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On the synthesis of some reactive triazine azodyes containing tetramethylpiperidine fragment

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Abstract

The synthesis of five new reactive triazine azodyes and their intermediates was investigated. Three of these dyes contained a tetramethylpiperidine (TMP) fragment and four of them contained a polymerizable group in their molecule. Two different reaction schemes for synthesis were studied and the most suitable one was found. The quantitative thin-layer chromatography (Tlc) to monitor the synthesis was applied. Cotton fabrics were dyed and their color characteristics were measured. The dyes copolymerized with acrylamide (ACA) and acrylonitrile (AN) and the copolymers with an intense orange color that is stable to solvent extraction were obtained. The photostability of the dyes in solution and on cotton fabrics was studied and it was found that two of the dyes, containing a TMP fragment, had good photostability and can be recommended.

Keywords: Triazine azodyes; Tetramethylpiperidine stabilizer; Photostability; Coloured copolymers of AN and ACA

1. Introduction

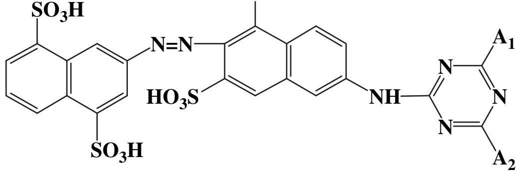
A polymeric modification of organic products including dyes and pigments is a modern approach for their more tolerant ecological application [1,2]. The photostability of the dyes and colored materials is of importance for their application. We have previously reported the synthesis of some polymerizable dyes containing a stabilizer in their molecule, suitable for "one-step" coloration and stabilization of materials [3,4]. Azodyes are widely applied in practice, but their photostability is not very high. Among them triazine derivatives have an important place.

The 1,3,5-triazine molecule affords an opportunity for modification by replacing some of the traditionally applied amine residues with some unsaturated group and/or with a stabilizer's fragment. Based on our experience, it was of interest to synthesize some reactive triazine azodyes, containing a TMP fragment and a polymerizable group in their molecule. Therefore, this was the aim of the present study.

2. Results and discussion

2.1. Synthesis of dyes

The dyes object of the present study can be presented by the general formula I, where meanings of A_1 and A_2 are presented in Table 1. Dye **1.1** (CI Reactive Orange 20) was used as a model dye:



Formula I

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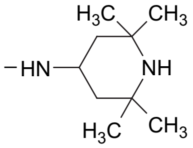
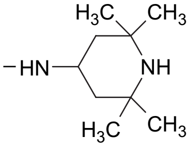
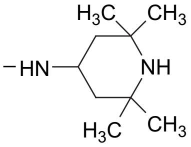
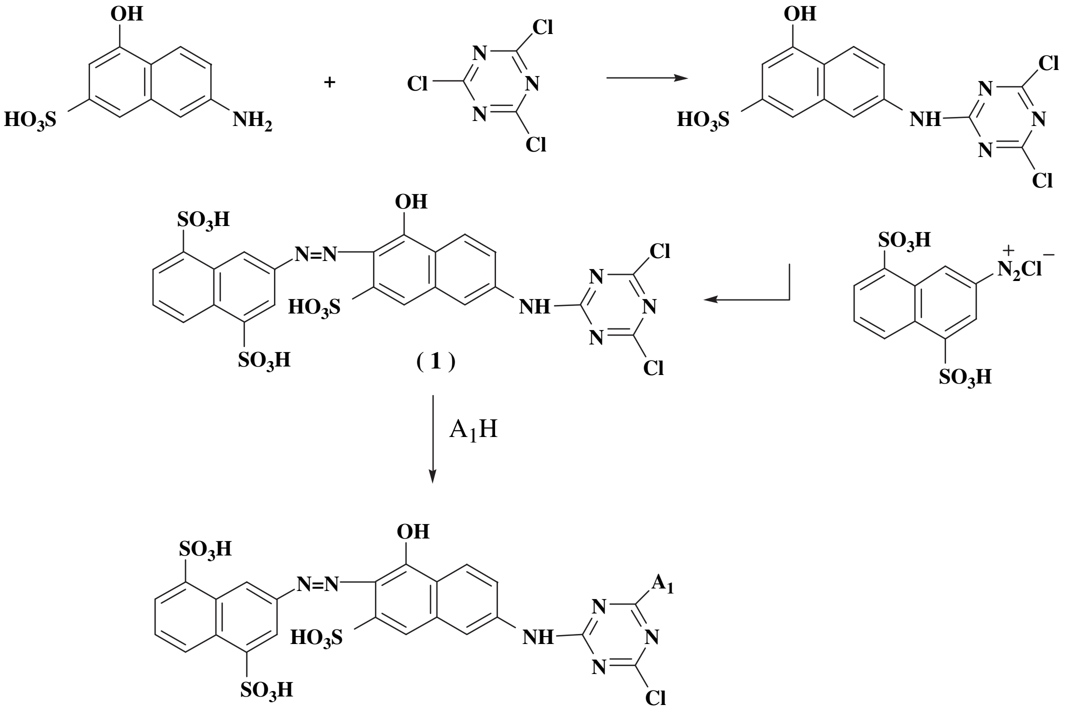
Table 1
Characteristic data for the dyes with formula I

