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The Synthesis, Properties and Application of Some 9-Phenylxanthene Dyes

T. Konstantinova,[a] G. Kirkova[a] & R. Betcheva[b]

[a]Organic Synthesis Department, University of Chemical Technology & Metallurgy, 8 Kl. Ohridsky str., Sofia 1756, Bulgaria
[b]Textile Chemistry Department, University of Chemical Technology & Metallurgy, 8 Kl. Ohridsky str., Sofia 1756, Bulgaria

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ABSTRACT

Three dyes, allyloxy ether–esters of 9-phenylxanthene, were synthesised and some of their characteristics determined. Their copolymers with methyl methacrylate (MMA) were stable to solvents and their colour and fluorescence parameters were obtained. Wool, polyacrylonitrile (PAN) and polyamide (PA) were dyed with them and some colour characteristics of the dyed fabrics using the Data Color technique were measured.

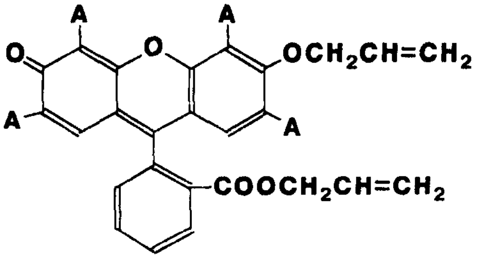
INTRODUCTION

Among various classical dyes, luminophores, with their bright colour and fluorescence, have been successfully applied for the coloration of natural and synthetic materials. A serious disadvantage of such dyes is their low photostability, which has been detrimental to their application in the textile industry [1]. The most significant part of their non-textile application is as laser and food dyes. The poor light fastness of laser dyes is also a serious problem, and one possibility to resolve this is polymer modification. A lower toxicity and more tolerant ecological behaviour of dyes and pigments applied in food can also be achieved by appropriate polymer modification [2]. Among the above mentioned dyes, derivatives of 9-phenylxanthene are well known and have been widely utilised [1, 2]. We have previously reported the synthesis of two dyes, viz. allylic ether-esters of fluorescein and eosin, able to copolymerize with styrene and acrylonitrile [3]. It was of interest to synthesize a similar rhodamine derivative to study the properties of all three dyes, the possibilities for their polymeric modification (obtaining of copolymers), and application for coloration of natural and synthetic materials.

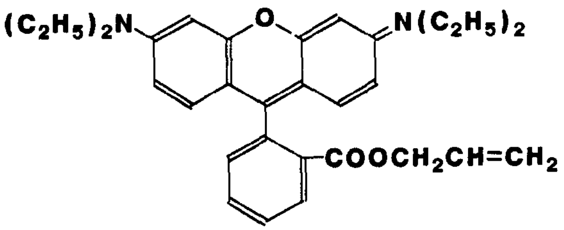
RESULTS AND DISCUSSION

Synthesis of the dyes

We have earlier reported [3] the synthesis of two dyes of general formula 1 viz. allylic ether–esters of fluorescein (I) and eosin (II).



where A = –H for dye I and A = –Br for dye II. No information is available for the synthesis of a similar rhodamine derivative. Having in mind the bright colour and very intensive fluorescence of rhodamine, the possibility of obtaining the allylic ester (III) has been studied.



The route employed for the synthesis was the same as for dyes I and II using phase transfer catalysis (PTC) conditions [3]: catalyst 18-crown-6 (10 mol%), rhodamine, allyl bromide and KOH in mole ratio 1:1:1.5 were used. The reaction was carried out in boiling acetonitrile and was monitored by thin-layer chromatography on silica gel. After 2 h the target product (formula III) with 60% yield was obtained, characterised and identified by mp, R_f, elemental analysis, UV/Vis, IR and ^{1}H NMR spectra. Some of these data are presented in the Experimental section.

TABLE 1

λ_{max} (nm) for the Dyes in Different Solvents

Dye no.	C_2H_5OH	*DMF*	$CHCl_3$	C_6H_6
I	458	456	456	456
II	544	542	542	542
II	552	552	554	556

Investigations on the properties of the dyes

Spectrophotometric investigations

The absorption spectra of the dyes I–III were recorded in different solvents and relevant data are presented in Table 1. The polarity of the solvents increased from toluene to methanol but neither bathochrome nor hypsochromic shifts of λ_{max} were observed. On the basis of such data, we can conclude that there is an $\mathbf{n} \rightarrow \pi*$ charge transfer transition [4]. A similar observation was made for fluorescein and eosin, which is an indication that the presence of one or two allyloxy groups in the dye molecule did not affect the character of the electron transfer transition in the basic chromophore.

