfuric acid (6 mL) was used instead of $ZnCl_2$ to precipitate the diazonium salt, the MDDS with HSO_4^- as a counteranion was obtained (mp: 195–197°C).

^{1}H-NMR (DMSO, ppm): 4.05 (3H, OCH_3), 6.7–8.1 (8H, aromatic nuclear), 10.8 (1H, HSO_4).

The elementary analysis data of **II**, **IV**, **V**, and **VI** are listed in Table I.

Polycondensation of MDDS with Formaldehyde

Referring to ref. 10, **VI** (23.5 g, 0.06 mol) was added into a 200-mL three-neck flask and 80-mL concentrated H_2SO_4 was added dropwise with stirring. The flask was cooled by an ice-water bath. After addition of H_2SO_4, paraformaldehyde (2.16 g, 0.072 mol) was added in batches at a temperature less than 5°C and the reaction was continued at 0–5°C for 2 h. The reactant was poured carefully into 400 mL of the ice water and filtered. $ZnCl_2$ (40 g, 0.294 mol) in 60 mL water was added into the filtrate, and the diazoresin as a $\frac{1}{2}$ $ZnCl_2$ complex with a yellow–green color was precipitated, washed with saturated $ZnCl_2$ aqueous solution twice, and dried at room temperature in a vacuum (19.6 g, 81%). η_{sp}/C (in water) = 0.12 dL g^{-1}; M_n = 1654 g/mol. All the procedures for the preparation of MDDS and its diazoresin should be carried out in the dark.

MEASUREMENT

The photo- and thermal decomposition of MDDS was monitored by a UV-vis spectrophotometer (Shimadzu UV-2100). The decomposition percent was calculated from the equation

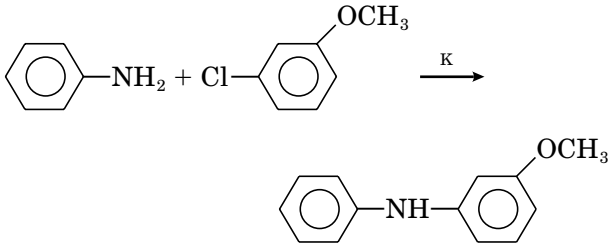
$$\text{Decomposition (mol \%)} = (A_0 - A_t)/A_0 \times 100\%$$

where A_0 and A_t represent the absorbance of the sample at time = 0 and time = t, respectively. The molecular weight of the diazoresin was determined by gel permeation chromatography (GPC, Waters 208) with polystyrene as the standard. The thermal decomposition temperature (T_c) was measured by a differential scanning calorimeter (DSC, Shimadzu-50).

RESULTS AND DISCUSSION

Synthesis of MDDS

The key material in the synthesis of MDDS is 3-methoxydiphenylamine (MDA). Referring to ref. 10, the MDA can be prepared from aniline and 3-methoxychlorobenzene:

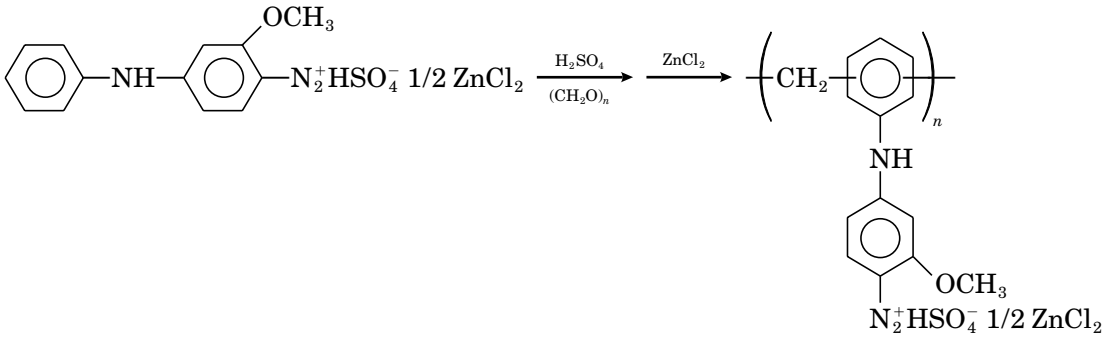


The main defects of the method are a safety problem as well as the price of 3-methoxychlobenzene being too expensive.