Dye No	A_1	A_2	λ_{max} (nm)	ε ($\times 10^{-4}$)
1.1	$-NH_2$	$-Cl$	502	1.61
1.2		$-Cl$	504	2.48
1.3	$-NHCH_2CH{=}CH_2$	$-Cl$	496	4.55
1.4	$-OCH_2CH{=}CH_2$	$-Cl$	496	1.51
1.5	$-NHCH_2CH{=}CH_2$		484	3.1
1.6	$-OCH_2CH{=}CH_2$		489	1.33

The dyes can be obtained according to two routes. The first one is presented in Scheme 1. According to the scheme the dichlorotriazine dye (**1**) and the model dye **1.1** were obtained by a traditional procedure [5,6]. For the synthesis of dye **1.2** at the last stage of the scheme we experimented with different reaction conditions—temperature was varied from 40 °C to 80 °C.

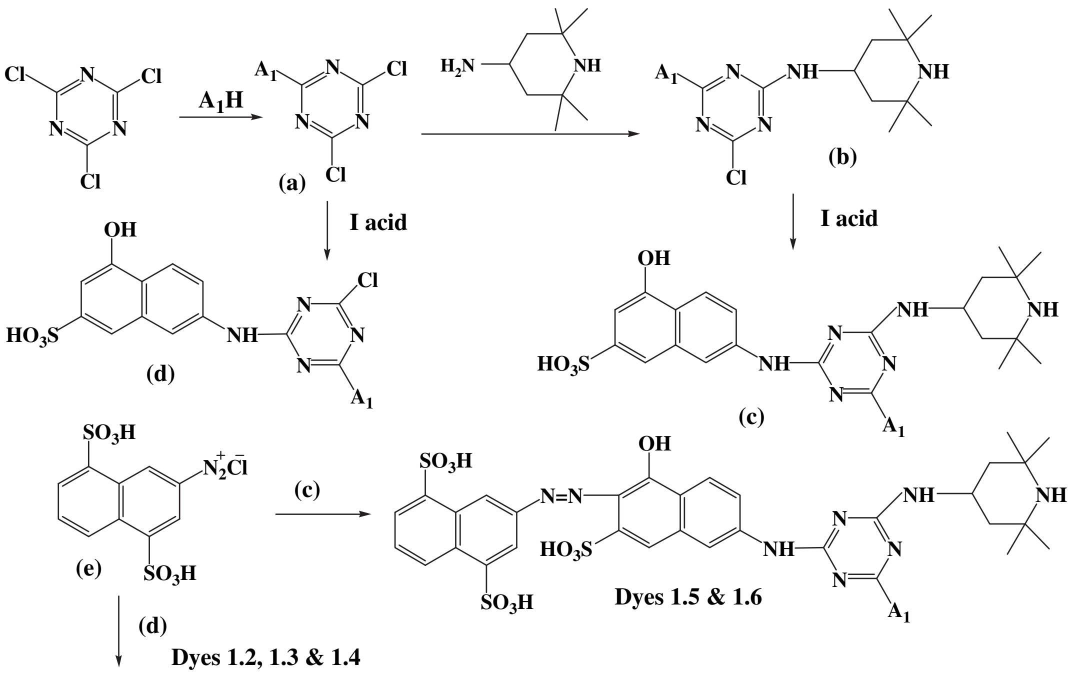
Thin-layer chromatography (Tlc) was a very suitable method for providing rapid reliable information about the course of the reaction, i.e. the conversion ratio and the duration of the synthesis. Therefore, a quantitative Tlc to monitor the process was applied. For this purpose, we had to find the most appropriate mobile phase (presented in Section 3) for separation of the final products from their starting compounds. For dye **1.2** the eluent system *n*-propanol–ammonia (1/1, v/v) was found to be suitable, furnished compact spots of regular shape, which resulted in subsequent detection with high sensitivity. After scanning, on the basis of the data for percentage correlation between the spots of the final product and its starting compound (**1**), the conversion ratio at the corresponding reaction time was estimated. Following this procedure it was found that a new product (**1.2**) was recorded at 80 °C only. After 3 h at this temperature and keeping pH neutral the synthesis was completed (95% conversion ratio that was not changed within 30 min). The dye **1.2** was isolated using 15% of NaCl, filtered and dried under vacuum at 40 °C till constant weight. The dye was characterized and identified by Tlc (R_f value), UV–vis, IR and ^{1}H NMR spectra. The data are given in Section 3.

It is well known that the reaction of cyanuric chloride (CC) with alcohols was more difficult to perform than



Dyes 1.1, 1.2

Scheme 1.