Polymerization

Polymethylmethacrylate (PMMA) is a widely utilised material and its coloration in bright colours is of interest. PMMA also has very good optical properties, so polymeric modification of dyes, i.e. copolymers with MMA, would be useful. We investigated the possibility of obtaining copolymers of MMA with the above mentioned dyes. The copolymerization was performed in bulk in the presence of 0.5% of azo-bisisobutyronitrile (ABIN) as initiator and at three different concentrations (0.05–0.2 wt.%) of the appropriate dye at 70°C. After 8 h, transparent coloured polymers with an intense fluorescence were obtained. They were several (3–4)-fold precipitated to remove unreacted monomers. All of them retained their colour, indicating that the copolymer had been formed. The absorption spectra for the polymers thus treated showed the same λ_{max} as the pure dyes, thus indicating that the basic chromophore did not change either during the polymerization or as a result of the bonding to the polymer chain. Using the standard curve colorimetric method, it was established that 45–55% of the initial amount of dyes I and II and 65% for dye III was incorporated (chemically bonded) into the macromolecule. These values are satisfactory for the production of intensively coloured polymers. More detailed investigations on the kinetics of the process will be an object of our future investigations.

Photostability of the dyes

Films prepared from precipitated polymers were irradiated in a Suntest equipment at room temperature for 10 h, and after that colorimetrically investigated. Absorption spectra showed no change in λ_{max}. The quantity of the dye in the irradiated polymers, compared to their concentration in the same polymers before irradiation (Table 2) showed a very significant increase of photo-stability of the dyes. It is evident that more than 60% of the chromophores remained unchanged, while pure dyes, irradiated under the same conditions, lost their colour over 1 h. On the basis of these results we can assume that polymeric modification (copolymers with MMA) of the dyes is a promising possibility to improve their photostability. Further investigations on the kinetics of the process are being carried out.

Dyeing of textile materials

Polyamide (PA), polyacrylonitrile (PAN) and wool fabrics were dyed by the disperse method at 1% depth o.w.f. with fluorescein, eosin, rhodamine and their allylic derivatives (dyes I–III). After 30 min materials with an intensive colour and bright fluorescence were obtained. Using the Data Color technique, some colour characteristics of the dyes were recorded; results are given in Figs 1–3. It is apparent from these figures that the intensity of the colour obtained with dye I on wool and PA (Fig. 1) decreased in comparison to that from fluorescein; the opposite effect was evident on PAN. The data for dye II on wool and PA were very close to those obtained with eosin, but the intensity of colouration on PAN was higher. The colour intensity for dye III on wool (Fig. 3), in comparison to rhodamine decreased, while on PA and PAN fabrics it increased significantly.

Other characterisation data, i.e. λ_{min} of reflection, percentage of emission (R), Kubelka–Munk values (K/S) and strength of colour (%) were measured and are shown in Table 3.

Wash fastness of the dyed materials was measured using standard methods (Table 4). From the results, it can be seen that there is a tendency for increase in wash fastness when the functionalized dyes were used. This effect is probably due to some additional linkages arising in the treated material,