In the reaction of resorcinol and aniline, NH_4Cl or $CaCl_2$ can also be used as a catalyst. We used H_3PO_4 as the catalyst because with it the repeatability of the reaction as well as the yield and the purity of the product are satisfactory. The preferable reaction condition of aniline and resorcinol was selected at 180°C for 12 h. The product obtained in this condition can be used in next reaction directly. The compound **V** was prepared via the reaction of a nitroso group transfer from the N atom to the C atom. The reaction is known as the Fischer–Hepp rearrangement in which only a *para*-substituted compound was formed.[11]

Preparation of Diozoresin

The polycondensation of MDDS and formaldehyde was carried out in sulfuric acid:



In the polycondensation, the CH_2O reacts only with the benzene ring far from the diazonium group because the polycondensation in the acidic medium follows the electrophilic-substituted mechanism.

The suitable molecular weight of diazoresin re-

Table II T_c (°C) of MDDS and Its Diazoresin with Different Organic Anions

Anion	HMDS	DBNS	NS	DSS	DS	PSS
Salts	173.4 (148.0)	163.1 (141.9)	174.5 (143.7)	155.8 (142.1)	146.4 (132.0)	176.4 (146.0)
Resins	181.0 (155.3)	174.2 (154.1)	176.2 (156.2)	177 (—)	160.7 (—)	175.7 166.5

The values in parentheses represent the T_c of DDS and its diazoresins with corresponding anions. HMDS: 2-hydroxy-4-methoxy-diphenyl ketone-5-sulfonic anion; DBNS: dibutyl naphthalene sulfonic anion; NS: naphthalene sulfonic anion; DSS: dioctyl sulfosuccinic anion; DS: dodecylsulfonic anion; PSS: polystylene sulfonic anion.

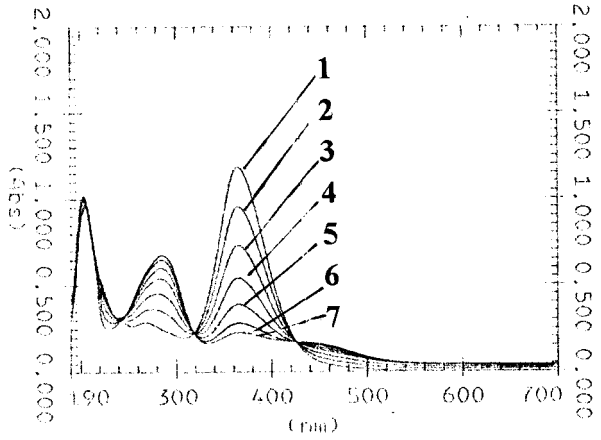


Figure 1 UV-vis spectrum of aqueous solution of MDDS under irradiation. [MDDS]: $4 \times 10^{-5} M$; intensity of irradiation (at 360 nm): 880 μw/cm^2; irradiation time (s): 1 (0); (2) 10; (3) 20; (4) 30; (5) 40; (6) 50; (7) 60.

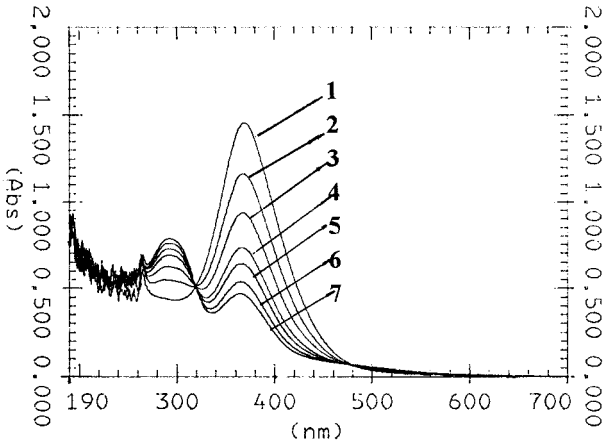


Figure 2 UV-vis spectrum of aqueous solution of diazoresin under irradiation. [Diazoresin] (as diazonium group unit): $4 \times 10^{-5} M$; intensity of irradiation (at 360 nm): 880 μw/cm^2; irradiation time (s): (1) 0; (2) 10; (3) 20; (4) 30; (5) 40; (6) 50; (7) 60.

quired in preparing a negative PS plate is in the region of M_n = 1200–1800 g/mol ($\eta_{sp}/C \sim 0.12$–0.15 g^{-1} dL). To obtain the required diazoresin, the polycondensation condition was controlled:

CH_2O/—$N_2^+ X^-$ (molar ratio)

$\sim$ 1.20, $\sim$ 2–4 h/0–5°C

The diazoresin with HSO_4^- as a counteranion is water-soluble; its complex with $ZnCl_2$ is insoluble in water. Therefore, $ZnCl_2$ was added to precipitate the diazoresin.