Scheme 2.

the reaction of CC with amines. Our earlier studies [8] showed that the replacement of the second chlorine atom in the CC with allylic alcohol took place above 80 °C in alkaline media, where hydrolysis also occurred. That is why for the synthesis of dyes **1.4** and **1.6**, we experimented with another route as presented in Scheme 2.

According to this scheme, first, CC reacted with allylic alcohol under the phase-transfer catalysis (PTC) conditions according to a method described in our earlier papers [8] at 0–5 °C and 2-allyloxy-4,6-dichlorotriazine ($\mathbf{a}_2$) for 1 h and a quantitative yield was obtained. For the synthesis of dye **1.4** the product $\mathbf{a}_2$ thus obtained reacted with I acid at 40 °C and pH = 6 and semi-product $\mathbf{d}_2$ after 1 h (conversion ratio 98%) was isolated by filtration only, characterized and identified by Tlc, UV–vis, IR and ^{1}H NMR spectra (data presented in Section 3). The subsequent step of the synthesis was the reaction of $\mathbf{d}_2$ with diazo amino C acid (**e**). This reaction was carried out at 0–5 °C, pH = 7 and was completed after 1 h (conversion ratio 97%). Dye **1.4** was isolated using 15% NaCl and identified by Tlc, UV–vis, IR and ^{1}H NMR spectra.

We decided to apply this scheme for the synthesis of dyes **1.2** and **1.3** as well. The product $\mathbf{a}_1$ was obtained according to the method described in our earlier papers [7], while $\mathbf{d}_1$ was obtained under similar conditions as described above (temperature and time) and identified by Tlc, UV–vis, IR and ^{1}H NMR spectra. After the reaction of $\mathbf{d}_1$ with (**e**) at 0–5 °C and pH = 7.5 (1 h) the dye **1.3** was obtained (conversion ratio 98%), isolated and characterized by Tlc, UV–vis, IR and ^{1}H NMR spectra.

The first step of the reaction for synthesis of dye **1.2** was carried out at 0–5 °C and pH = 7.5, thus product $\mathbf{a}_3$ with 87% yield (filtration only) was isolated, characterized and identified by Tlc, UV–vis, IR spectra and elemental analysis. Reaction of $\mathbf{a}_3$ with I acid at 45 °C and pH = 7.5 was completed after 2 h. The corresponding product $\mathbf{d}_3$ (98% conversion ratio) by filtration only was isolated, characterized and identified by Tlc, UV–vis, IR and ^{1}H NMR spectra. The last step of the synthesis of dye **1.2** was performed under the same conditions as for dyes **1.3** and **1.4** and it was isolated (conversion ratio 93%) and characterized. Its characteristics entirely corresponded to those for the product obtained according to Scheme 1.

The advantages of this scheme were that the time of the total reaction was shorter, steps at lower temperature (the highest one was at 45 °C) were performed, and semi-products could be easily isolated, purified and identified. Bearing this in mind, we accepted that the second route (Scheme 2) was the better one.

Dyes **1.5** and **1.6** were synthesized according to the same scheme. According to this the products $\mathbf{a}_1$ and $\mathbf{a}_2$ reacted with TMP in a water–acetone media at 15–20 °C and pH = 7.5. The course of the reaction was monitored again by a quantitative Tlc. After 7 h the corresponding products $\mathbf{b}_1$ and $\mathbf{b}_2$ were isolated by filtration only and identified by Tlc, UV–vis, IR, ^{1}H NMR spectra and elemental analysis. Data are given in Section 3. Products $\mathbf{b}_1$ and $\mathbf{b}_2$ thus obtained, reacted with I acid in water media at 35–55 °C (35–40 °C for $\mathbf{b}_1$ and 50–55 °C for $\mathbf{b}_2$) and pH = 7.5–8 to produce $\mathbf{c}_1$

Table 2
Color data of dyes, exhaustion, fixation and wash fastness on cotton fabrics

Dye number	**1.1**	**1.2**	**1.3**	**1.4**	**1.5**	**1.6**
Y^a (%)	69.12	63.20	69.20	72.87	44.91	39.60
x^b	0.5516	0.5356	0.5531	0.5624	0.4560	0.361
y^b	0.3386	0.3336	0.3374	0.3412	0.3482	0.282
Exhaustion (%)	75	83	83	85	85	89
Fixation^c (%)	75	92	91	91	95	98
Wash fastness	5/5/5	5/5/5	5/5/5	5/5/5	5/5/5	5/5/5

Achromatic PT $x = 0.3137$, $y = 0.3308$.

[a] Luminance.

[b] Chromaticity.

[c] Fixation as a percentage of the exhausted amount of dye.

and $\mathbf{c}_2$. The process was completed after 3 h (Tlc control). The products $\mathbf{c}_1$ and $\mathbf{c}_2$ reacted with (**e**) at 0–5 °C and pH = 7.5 and after 1 h the target dyes **1.5** (conversion ratio 96%) and **1.6** (conversion ratio 93%) were isolated, characterized and identified by Tlc, UV–vis, IR and ^{1}H NMR spectra.

