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### Water Soluble and Photoactive Copolymers Containing Amidic Aryldiazosulfonate Groups

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## WATER SOLUBLE AND PHOTOACTIVE COPOLYMERS CONTAINING AMIDIC ARYLDIAZOSULFONATE GROUPS

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***Dedicated to Professor Max Herberhold on the occasion of his 60th birthday.***

### ABSTRACT

Photoactive polymers could be synthesized by copolymerization of methyl methacrylate and sodium-(4-methacryloylaminophenyl)-diazosulfonate which became water soluble at high azo content. Determination of the copolymerization parameters revealed an almost ideal copolymerization behavior of the two monomers. The photoactivity of the azo chromophore could be further increased by introduction of two methoxy substituents into the aromatic unit which renders these polymers more suitable for application as photo resins.

### INTRODUCTION

The diazosulfonate chromophore, synthesized by the coupling reaction of an aromatic diazonium salt with sodium sulfite in an acetate buffered aqueous solution, is well known since 1869 [1]. It is highly water soluble, thermally stable up to 230 °C, of yellow color, and photosensitive. In previous work we studied the photochemistry of several low molar mass diazosulfonates as well as of polymeric analogs [2,3] and the possibility to use these structures in photo resins [4]. The polymeric materials

have been synthesized via free radical copolymerization or via polymer analogous reaction [4-6]. The latter showed some disadvantages regarding adhesion on a substrate and film forming properties [4].

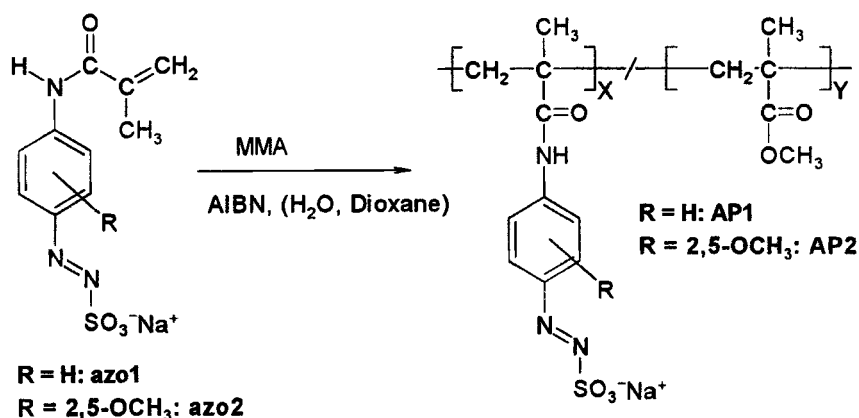
The photochemical decomposition of the chromophore in aqueous solution follows mainly an ionic pathway with diazonium salt intermediates and phenolic products. In contrast to this, radicals are formed by photolysis in bulk which can lead to crosslinking in a thin polymer film. For application in photo resin the water solubility of polymers with high content of diazosulfonate groups is a great advantage compared to commercial systems [7]. Furthermore, the crosslinking reaction upon irradiation and the loss of the polar groups lead to a polymer which does not swell in water nor in organic solvents. Therefore, cast on a hydrophilic support, photo resins based on polymeric diazosulfonates proved to be very suitable for the preparation of offset printing plates [4].

First studies on copolymers of sodium-(3-vinylphenyl)-diazosulfonate with MMA [5] revealed a non-ideal copolymerization with preferred incorporation of the azo compound and therefore, formation of heterogeneous products. Furthermore, the UV-absorption (maximum at ~ 290 nm) of an alkyl-substituted phenyldiazosulfonate does not match well with the emission spectrum of commercial UV-irradiation lamps (maximum at ~ 360 nm) used for photolithography which reduces the photo sensitivity. Therefore, diazosulfonate acrylates with amidic functionalities in para-position to the azo function have been studied which should reveal a more ideal copolymerization behavior and a bathochromic shift in UV-absorption.