If the organic sulfonic acids were used instead of H_2SO_4, the diazoresins with the organic sulfonic counterion do not dissolve in water but dissolve in organic solvents. The diazoresins with the organic sulfonic anion exhibit better antiaging properties especially to weather; another advantage is that the resins dissolve easily in glycol monomethyl ether (GME) or *N*,*N*-dimethylformamide (DMF), which are common solvents used in the preparation of a negative PS plate.

A series of MDDS and its diazoresins with different organic anions was prepared. The thermal decomposition temperatures (T_c) were determined and are summarized in Table II. The T_c's of MDDS or its diazoresins with different organic anions are higher than that of the diphenylamine-4-diazonium salt (DDS) with corresponding anions (values in parentheses).

Photodecomposition of MDDS and Its Diazoresins

The photo- and thermal decomposition behaviors of diazonium salt or its resin are generally considered as a key property of the compounds because the former determines the photosensitivity toward the UV light, whereas the latter determines the storage life of the materials.

Figure 1 shows the photodecomposition of

Table III Thermal Decomposition of MDDS and DDS in Solid State at 80°C

	Diazonium Salt[a]									
	MDDS					DDS				
	Heating time (h)									
Measurement	0	24	48	96	192	0	24	48	96	192
Decomposition (mol %)	0	3	5	8	10	0	55	97	—	—

[a] The solid sample was grounded carefully to fine powder before heating.

Table IV Thermal Decomposition of MDDS and DDS in Aqueous Solution (pH 2) at 70°C

	Diazonium Salt							
	MDDES				DDS			
	Heating Time (h)							
Measurement	0	1	3	6	0	1	3	6
Decomposition (mol %)	0	7	18	28	0	37	76	94

[MDDS] = [DDS] = 4×10^{-5} *M*.

MDDS in an aqueous solution. The λ_{max} appears at 365 nm with a molar extinction coefficiency of 3.4×10^4 L mol^{-1} cm^{-1}. The result shows that the photodecomposition of MDDS is very rapid. It is almost complete within 1 min under experimental conditions. With decreasing of the absorbance at 365 nm, a new band with λ_{max} = 290 nm appears, which was originated from the decomposition product of MDDS, probably 4-hydroxy-3-methoxydiphenylamine. A weak absorption that appeared in the 430–700 nm region can be ascribed to the oxidation, because as the decomposition was carried out in the absence of oxygen, the colored material was not detected.

The photodecomposition of diazoresins with different anions was also performed. The profiles of the UV-vis absorption of the diazoresins are very similar to that of MDDS. A typical UV-vis absorption is shown in Figure 2. The λ_{max} of the resin still remains at 365 nm, indicating that the excitation energies of the diazonium groups in the salt and in the resin are at the same level.

Thermal Decomposition of MDDS and Its Resins

The thermal decomposition of MDDS in the solid state or in solutions was carried out. The decompositions represented as mol percent were measured by a spectrophotometric method and calculated from the decreasing absorbance after heating. The data are summarized in Tables III and Table IV.

As a comparison, the data of DDS in the same condition are also listed. From the data, we can see that the thermal decomposition of MDDS, especially in the solid state, is remarkably slow as compared with DDS. The thermal decomposition in an aqueous solution is affected severely by the pH. It is easy to understand that the thermal decomposition of diazonium salt in an aqueous solu-

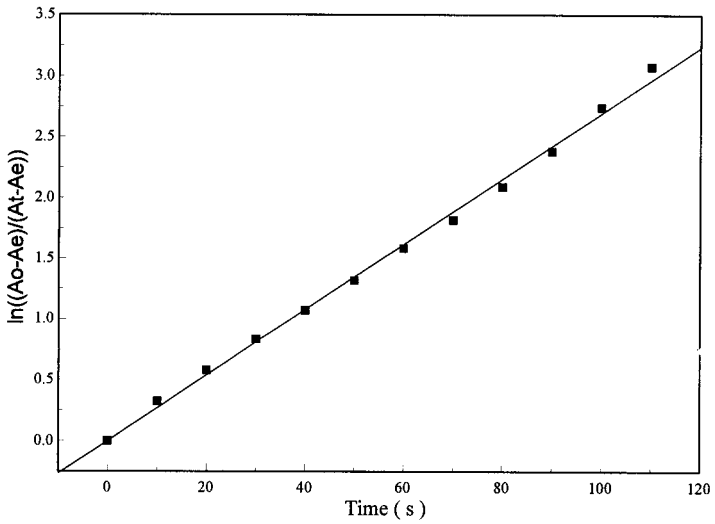


Figure 3 Plot of $\ln(A_0 - A_e/A_t - A_e)$ versus time in photodecomposition of MDDS. Intensity of irradiation (360 nm): 230 μw/cm^2; solvent : ethanol.