TABLE 2
Concentration of the Dye in Polymer (%) after 10 h Irradiation

Dye no.	*Dye concentration (%)*
I	70
II	60
III	85

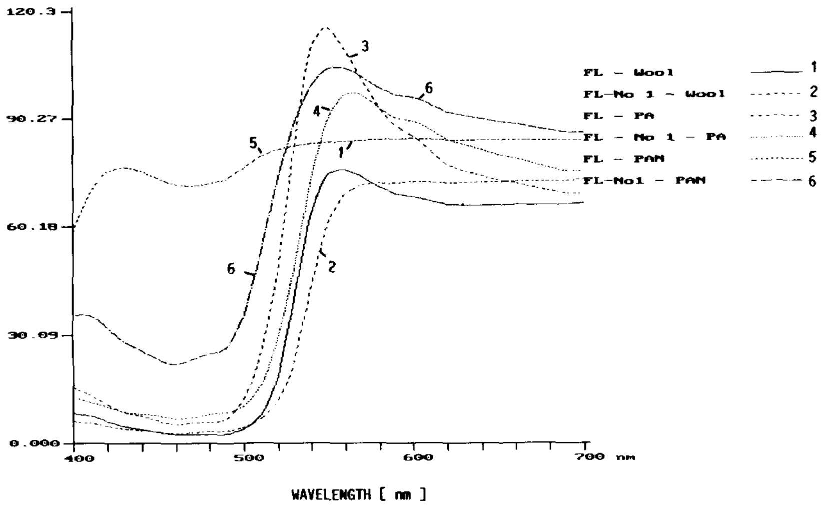


Fig. 1. Dependence of reflectance (%) on the wavelength (nm) of the dyed materials: **1**, wool with fluorescein; **2**, wool with dye I; **3**, PA with fluorescein; **4**, PA with dye I; **5**, PAN with fluorescein; and **6**, PAN with dye I.

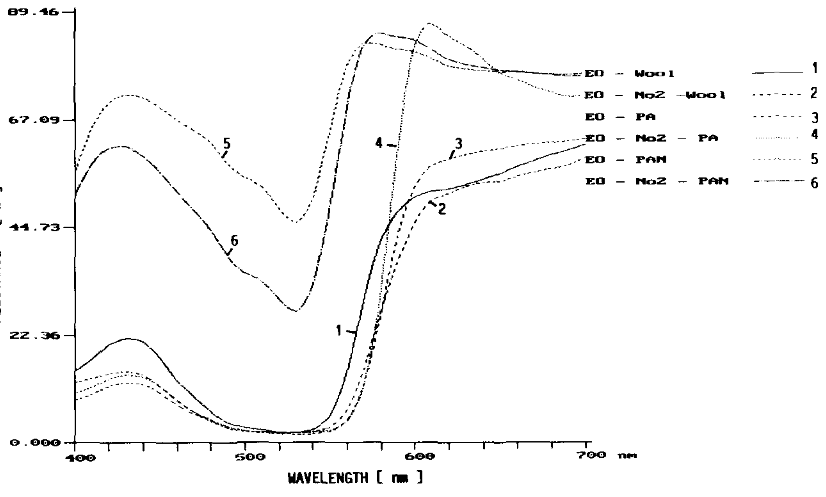


Fig. 2. Dependence of reflectance (%) on the wavelength (nm) of the dyed materials: **1**, wool with eosin; **2**, wool with dye II; **3**, PA with eosin; **4**, PA with dye II; **5**, PAN with eosin; and **6**, PAN with dye II.

and more detailed investigations to determine the mechanism of the dyeing process and character of such linkages is necessary. These preliminary results could be very useful in the dyeing of mixed (natural and synthetic) materials to obtain colours of high quality.

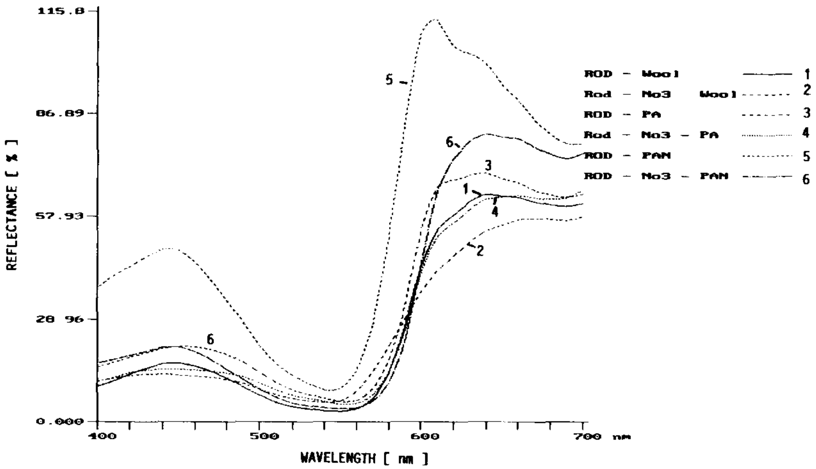


Fig. 3. Dependence of reflectance (%) on the wavelength (nm) of the dyed materials: **1**, wool with rhodamine; **2**, wool with dye III; **3**, PA with rhodamine; **4**, PA with dye III; **5**, PAN with rhodamine; and **6**, PAN with dye III.