## RESULTS AND DISCUSSION

In a previous work [4] we already described the feasibility of the copolymerization of sodium-(4-methacryloylamino-phenyl)-diazosulfonate **azo1** and methyl methacrylate and the photolithographic behavior of the products. Copolymers with 40 mol% of **azo1** were fully water soluble and showed very good properties as photo resins. Now we would like to discuss the copolymerization of these two monomers more in detail.

For the determination of the copolymerization parameter the **azo1** content in the monomer mixture was varied from 10 to 90 mol%. The free radical copolymerization was carried out in a dioxane/water mixture (4:1) at 70°C. The polymerization was quenched with hydroquinone after 15 min in order to keep the polymer yield below



Scheme 1

5%. AIBN (2 mol% based on the total monomer amount) was used as initiator. The polymer was isolated by precipitation in diethylether. In addition the isolated product was dialyzed in water for 3 days in order to remove all unreacted **azo1**. The composition of the copolymers was analyzed by proton NMR and the copolymerization parameters were determined using the Fineman-Ross equation (eq.1):

$$\frac{[M_1]}{[M_2]} \left(1 - \frac{m_1}{m_2}\right) = -r_2 + r_1 \left(\frac{[M_1]}{[M_2]}\right)^2 \frac{m_2}{m_1} \quad (\text{eq.1})$$

$[M_1], [M_2]$  = molar concentration of the monomer in the feed;  $m_1, m_2$  = molar content of the monomer in the polymer;  $r_1, r_2$  = copolymerization parameter

An almost ideal copolymerization behavior was found (Fig.1). The copolymerization parameters of  $r_1 = 0.96$  and  $r_2 = 0.94$  ( $M_1 = \text{azo1}$ ) indicate a nearly ideal azeotropic copolymerization ( $r_1 = r_2 = 1$ ). This result was not fully expected due to some differences in the polymerizable groups of **azo1** (acrylamide) and MMA (acrylester), but it is very favorable for the synthesis of copolymers with a homogeneous composition. In similar experiments, for the copolymerization system (3-vinylphenyl)-diazosulfonate ( $M_1$ ) and MMA ( $M_2$ ) a large difference in the copolymerization parameters has been observed:  $r_1 = 23$ ,  $r_2 = 0.8$  [8]. In this case, polymers with high chemical inhomogeneity had to be expected.

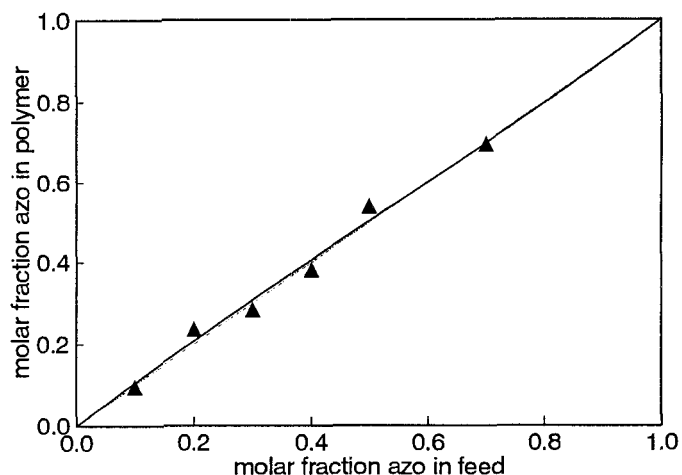


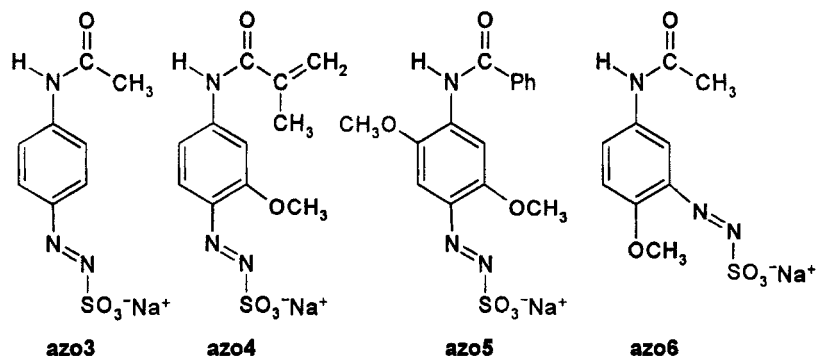
Fig. 1: Copolymerization diagram for the system **azo1**/MMA (diagonal represents ideal copolymerization)

