

# Syntheses of Azo Dyes

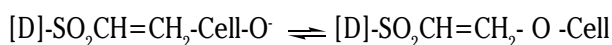
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The present paper describes the synthesis of some new monoazo-dyes for textile fibers and also for polymeric liquid crystals. They have been obtained from the reaction between a monoazo component (4-N,N-dimethyl-4'-carboxyazobenzene; 4-N,N-diethyl-4'-carboxyazobenzene; 4-N,N-diethyl-2-methoxy-4-carboxyazobenzene; 4-cyanoethyl-4-carboxyazobenzene; 4-N,N-cyano-carboxyethyl-2-azocarboxy-4-methoxy-4-carboxyazobenzene) and a polymerisable one (p-chlorine-methyl styrene). The synthesis of azo monomers is carried out by using the catalysis technique through phase transfer, the reaction agent being DMSO. Dyes were analyzed by TLC, elemental analyses (C, H, N), FT-IR and UV spectra.

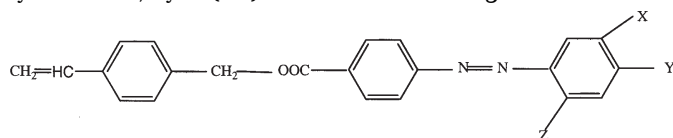
**Keywords:** monoazo-dyes, monoazo component, 4-N,N-dimethyl-4'-carboxyazobenzene, p-chlorine-methyl styrene, FT-IR and UV spectra

The dyes have in their molecule structures with vinylic systems which are fixed to textile surface via nucleophilic addition. The most important groups of this type are the vinylsulphonic dyes and the arylamidic ones. The dyes are fixed on the textile surface, the reaction proceeding in this manner:



The stationary vinylsulphonic reactive group is not usually present in the commercialised dyes involved in this process. A more stable precursor is used instead, mainly a  $\beta$ -sulphatoethylsulphonic group [1-4].

In the present study was performed synthesis and characterization of photochromic dyes used for textile fibers monoazoic [5] and the possibilities of use for polymer liquid crystals. [6]. Due to their similar structure synthesized, dyes (I-V) have the following structure:



- I. X, Z= H, Y= N(CH<sub>3</sub>)<sub>2</sub>
- II. X, Z= H, Y= N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>
- III. X= H, Y= N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, Z= NHCOCH<sub>3</sub>
- IV. X, Z= H, Y= N(CH<sub>2</sub>-CH<sub>2</sub>-CN) (CH<sub>2</sub>-CH<sub>2</sub>-COCH<sub>3</sub>)
- V. X=OCH<sub>3</sub>, Y= N(CH<sub>2</sub>-CH<sub>2</sub>-CN) (CH<sub>2</sub>-CH<sub>2</sub>-COCH<sub>3</sub>), Z= NHCOCH<sub>3</sub>

## Experimental part

The dyes from the polymerisable monoazo dyes series can be obtained from the direct reaction between a monoazo component and a polymerisable one, p-chloromethyl styrene in this case. The monoazo intermediate can be obtained by two methods. The first one consists of adding the coupling component to the diazoderivative solution. Then, a solution of sodium acetate is added, being further finalized for 14 h at low temperature. The mixture is kept for 24 h with continuous stirring, then a NaOH solution 40% is added. The mixture is left to rest 48 h, afterwards it is filtered and the precipitated dye is processed. The second method is performed by adding the coupling component over the diazoderivative solution in ethanol, at low temperature. The mixture is heated and drained in cold water and this the way the dye is

precipitated as a free acid. It is processed after being filtered. This second method is usually preferred due to the shorter period in which the work is done and the fewer intermediate steps involved. The monoazo component must be turned into a sodium salt in order to be used in the next phase. To achieve this, the product is dissolved into ethanol and then it is precipitated as sodium salt with NaOH solution 30% until pH=8-8.5. The salt is separated from the solution by filtration. The synthesis of azo monomers is performed via catalysis by phase transfer, the transfer agent being 2,3-dimercapto-1-propanol, and the reaction medium is DMSO. The reaction for the preparation of the monoazo intermediate and its salt was done via para-amino benzoic acid diazotization, after the model of anthranilic acid diazotization. The synthesis of intermediates was carried out according to data from the literature [7].

### Diazotization of para-aminobenzoic acid

An amount of 6.8g (0.05 moles) of para-amino benzoic acid (Merck) is dissolved into 111.2g (138 mL) ethanol 95%, then 25g (21.7 mL; 0.2 moles) HCl 30% are poured, while the mixture is being cooled on the outside. Diazotization follows by dripping 11.5g (9.5 mL; 0.05 moles) NaNO<sub>3</sub> solution 30%, the temperature being kept all this time at 5-10°C. The organic phase is extracted with ethylic ether which is separated from the product by distillation.