Following these two schemes five new dyes were synthesized—three of them containing a TMP fragment in their molecule and four of them an unsaturated group.

2.2. Color assessment

In order to study the properties of the dyes their absorption spectra in water were recorded. Data for $\lambda_{\max}$ and molar extinction coefficient are presented in Table 1. One can see from these data that the replacement of the amino group in the model dye **1.1** with TMP, allylamino or allyloxy-residues in dyes **1.2**, **1.3** and **1.4** caused neither hypsochromic nor bathochromic shift in $\lambda_{\max}$, but the effect of simultaneous presence of allylic and TMP groups was a 10–15 nm hypsochromic shift in the absorption maximum.

Cotton fabrics were dyed with dyes at 3% depth o.w.f. and materials with an intense orange color were obtained. The percentage of exhaustion, fixation and wash fastness was measured [9]. The data are given in Table 2. One can see from these data that the modification of the model dye **1.1** improved the exhaustion and fixation properties and the best results were for dye **1.6**. Using the Data Color technique and associated software some color characteristics of the dyes were recorded (Table 2). It is apparent from these data that practically no movement in the CIE coordinates for the new dyes was observed.

2.3. Photostability of dyes

To study the photostability of dyes, their water solutions were subjected to irradiation with UV light ($\lambda_{\max} = 290$ nm, Suntest equipment). During the irradiation since no change in $\lambda_{\max}$ of the dyes was observed, the kinetics of their photodegradation was monitored colorimetrically. The dependence of the dye concentration on the time of irradiation was determined by the method of standard calibration curve. The data obtained are presented in Table 3. One can see from these data that under these conditions the TMP fragment in the dye **1.2** practically did not affect positively the photostability of the dye, but in combination with an allylamino or allyloxy group (dyes **1.5** and **1.6**) the photostability increased (it was >90%).

It was of interest to study the photostability of dyes on the dyed material. The dyed cotton fabrics were subjected to irradiation under the same conditions as it was described before [10] and were tested measuring reflectance and Kubelka–Munk (K/S) function (data presented in Table 4). On the basis of these data, the percentage of color lost was calculated. These data for the dyes were as follows: **1.2** = 38%; **1.5** = 33% and **1.6** = 23%.

One can see from these results that dye **1.5** and especially dye **1.6** had good photostability and can be recommended.

2.4. Copolymerization

Having in mind the possibility for application of the dyes for coloration of polymers, we studied their ability to copolymerize with two monomers ACA and AN.

2.4.1. Copolymerization with ACA

Polyacrylamide is a water-soluble polymer widely applied as an ecologically suitable material. It polymerizes easily in water media at 60 °C. We used this monomer

Table 3
Concentration of the dyes in water solution (%) after 60 min irradiation at 290 nm

Dye number	Concentration of dye (%)
1.1	70
1.2	66
1.3	88
1.4	90
1.5	94
1.6	93

Table 4
Data for K/S and reflectance R (%) for the dyed fabrics during irradiation with UV light (min)

Time (min)	Dye **1.2**		Dye **1.5**		Dye **1.6**	
	R (%)	K/S	R (%)	K/S	R (%)	K/S
0	4.17	11.006	9.87	4.1157	7.90	5.3686
30	5.14	8.7575	12.04	3.2137	8.91	4.6562
60	5.37	8.3304	14.69	2.4762	7.63	5.5912
90	6.04	7.3148	16.37	2.1369	8.95	4.6313
120	5.67	7.8453	18.15	1.8457	8.65	4.8236

as a model one and studied the copolymerization of dyes **1.3**–**1.6** with ACA by a procedure described before [11]. After 4 h intensive orange polymers were isolated and purified by precipitation. The polymers retained their color, which was an indication that the dyes were covalently bonded to the polymer chain.

2.4.2. Copolymerization with AN

Polymers and copolymers of AN are widely applied in industry, that is why we studied the copolymerization of AN with the above dyes. The process was performed according to the method described before [12] in DMFA solution. After 7 h intensive orange polymers were obtained. They were isolated and purified as described before [12]. Their color was stable to solvents, which was an indication for obtaining copolymers.

Absorption UV–vis spectra of the colored purified polymers were recorded and compared to those of the dyes. They showed the same λ_{max} as the parent dyes, an indication that the basic chromophore did not change either during the polymerization or as a result of its incorporation in the polymer chain. Therefore, by the method of the standard curve, the percentage of the chemically bound dye was calculated. The data obtained were 85–96%. The basic conclusion from these experiments was that the dyes are able to copolymerize and can be applied for chemical dyeing of polymers.