The ideal copolymerization behavior of **azo1** and MMA led to excellent copolymers with high photoactivity which proved to be suitable for photolithography. However, the already described photo activity of these products [4] is still not high enough for a commercial application. In order to improve the photo sensitivity we have studied the UV-absorption of derivatives of **azo1** with methoxy substituent at the aromatic unit. For some model compounds the UV-absorption maxima and the irradiation time which was necessary to reduce the UV-absorption by half are given in Table 1. As described before [2], it is not possible to evaluate the photolytic decomposition of diazosulfonates in water by a simple first order kinetics, therefore these estimated values are given as a measure for the photo sensitivity. From the studies one can conclude, that para-position of the azo group to the amidic function is absolutely required and that two methoxy substituents result in the highest photoactivity of these model compounds.

Therefore, a diazosulfonate monomer with two methoxy substituents (**azo2**) has been synthesized (scheme 2). Its copolymerization with MMA (**AP2**, scheme 1) was readily achieved under similar conditions as described for **azo1** [4]. Again, water solubility was achieved for a copolymer with 40mol% azo content. Molar mass determination was not suitable due to aggregate formation of the polymers but high solution viscosities in water and excellent film forming properties indicate high molar mass products. The UV-absorption of the chromophore incorporated into the polymer chain was only slightly shifted to smaller wavelength (319 nm and 396 nm)

TABLE 1

UV-absorption and photolytic decomposition time in water (RT) of some diazosulfonate model compounds



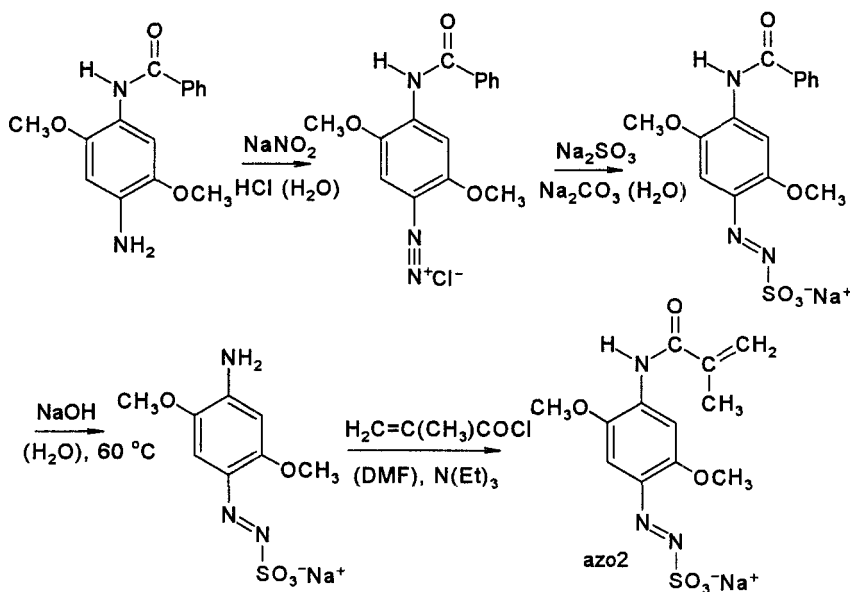
	<b>azo3</b>	<b>azo4</b>	<b>azo5</b>	<b>azo6</b>
$\lambda_{\max} / \text{nm}^a$	330	349	326,403	374
$t_{1/2} / \text{s}^b$	45	22	11	180

a) wavelength of the maximum UV-absorption,

b) irradiation time in sec. (solvent = water, Hg-Xe-High pressure lamp, fluence = 100mW/cm<sup>2</sup>) which was necessary to reduce the original UV-absorption by half

compared to the model compounds and still two almost equally strong absorptions could be observed. Photolysis in aqueous solutions confirmed the results from the model compounds: the decomposition of **AP2** was about three times faster than that of **AP1**.