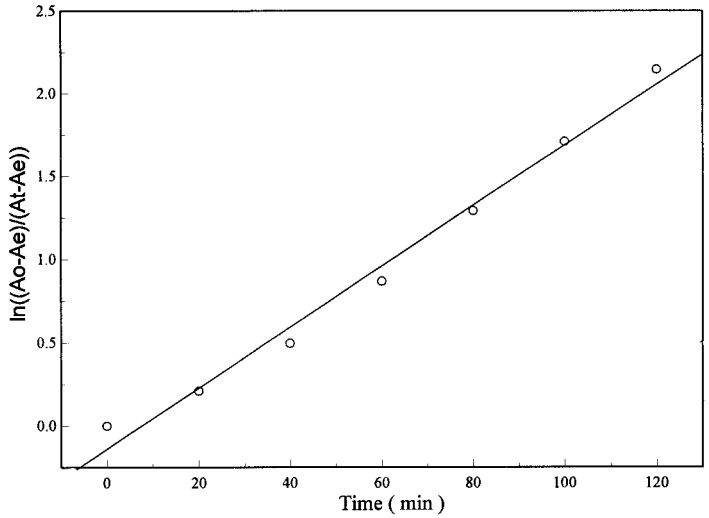


Figure 4 Plot of $\ln(A_0 - A_e/A_t - A_e)$ versus time in thermal decomposition of MDDS. Decomposition temperature: 75.9°C; solvent : ethanol.

tion should be ascribed to the nucleophilic substitution of the diazonium group by $^-$OH. The proton will suppress the $^-$OH formation so that the stability of MDDS in an aqueous solution will be improved. This fact is in accordance with that MDDS or its diazoresin exhibits a higher stability in DMF than in H_2O or ROH. It is very important in practice that the MDDS solution should be stored in an acidic condition.

Kinetics of Photo- and Thermal Decomposition of MDDS

To understand the photo- and thermal decomposition of MDDS quantitatively, the kinetics of MDDS in photo- and thermal decomposition with ethanol as a solvent were investigated and compared with that of DDS. Figures 3 and 4 give the relation of $\ln(A_0 - A_e/A_t - A_e)$ and the decomposition time for MDDS in photo- and thermal decomposition, respectively, where A_o, A_t, and A_e represent the absorbance of the sample solution irradiation by UV light or heating at time = 0, t, and that at the end of the experiment, respectively. In the case of photodecomposition, the experimental period was controlled for less than 10 min. The thermal decomposition was performed usually for 5 h.

Both in photo- and in thermal decomposition, the decomposition of MDDS follows the kinetics of the first-order reaction as shown in Figures 1 and 2. The velocity constant k_d and the half-life period $t_{1/2}$ were calculated from the scope of straight line of the Figures 3 and 4, respectively, and the values obtained are listed in Table V. By comparison, the k_d and $t_{1/2}$ of DDS in the same condition are also listed in Table V. The k_d and $t_{1/2}$ of MDDS are not different obviously from those of DDS in photodecomposition, but in thermal decomposition, the differences are remarkable. The superior thermostabilities of MDDS and its resin are very important in the preparation of a negative PS plate.

Table V k_d and $t_{1/2}$ of MDDS in Photo- and Thermal Decomposition (in Ethanol)

	Photodecomposition (22°C)[a]		Thermal Decomposition (75.9°C)	
Diazonium Salt	k_d (s^{-1})	$t_{1/2}$ (s)	k_d (min^{-1})	$t_{1/2}$ (min)
MDDS	0.0270	25.7	0.0183	37.9
DDS	0.0326	21.3	0.0354	19.6

[a] Light intensity (at 365 nm): 230 $\mu w/cm^2$.

CONCLUSIONS

MDDS was synthesized with aniline and resorsinol as major rough materials via six steps. The diazoresin prepared from the polycondensation of MDDS and paraformaldehyde with different counteranions was reported. The photochemical and thermal properties of MDDS and its diazoresin were investigated and showed that both the diazonium salt and the diazoresin exhibit extraordinary thermal properties as well as high photosensitivity. The kinetics of photo- and thermal decomposition of MDDS in ethanol was also reported.

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