3. Experimental

3.1. Materials

Cyanuric chloride (CC) (98%), 6-amino-1-naphthol-3-sulfonic acid (I acid) (71%), 2-amino-4,8-naphthalene disulfonic acid (Amino C acid) (73%), 4-amino-2,2,6,6-tetramethylpiperidine (TMP), acrylamide (ACA), acrylonitrile (AN), ABIN and potassium persulfate were Fluka (Swiss) products; solvents are of p.a. or analytical grade (Fluka).

3.2. Analysis and equipment

Tlc analysis was made on silica gel plates (Fluka, $F60_{254}$, 5×10 cm, 0.2 mm thickness, ready-to-use) using a Camag (Swiss) Tlc equipment, comprising a Linomat IV device for sample application, a Scanner II and an SP429 Integrator. pH values were monitored using a 704 pH-meter (Metrohm, Swiss). Electronic spectra were recorded in water and DMF (2×10^{-4} g/ml) on a Hewlett Packard 8452A UV–vis spectrophotometer; IR spectra on Specol (DDR) using KBr pellets; ^{1}H NMR spectra were measured in H_2O on DRX-250-Brucker equipment operating at 250 MHz.

3.2.1. Procedure for Tlc analysis

To monitor the synthesis of the products, samples (1 μL) of the standard solutions prepared from reaction solution at every 30 min were spotted on the plates by means of Linomat IV device. The chromatograms were developed with the appropriate mobile phases, the spots were visualized under UV light and R_f values for each spot were measured. Quantitative analysis was performed by scanning the chromatograms with a Camag Scanner II. The scanning data for the area of each spot were recorded and percentage correlation between the spots, produced from each initial starting point, was calculated; the error was 1.5–3% from three replicate analyses.

Dyeing of 100% cotton fabrics according to a standard procedure [9] (official Bulgarian standard) at 3% depth o.w.f. and color assessment measurements were performed in a specialized laboratory at the University on Data Color equipment under illuminant D_{65}. Photostability of the dyes in water solution (concentration 2×10^{-4} g/ml H_2O) and on cotton fabrics was studied by a Suntest CPS equipment (Heraeus) supplied with a Xenon lamp (Hanau, 1.1 kW, 765 W/m^2, wavelength $\lambda_{max} = 290$ nm). The photodegradation was monitored spectrophotometrically using the method of standard calibration curve (1 h for dyes and 2 h for textile samples).

3.3. Synthesis of dyes

Dye **1.1** was obtained following the procedure described elsewhere [5,6].

3.3.1. Synthesis of dye **1.2** (method 1)

7.4 g of dye **1** was dissolved in 40 ml water and to this solution 1.75 ml of 4-amino-2,2,6,6-tetramethylpiperidine (TMP) was added. Temperature was maintained at 70–80 °C and pH = 8.5 by adding 20% Na_2CO_3. After 3 h [Tlc control on silica gel plates and eluent system *n*-propanol–ammonia (1/1, v/v)], when the process was completed, the dye **1.2** was isolated using 15% of NaCl, filtered off and dried at 40 °C under vacuum. $R_f = 0.84$, IR spectra data (KBr): $\nu_{-OH} = 3400\ cm^{-1}$, $\nu_{-NH-} = 3300\ cm^{-1}$, $\nu_{-CH3} = 2960\ cm^{-1}$, $\nu_{-CH2} = 2920\ cm^{-1}$, $\nu_{-CH-} = 2900\ cm^{-1}$, $\delta_{-NH-} = 1570\ cm^{-1}$, $\nu_{-CH3} = 1370\ cm^{-1}$, $\nu_{-C-OH} = 1180\ cm^{-1}$, $\nu_{-C-NH-} = 1100\ cm^{-1}$, $\nu_{-SO2-} = 1040\ cm^{-1}$, $\nu_{-C-Cl} = 770\ cm^{-1}$, ^{1}H

NMR spectra (DMSO, 250 MHz) δ ppm: 7.27–8.87 (m, 9H, ArH); 4.35 (m, 1H, $-\mathrm{C}H$ of piperidine); 3.14 (s, 1H, $-\mathrm{N}H$ of piperidine); 1.88 (m, 2H, $-\mathrm{C}H_2$ of piperidine); 1.76 (m, 2H, $-\mathrm{C}H_2$ of piperidine); 1.14 (s, 6H, $2 \times \mathrm{C}H_3$ of piperidine); 1.09 (s, 6H, $2 \times \mathrm{C}H_3$ of piperidine).