For the application as photo resin the photo decomposition of **AP2** in bulk has been studied and the lithographic properties of a film cast on a hydrophilic PET support were evaluated by irradiation through a mask and application of the developed structures in a printing process. The decrease of absorption versus irradiation time (fluence = 1mW/cm<sup>2</sup>) of **AP2** and, for comparison, of **AP1** cast as an approximately 1µm thick film from water solution (at pH 2 and pH 7) is given in Fig.2. For both polymers decrease of pH accelerates the decomposition and the photoactivity of **AP2** exceeds that of **AP1** approximately by the factor of 2. This result was confirmed in the lithographic test: Similar good adhesion to the substrate, film forming properties, mechanical properties, and long time stability were found for



Scheme 2

**AP1** and **AP2**. The possible line resolution of the structures was in the range of  $4\mu\text{m}$  for both and no veils remained on the structures after development in pure water. However, whereas the best results for **AP1** were obtained after 500s irradiation time, the same was achieved with **AP2** after only 250s irradiation time due to the higher photo activity of the chromophores. Even though this increase in photo sensitivity is not dramatic, it still places photo resins based on diazosulfonate chromophores extremely close to commercially interesting systems.

## EXPERIMENTAL PART

### Materials

All chemicals were commercial products and applied without further purification. Methyl methacrylate was destabilized by passing through a column filled with basic aluminum oxide and then distilled. The synthesis of **azo1** and **AP1** has been described before [4]. Model compounds **azo3** and **azo5** are intermediates in the synthesis of **azo1** and **azo2**.

The UV-irradiation in solution and in bulk, the lithographic test, and the copolymerization was carried out as described before for **azo1** [4].

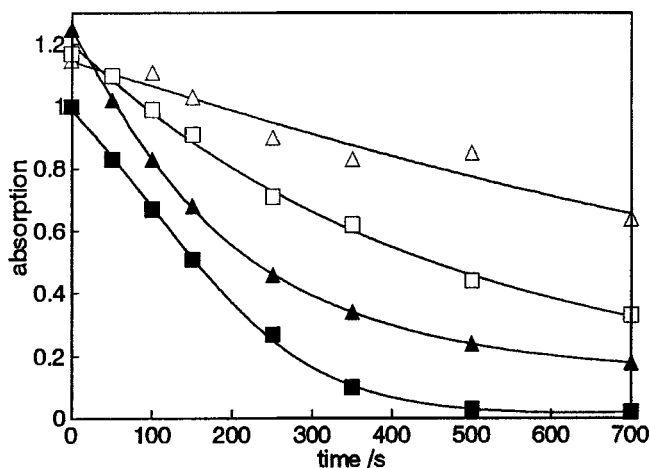


Fig.2: Decrease of absorption upon irradiation with UV-light (DL 2000 irradiation apparatus,  $1\text{mW}/\text{cm}^2$ ) of a film cast from AP1 (pH7  $\Delta$ ; pH2  $\blacktriangle$ ) and from AP2 (pH7  $\square$ ; pH2  $\blacksquare$ ).

#### *Sodium-(2,5-dimethoxy-4-methacryloylaminophenyl)-diazosulfonate (azo2)*

The synthesis of **azo2** (scheme2) was carried out analogous to that of **azo1** [4] with the exception that the reaction with the methacryloyl chloride and the intermediately formed amine was carried out in dimethyl formamide (DMF) and not in water. In the last step of the synthesis the product precipitates together with triethyl ammonium chloride. The precipitate was dissolved in water, excess of sodium carbonate was added, triethyl amine was distilled off in vacuum and the product was isolated by removal of the solvent. The crude product was stirred in DMF for 3 hrs, undissolved salt was separated by filtration and the product was isolated by pouring the DMF-solution into an 20 fold excess of diethyl ether. After collection by filtration the product was dried over  $\text{P}_2\text{O}_5$  in vacuum.