### Coupling with N,N-dimethylaniline

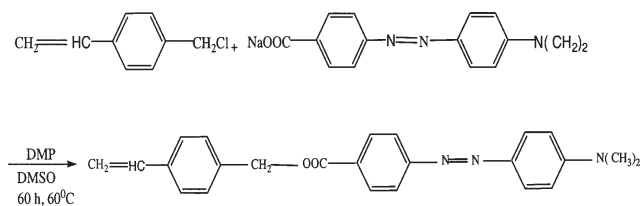
An amount of 6.2g (6.5 mL; 0.05 moles) of N,N-dimethylaniline (Merck) is dissolved into 33.5mL ethanol 95%. The next step is the addition of 7.8g (6.8mL; 0.05 moles) HCl 30% and the solution is cooled at 5-10°C on the outside. The diazoderivative solution is cooled and stirred and coupling occurs rapidly. The mixture is heated at 60-65°C dipped in water bath, then it is drained into 0.5 L cold water. The intermediate is precipitated as free acid and it is then filtered, washed with water on the filter until the filtered liquid does no longer have a positive reaction to red Congo paper. The product is pressed and dried at 50°C. The resulted amount is 11.7g fine crystals of dark red product, at a yield of 89.2%.

The transformation into the sodium salt of the resulted product is made by dissolving into 95% ethanol and it is

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brought to  $pH=8$  with a 30% NaOH solution, until the sodium salt of the dye precipitated. It is separated from the solution by filtration, the result being 13.5g product as bright orange crystals.

### The synthesis of dye 1



3.5 g of azo dye salt ( $12.4 \cdot 10^{-3}$  moles), 0.27g (0.2 mL;  $2.2 \cdot 10^{-3}$  moles) 2,3-dimer-capto-1-prophanol and about 300 mL, DMSO are introduced into a balloon equipped with ascending cooler, dripping funnels, stirrer and thermometer. The resulted solution is then cooled at  $0^{\circ}C$ . A halogenated derivative (para-chloro methyl-styrene), 16.77g (0.11 moles) is slowly added upon stirring, Keeping the reaction temperature at  $0-2^{\circ}C$ . After this addition is completed, the temperature is increased to  $60^{\circ}C$ , this temperature being kept for about 24-60 h, while stirring continuously. At the end the reaction mixture is poured into 1L of iced water. The resulted product (3.45g) is a bright red powder with a boiling point of  $94-95^{\circ}C$ , the yield being 75%. Dyes II-V are obtained in a similar manner. The reaction conditions are presented in table 1.

The experimental study which led to the preparation of dyes involved the condensation of monoazo dyes with para-dimethyl styrene. Condensation was completed with good results. The synthesis of monoazo dyes goes through diazotization, coupling and condensation with para-dimethyl styrene, with 70-90% reaction yield. The purity of the synthesized products was tested via thin layer chromatography; the fixed and mobile phases were determined for each separate product [8]. For all the dyes, the optical separation method, the ascending method on silicagel prop were used. The latter one contained silicagel 600 G (Merck) as stationary phase, deposited on plastic paper and having a mixture of pentanol- ethanol solution of  $NH_3$  25% as a stable phase, in a 10:5:1 ratio.

The sample solubility was tested with ethyl alcohol 5%. The analysis solutions were applied at 3 mL. Dyes I-V were purified via recrystallization from 95% ethanol and precipitated as sodium salts with 30% NaOH solution. The purified products were subjected to IR spectral analysis in a SPECORD M 80 (Carl Zeiss) in KBr prop. The dyes were analysed in UV-VIZ in methanol solution [9-10].

### Results and discussions

The elemental analysis showed that the experimental values and the calculated ones were consistent with each other. (table 2).

To verify the purity of compounds thin layer chromatography was used with aluminum silicate as stationary phase [8], the results being those in table 3.