*3.3.2. Synthesis of dye **1.2** (method 2)*

A solution of 1.75 ml of TMP in 5 ml of acetone was added dropwise to a suspension of 1.87 g CC in water. The temperature was maintained at 0–5 °C and pH = 7.5. The reaction was monitored using Tlc analysis [silica gel plates and eluent system *n*-propanol–ammonia (1/1/, v/v)]. After 3 h when the synthesis was completed the product 2-tetramethylpiperidinilamino-4,6-dichlorotriazine ($\mathbf{a}_3$) was isolated with an yield of 87%. It was characterized and identified by $R_\mathrm{f} = 0.88$, λ_max (acetone) = 238 nm. IR spectra data (KBr): $\nu_{-\mathrm{NH}-} = 3200\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{CH3}} = 2960\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{CH2}-} = 2920\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{CH}-} = 2900\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{C=N}-} = 1580\ \mathrm{cm}^{-1}$, $\delta_{-\mathrm{NH}-} = 1550\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{CH3}} = 1370\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{C-NH}-} = 1100\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{C-Cl}} = 770\ \mathrm{cm}^{-1}$. Elemental analysis for $\mathrm{C}_{12}\mathrm{H}_{19}\mathrm{N}_5\mathrm{Cl}_2$ calcd.: N = 23.03%, found: N = 23.16%.

A solution of 4.5 g I acid in water was added to the suspension of 3.05 g of $\mathbf{a}_3$ in 25 ml water. The temperature was maintained at 45 °C and pH = 7.5. After 2 h [Tlc control, eluent system *n*-butanol–acetic acid–$\mathrm{H_2O}$ (4/1/5, v/v/v)], the product ($\mathbf{d}_3$) was obtained. It was characterized by $R_\mathrm{f} = 0.51$, λ_max ($\mathrm{H_2O}$) = 330 nm, IR spectra (KBr): $\nu_{-\mathrm{OH}} = 3400\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{NH}-} = 3280\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{CH3}} = 2960\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{CH2}} = 2920\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{CH}-} = 2900\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{C=N}-} = 1580\ \mathrm{cm}^{-1}$, $\delta_{-\mathrm{NH}-} = 1570\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{CH3}} = 1370\ \mathrm{cm}^{-1}$, $\delta_{-\mathrm{C-OH}} = 1190\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{C-NH}-} = 1100\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{SO3H}} = 1040\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{C-Cl}} = 770\ \mathrm{cm}^{-1}$ and $^1\mathrm{H}$ NMR spectra ($\mathrm{D_2O}$, 250 MHz) δ ppm: 7.01–8.46 (m, 5H, ArH); 1.92 (m, 1H, $-\mathrm{C}H$ of piperidine); 1.43 (m, 4H, $2 \times -\mathrm{C}H_2$ of piperidine); 1.19 (s, 12H, $4 \times \mathrm{C}H_3$ of piperidine). Diazotation of amino C acid [6] and subsequent reaction of the diazo compound with $\mathbf{d}_3$ was performed at 0–5 °C and pH = 7.5 for 1 h. The dye was isolated using 15% NaCl, filtered off and dried under vacuum at 40 °C till constant weight. The characteristic data (Tlc, UV–vis, IR and $^1\mathrm{H}$ NMR) of the product thus obtained corresponded to dye **1.2** obtained according to method 1 (See Section 3.3.1).

Dye 1.3: First, 2-allylamino-4,6-dichlorotriazine ($\mathbf{a}_1$) was obtained by a method described before [7]. Semi-product $\mathbf{d}_1$ was isolated with 90% yield, characterized by $R_\mathrm{f} = 0.64$ and λ_max ($\mathrm{H_2O}$) = 268 nm. $^1\mathrm{H}$ NMR spectra data: [$\mathrm{D_2O}$] δ ppm: 6.7–7.05 (m, 5H, ArH) 5.85 (m, 2H, CH=, −OH) 5.24 (dd, 2H, $\mathrm{NCH_2}$) 4.0 (d, 2H, $\mathrm{CH_2}$=). The reaction of $\mathbf{d}_1$ with (**e**) at 0–5 °C and pH = 7.5 for 1 h was performed. Dye **1.3** was isolated using 15% NaCl, filtered, dried under vacuum at 40 °C till constant weight and analyzed. $R_\mathrm{f} = 0.5$ [*n*-propanol–ammonia (2/1)], λ_max ($\mathrm{H_2O}$) = 492; $^1\mathrm{H}$ NMR spectra (DMSO) δ ppm: 10.53 (d, H, OH), 7.4–8.8 (m, 11H, ArH, 2 × OH), 6.4 (s, H, OH), 5.9 (m, H, CH=), 5.18 (dd, 2H, $\mathrm{NC}H_2$), 3.9. (d, 2H, $\mathrm{C}H_2$=).