Yield: overall 20% (based on 4-amino-2,5-dimethoxybenzanilide)

$^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$  in ppm): 2.00, 3.85, 3.88, 5.59, 5.91, 7.11, 8.10, 8.93 (NH)

$^{13}\text{C}$  NMR (DMSO- $d_6$ ,  $\delta$  in ppm): 19.1, 57.1, 57.3, 98.7, 107.0, 122.1, 133.2, 134.9, 140.6, 144.3, 153.1, 167.0

#### *Sodium-(2-methoxy-4-methacryloylaminophenyl)-diazosulfonate (azo4)*

Starting from the hydrate of sodium-(2-methoxy-4-aminophenyl)enediamine)-sulfate sodium-(2-methoxy-4-aminophenyl)diazosulfonate was prepared in 30% yield following a known procedure [9]. The diazosulfonate was then reacted with methacryloyl chloride via a Schotten-Baumann reaction similarly as described for **azo1** [4]: 3 g of sodium-(2-methoxy-4-aminophenyl)diazosulfonate were dissolved in



40 ml water and 10 ml aqueous solution of pikrinic acid (1%); 2.28 ml methacryloyl chloride, dissolved in diethyl ether, and 0.96g NaOH, dissolved in water, were added simultaneously at 0°C and the reaction mixture was kept at 4 °C for 24hrs. The product precipitated and was isolated by filtration.

Yield: 3.6% (based on sodium-(2-methoxy-4-aminophenylenediamine)

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ in ppm): 1.97, 3.89, 5.58, 5.86, 7.41, 7.75, 10.07 (NH)

<sup>13</sup>C NMR (DMSO-d<sub>6</sub>, δ in ppm): 19.5, 56.6, 105.0, 112.6, 117.6, 121.5, 135.7, 141.0, 145.0, 158.3, 168.0

#### *Sodium-(2-methoxy-5-acetylaminophenyl)-diazosulfonate (azo6)*

The synthesis of **azo6** started from 3-amino-4-methoxyacetanilide and followed standard procedure for the diazotation and diazosulfonate coupling reaction [1,2]. The product precipitated during the coupling reaction, was isolated by filtration, purified by recrystallization from water, and dried over P<sub>2</sub>O<sub>5</sub>.

Yield: 88% (based on 3-amino-4-methoxyacetanilide)

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ in ppm): 2.09, 3.89, 7.18, 7.69, 7.71, 10.14 (NH)

<sup>13</sup>C NMR (DMSO-d<sub>6</sub>, δ in ppm): 24.7, 56.9, 107.9, 114.5, 124.9, 133.5, 139.6, 153.6, 168.9

### ACKNOWLEDGMENT

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### REFERENCES

- [1] R. Schmidt, L. Lutz, Ber. Dtsch. Chem. Ges. **2**, 51 (1869)
- [2] O. Nuyken, T. Knepper, B. Voit, Makromol. Chem. **190**, 1015 (1989)
- [3] A. Stasko, O. Nuyken, B. Voit, S. Biskupic, Tetrahed. Lett. **31**, 5737 (1990); P. Rapta, A. Stasko, D. Bustin, O. Nuyken, B. Voit, J. Chem. Soc. Perkin Trans. **2**, 2049 (1992)
- [4] P. Matusche, O. Nuyken, B. Voit, M. Van Damme, J. Vermeersch, W. De Winter, L. Alaerts, Reactive Polymers **24**, 271 (1995)
- [5] O. Nuyken, B. Voit, Makromol. Chem. **190**, 1325 (1989)
- [6] J. Dauth, O. Nuyken, P. Strohhriegl, B. Voit, Makromol. Chem. **193**, 723 (1992)
- [7] J.R. Williams, M.F. Molaire, in Kirk-Othmer: *Encyclopedia of Chemical Technology*, Vol. **17**, p. 680f., John Wiley & Sons, New York 1982; Y. Tabata,

I. Mita, S. Nogogaki, K. Horie, S. Tagawa (Eds.), *Polymers for Microelectronics, PMS'89*, Kodansha and VCH, Tokyo 1990.

[8] B. Voit, PhD thesis, University of Bayreuth (1990)

[9] J. Dauth, PhD thesis, University of Bayreuth (1991)