EXPERIMENTAL

Fluorescein, eosin, rhodamine and dyes I and II were synthesized as described elsewhere [3, 5]. UV/Vis spectra were recorded on a Hewlett Packard 8452A spectrophotometer. Films of precipitated polymers ($d = 94$ mm, 2 mm thickness) were irradiated in a Suntest equipment (Heraes, Germany),

TABLE 3

Colorimetric Data for Wool, PA and PAN Materials dyed with 9-Phenylxanthene Dyes

Dyed material/dye	λ_{min} *(nm)*	*Remission R(%)*	*K/S*	*Strength of colour(%)*
Wool fluorescein	480	2.41	19.7715	100
Wool I	480	3.34	13.9712	70.7
PA fluorescein	480	5.93	7.4655	37.8
PA I	480	8.20	5.1364	25.9
PAN fluorescein	480	72.06	0.0542	0.3
PAN I	480	24.81	1.1392	5.8
Wool eosin	530	1.96	24.5774	100
Wool II	530	1.58	30.6257	124.6
PA eosin	530	1.92	25.0579	101.9
PA II	530	1.97	24.3925	99.2
PAN eosin	530	45.52	0.3260	1.3
PAN II	530	27.19	0.9751	3.9
Wool rhodamine	550	2.97	15.8380	100
Wool III	550	5.75	7.7184	48.7
PA rhodamine	550	6.04	7.3022	46.1
PA III	550	4.99	9.0518	57.1
PAN rhodamine	550	9.49	4.3137	27.2
PAN III	550	3.69	12.5745	79.4

TABLE 4
Wash Fastness Data for Wool and PA Dyed with the Synthesized Dyes

Dye no.	*PA*	*Wool*
Flourescein	3	3
I	3/4	3/4
Eosin	2/3	2
II	3	2/3
Rhodamine	3	3
III	3	3

equipped with a Xenon lamp (1,1 kW). ^{1}H NMR spectra were made on a Jeol JNM-PS-100 in $CDCl_3$. TLC analysis were performed on silica gel plates (Fluka, F_{60} 254). Acetonitrile, 18-Crown-6, allyl bromide, azobis-*iso*-butyronitryle (ABIN), benzene, methanol, ethanol, chloroform and DMF were Fluka products of p.a., chromatographic or spectrophotometric grade. MMA (Agrobiochim, Bulgaria) was redistilled under vacuum in a nitrogen atmosphere.

Synthesis of dye III. 0.01 mol of rhodamine, 0.001 mol of 18-Crown-6 and 0.015 mol of finely ground KOH were dissolved in 150 mL of acetonitrile. Allyl bromide (0.01 mol) was added dropwise to this solution at room temperature. The mixture was stirred under reflux and the process was monitored by TLC (silica gel plates, using benzene-methanol (1:1, v/v) as eluent). After 2 h the organic phase was separated and the solvent evaporated under vacuum to give the target dye in 62% yield. mp = 130–132°C, $R_f = 0.75$, $\lambda_{max} = 552$ nm (in ethanol).

^{1}H NMR [$CDCl_3$, 100 MHz) δ ppm: 4.7–4.8 (d, 2H,- OCH_2) 5.3–5.5 (d, 2H, $CH_2=$) 6.0–6.2 (m, 1H, $CH=$) 6.3–7.5 (m, 10 H, Ar*H*).

Polymerization. A mixture of 10 g of MMA, 0.05 g of ABIN and 0.0025 g (0.005, 0.01 or 0.02 g) of the appropriate dye was heated at 70°C for 8 h in a sealed ampoule (flushed with dry N_2). Transparently coloured polymers with an intense fluorescence were obtained and these were dissolved in chloroform and precipitated by ethanol (3–4 times) until the filtrates were colourless. The polymers thus treated were dried in vacuum at 40°C to constant weight.

Spectrophotometric analysis. Absorption spectra of DMF solutions of the dyes (2.10^{-5} g cm^{-3}) and the polymers (6.10^{-2} g cm^{-3}) were recorded.

Dyeing. Polyamide (PA), polyacrylonitrile (PAN) and wool fabrics were dyed by the disperse method at 1% depth o.w.f. Colour assessment measurements were performed on a 'Data Color' equipment. Wash fastness was determined by standard methods.

ACKNOWLEDGEMENT

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