Dye 1.4: $\mathbf{a}_2$ obtained according to a method described before [8] reacted with I acid at 40 °C and pH = 6 for 1 h. $\mathbf{d}_2$ thus obtained was isolated by filtration (90% yield) and analyzed: $R_\mathrm{f} = 0.67$ and λ_max ($\mathrm{H_2O}$) = 268 nm. $^1\mathrm{H}$ NMR spectra data: [$\mathrm{D_2O}$] δ ppm: 7.0–7.8 (m, 5H, ArH) 5.9 (m, 2H, CH=, −OH) 5.3 (m, 2H, $\mathrm{OCH_2}$) 4.6 (d, 2H, $\mathrm{CH_2}$=). Reaction of $\mathbf{d}_2$ with (**e**) was performed at 0–5 °C and pH = 7 for 1 h and dye **1.4** was obtained. It was isolated using 15% NaCl, filtered, dried under vacuum and analyzed. $R_\mathrm{f} = 0.5$ [*n*-propanol–ammonia (2/1)], λ_max ($\mathrm{H_2O}$) = 496; $^1\mathrm{H}$ NMR spectra (DMSO) δ ppm: 11.1 (bs, H, −OH), 7.3–8.7 (m, 11H, ArH, 2 × OH), 6.39 (s, H, −OH), 6.1 (m, H, CH=), 5.4 (dd, 2H, $-\mathrm{OC}H_2$), 4.9 (d, 2H, $\mathrm{C}H_2$=).

Dye 1.5: A solution of 1.75 ml TMP in 5 ml acetone was added to the suspension of 2.05 g of $\mathbf{a}_1$ in 25 ml ice-water. The temperature was maintained at 15 °C and pH = 7.5–8. After 7 h [Tlc control, silica gel and system *n*-heptan–diethyl ether (1/1, v/v)], the product $\mathbf{b}_1$ was filtered and isolated with an yield of 98%, dried under vacuum at 40 °C and analyzed. $R_\mathrm{f} = 0.47$, λ_max (acetone) = 338 nm. IR spectra data (KBr): $\nu_{-\mathrm{NH}-} = 3350\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{CH3}} = 2960\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{CH2}} = 2800\ \mathrm{cm}^{-1}$, $\delta_{-\mathrm{NH}-} = 1560\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{CH3}} = 1390\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{C-NH}-} = 1100\ \mathrm{cm}^{-1}$, $\delta_{-\mathrm{CH=CH2}} = 980\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{C-Cl}} = 773\ \mathrm{cm}^{-1}$. Elemental analysis, $\mathrm{C}_{15}\mathrm{H}_{25}\mathrm{N}_6\mathrm{Cl}$, calcd.: N = 25.89%; found: N = 25.67%. Reaction of product $\mathbf{b}_1$ with I acid was performed at 35–40 °C and pH = 7.5–8 for 3 h. Product $\mathbf{c}_1$ was isolated by filtration, dried under vacuum till constant weight (yield 88%) and characterized by $R_\mathrm{f} = 0.49$, λ_max ($\mathrm{H_2O}$) = 344 nm, IR spectra (KBr): $\nu_{-\mathrm{OH}} = 3400\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{NH}-} = 3310\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{CH3}} = 2960\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{C-NH}-} = 1100\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{SO2}-} = 1040\ \mathrm{cm}^{-1}$, $\delta_{-\mathrm{CH=CH2}} = 980\ \mathrm{cm}^{-1}$ and $^1\mathrm{H}$ NMR spectra ($\mathrm{D_2O}$, 250 MHz) δ ppm: 7.02–8.46 (m, 12H, ArH, $4 \times -\mathrm{O}H$, $3 \times -\mathrm{N}H-$); 5.90 (m, 1H, $\mathrm{C}H$=); 5.10 (m, 2H, $-\mathrm{NC}H_2-$); 3.96 (bd, 3H, $\mathrm{C}H_2$=, $-\mathrm{C}H$ of piperidine); 2.19 (m, 2H, $2 \times -\mathrm{C}H_2$ of piperidine); 1.53 (s, 6H, $2 \times \mathrm{C}H_3$ of piperidine); 1.43 (s, 6H, $2 \times \mathrm{C}H_3$ of piperidine). Reaction of $\mathbf{c}_1$ with (**e**) was performed at 0–5 °C and pH = 7–7.5 for 1 h. The dye **1.5** was isolated using 15% NaCl, filtered off and dried under vacuum at 40 °C. $R_\mathrm{f} = 0.80$, λ_max ($\mathrm{H_2O}$) = 486 nm. IR spectra data (KBr): $\nu_{-\mathrm{OH}} = 3400\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{NH}-} = 3310\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{CH3}} = 2960\ \mathrm{cm}^{-1}$, $\delta_{-\mathrm{NH}-} = 1570\ \mathrm{cm}^{-1}$, $\delta_{-\mathrm{C-OH}} = 1190\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{C-N}-} = 1180\ \mathrm{cm}^{-1}$, $\nu_{-\mathrm{SO2}} = 1040\ \mathrm{cm}^{-1}$, $\delta_{-\mathrm{CH=CH2}} = 980\ \mathrm{cm}^{-1}$, $^1\mathrm{H}$ NMR spectra ($\mathrm{D_2O}$, 250 MHz) δ ppm: 6.94–8.94 (m, 16H, ArH, $4 \times -\mathrm{O}H$, $3 \times \mathrm{N}H$); 5.58 (m, 1H, CH=); 4.92 (d, 2H, $-\mathrm{NC}H_2-$); 3.65 (m, 1H, $-\mathrm{C}H$ of piperidine); 3.53 (s, 1H, $\mathrm{N}H$ of piperidine); 3.44 (d, 2H, $\mathrm{C}H_2$=); 1.64 (d, 4H, $2 \times -\mathrm{C}H_2$ of piperidine); 1.09 (s, 12H, $4 \times \mathrm{C}H_3$ of piperidine).