Table 1

Dye	The amount of diazoderivative		The amount of coupling component		Reaction time (hours)	Yield %	Para-chloro styrene		Yield %	Colour
	g	moles	g	moles			g	moles		
II	6.8	0.05	7.67	0.05	0.1	87	16.7	0.11	70	orange
III	6.8	0.05	8.9	0.05	0.1	87.7	16.77	0.11	67	orange
IV	6.8	0.05	19	0.05	0.1	80	17.7	0.11	79	orange
V	6.8	0.05	19.8	0.05	0.1	82	16.77	0.11	69	yellow

Table 2

RESULTS OF ELEMENTAL ANALYSIS FOR DYES I-V

Dye	Molecular formula	Molecular mass	Elemental analysis %					
			C calc	C found	H calc	H found	N calc	N found
I	$C_{24}H_{25}O_2N_3$	385	74.31	74.28	6.46	6.42	10.85	10.81
II	$C_{25}H_{29}O_2N_3$	413	74.44	74.41	7.19	7.07	10.42	10.39
III	$C_{27}H_{33}O_2N_4$	458	74.04	74.00	7.31	7.29	12.63	12.60
IV	$C_{30}H_{28}O_2N_4$	468	71.94	71.90	6.05	6.02	12.02	12.00
V	$C_{32}H_{29}O_2N_5$	553	75.19	75.06	5.17	5.06	12.50	12.02

Table 3

$R_f$  VALUES FOR DYES I-V

Dyes	I	II	III	IV	V
$R_f$	0,92	0,94	0,96	0,91	0,99

Table 4  
RESULTS OF IR SPECTRA FOR DYES I-V

Dye	Characteristic frequencies $\text{cm}^{-1}$ and intensities
I	3500s 3020m 1500 960s 780s 1625 2925 i 2853i
II	3540s 3021m 1580 961 775s 1623 2925i 2853i
III	3500s 3019m 1500 960 779s 1620 2925i 2853i
IV	3500s 3020m 1580 962 780s 1625 2920i 2830i
V	3500s 3019m 1500 960s 779s 1620i 2924i 2852i

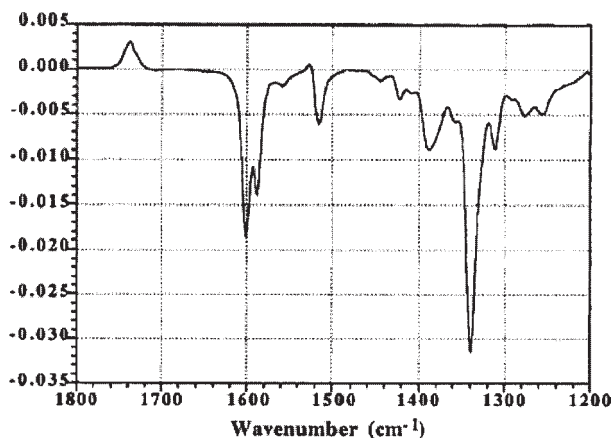


Fig. 1. IR spectra of compound I

Condensation has 70-90% yields and the resulted dyes are in yellow-orange shades. They were obtained via condensation with para-chloro-methyl styrene in the presence of dimer-capto-1-prophanol and DMSO. The structure of the dyes was tested in IR in KBr prop. (table 4). In IR spectra, the main functional groups of the dyes for the mentioned models are highlighted with the help of the absorption bands consistent with the data in the literature [10-11].

The condensation of the chloro-methyl styrene group with the methylcarboxyl group can be noticed. Carboxy methyl groups are identified of 1730  $\text{cm}^{-1}$  intense absorption. The spectra reveal the NCH groups at 1495  $\text{cm}^{-1}$  and C = O at 1600  $\text{cm}^{-1}$ . All the five synthesized compounds have a broad band absorption at 1610  $\text{cm}^{-1}$  specific to groups CH = CH. Bands appearing in the 1350 - 1500  $\text{cm}^{-1}$  are assigned to CH vibration of the R-CH<sub>3</sub> and O-CH<sub>3</sub>. Peaks appearing in the 1575  $\text{cm}^{-1}$  are assigned to groups N = N (table 4 and fig. 1).

The UV-VIZ spectra in methyl alcohol show the wavelengths ranging from 400 to 800 nm. Compound I had an absorption maximum around 364 nm, due to electron donor groups. The substitute can not be quantitatively correlated with structural changes. The colours of the five dyes range from yellow to orange. The solvent used was absolute methanol [10-12].

## Conclusions

The reaction conditions in the preparation of new polymerizable dyes are relatively simple, involving reactions of diazotization, coupling and condensation at good yields.

The synthesis dyes were recrystallized from ethanol and were tested via thin layer chromatography on silicagel prop, being pure.

The structure of dyes was verified with IR and UV-VIS spectra in methanol solution.

Synthesized dyes have structures similar to the dyes used for textile fibres and liquid crystals, which results from the analysis of IR spectra and UV-VIS.

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Manuscript received: 18.05.2010