Dye 1.6: **a**$_2$ reacted with TMP at 20 °C and pH = 7.5–8 for 7 h. Semi-product **b**$_2$ with an yield of 85% was isolated, dried and analyzed: $R_f = 0.42$, λ_{max} (acetone) = 324 nm, IR spectra data (KBr): $\nu_{-NH-} = 3360\ cm^{-1}$, $\nu_{-CH3} = 2940–2740\ cm^{-1}$, $\delta_{-NH-} = 1560\ cm^{-1}$, $\nu_{-C-O-C} = 1240\ cm^{-1}$, $\nu_{-C-NH-} = 1100\ cm^{-1}$, $\delta_{-CH=CH2} = 970\ cm^{-1}$, $\nu_{-C-Cl} = 773\ cm^{-1}$. Elemental analysis for $C_{15}H_{24}N_5OCl$, calcd.: N = 21.50%; found: N = 21.27%. **b**$_2$ reacted with I acid at 50–55 °C and pH = 7.5–8 for 7 h and product **c**$_2$ was isolated by filtration (yield 92%) and analyzed: $R_f = 0.44$, λ_{max} (H_2O) = 340 nm. IR spectra (KBr): $\nu_{-OH} = 3400\ cm^{-1}$, $\nu_{-NH-} = 3360\ cm^{-1}$, $\nu_{-CH=CH2} = 3100\ cm^{-1}$, $\nu_{-CH3} = 2890\ cm^{-1}$, $\nu_{-C-O-C} = 1230\ cm^{-1}$, $\nu_{-C-NH-} = 1100\ cm^{-1}$, $\nu_{-SO2-} = 1040\ cm^{-1}$, $\delta_{-CH=CH2} = 910\ cm^{-1}$; ^{1}H NMR spectra ($D_2O$, 250 MHz) δ ppm: 7.01–8.07 (m, 11H, Ar*H*, 4 × –O*H*, 2 × –N*H*–); 6.04 (m, 1H, C*H*=); 5.33 (m, 2H, –OC*H*$_2$–); 4.36 (bd, 3H, C*H*$_2$=, –C*H* of piperidine); 2.18 (m, 4H, 2 × –C*H*$_2$ of piperidine); 1.54 (s, 6H, 2 × C*H*$_3$ of piperidine); 1.43 (s, 6H, 2 × C*H*$_3$ of piperidine). Reaction of **c**$_2$ with (**e**) was performed at 0–5 °C and pH = 7.5 for 1 h. Dye **1.6** was isolated using 15% NaCl, filtered off, dried under vacuum till constant weight and analyzed. $R_f = 0.76$, λ_{max} (H_2O) = 498 nm, IR spectra (KBr): $\nu_{-OH} = 3400\ cm^{-1}$, $\nu_{-NH-} = 3360\ cm^{-1}$, $\nu_{-CH3} = 2890\ cm^{-1}$, $\delta_{-NH-} = 1560\ cm^{-1}$, $\nu_{-C-O-C} = 1240\ cm^{-1}$, $\delta_{-C-OH} = 1190\ cm^{-1}$, $\nu_{-C-N-} = 1180\ cm^{-1}$, $\nu_{-SO2} = 1040\ cm^{-1}$, $\delta_{-CH=CH2} = 910–880\ cm^{-1}$; ^{1}H NMR spectra ($D_2O$, 250 MHz) δ ppm: 6.69–8.88 (m, 16H, Ar*H*, 4 × –O*H*, 2 × N*H*); 5.83 (m, 1H, –C*H*=); 5.1 (m, 2H, –OC*H*$_2$–); 4.42 (d, 2H, C*H*$_2$=); 3.66 (m, 1H, –C*H* of piperidine); 1.75 (d, 4H, 2 × –C*H*$_2$ of piperidine); 1.19 (s, 12H, 4 × –C*H*$_3$ of piperidine).

3.4. Polymerization

3.4.1. Polymerization with ACA

The polymerization was performed as described before [11]. Intensively colored polymers obtained were subjected to threefold precipitation with methanol until the colorless filtrates were observed, an indication that the unreacted dye was removed. All polymers retained their color. The precipitated polymers were dried at 40 °C under vacuum till constant weight and analyzed.

3.4.2. Polymerization with AN

The polymerization was carried out at 70 °C for 6 h in DMF [12]. Colored polymers obtained were precipitated by hot water, which is a good solvent for the dyes, but not for PAN. After twofold precipitation the colorless filtrates were obtained, an indication that the unreacted dye was removed. The polymers retained their color. They were dried at 40 °C under vacuum till constant weight and analyzed.

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