

ON THE SYNTHESIS OF COPOLYMERS OF ACRYLAMIDE WITH FLUORESCENT DYES, DERIVATIVES OF 9-PHENYLXANTHENE

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Received 27 January 2006
Accepted 10 February 2006

ABSTRACT

The possibility for obtaining copolymers of acrylamide with 5 fluorescent dyes, derivatives of 9-phenylxanthene was investigated. At two concentrations of the dyes (0.1 and 0.2 wt. %) in the initial monomer mixture, coloured polymers with intensive fluorescence were obtained. Participation of the dyes in the copolymerization was proved and the quantity of the dye chemically incorporated in the polymer was determined. It was established that the participation of the dyes does not affect the copolymerization process and does not exert considerable influence on the properties of the polymer obtained. These investigations afford an opportunity of applying the dyes in an environmentally more tolerant polymer form for cosmetic and food products.

Keywords: monomer 9-phenylxanthene dyes, coloured copolymers of acrylamide.

INTRODUCTION

Dyes and pigments are widely applied for coloration of food, cosmetic and drug products. As it is well-known, for these purposes only specially permitted dyes and pigments are applied. Derivatives of 9-phenylxanthene, have an important place among them with their nice and vivid colours and intense fluorescence. They are in the List of permitted colorants for food and cosmetics [1]. Polymer modification of different organic products, such as dyes, stabilizers, pesticides and others, recently attained particular importance [2-6]. These modifications are of significance as an opportunity for durable coloration or stabilization of the respective materials and also with a view to improve their ecological behaviour [1,7]. As it is well-known, this is particularly important for food and cosmetic products, for such articles as toys, etc.

In previous works of ours, the synthesis of some polymerizable fluorescent dyes and their coloured copolymers were described [8-13]. Polyacrylamide (PACA) is among the polymers widely applied in medicine, cosmetics, the food processing industry and agriculture. It

is well soluble in water which is important for its successful application in these fields. In a previous work, we reported the possibility for obtaining copolymers of acrylamide (ACA) with some triazine herbicides and bactericides with more tolerant application [14]. Based on our experience the aim of the present study was to investigate the possibility for obtaining copolymers of ACA with 9-phenylxanthene dyes synthesized by us, in view of their more tolerant application in the polymer form.

EXPERIMENTAL

Materials

The dyes 1.1, 1.2, 1.3 and 3 were synthesized by a method described before [8, 9, 12]. All dyes were purified by column chromatography, on aluminium oxide (neutral) with an eluent system methanol: ethyl acetate (2:1, v/v) and analyzed by quantitative TLC and HPLC [15]. Eosin B, potassium peroxodisulfate (99 %) and 2-propanol were products of Merck; 18-Crown-6, allylbromide, acrylamide (>98 %) and formamide (>98 %) were products of Fluka. All solvents were of p.a.,

chromatographic or spectrophotometric grade (Fluka). Thin layer chromatography (TLC) was performed on silica gel plates ready-to-use (Merck, 60 F254, 5 x 10cm.), using toluene: ethyl acetate: ethanol (2:1:1, v/v) as eluents.

Analysis and equipment

UV/Vis absorption spectra of the dyes (2.10^{-4} g/ml) and the colored polymers (2.10^{-2} g/ml) in formamide were recorded on a Hewlett Packard 8452A spectrophotometer. TLC analysis was performed using a Camag (Switzerland) TLC system comprising a Linomat IV device for sample application and a Scanner II, equipped with an SP 429 integrator by a described procedure [15]. For determination of the intrinsic viscosity $[\eta]$ of the obtained colored polymers, Ubbelohde AV-1 viscometer and aqueous solutions of the polymers with concentrations from 0.2 upto 0.07 wt. % at 24[°]P were used. Data for average molecular masses were calculated according to ref. [16, 17].

Synthesis of dye 2

In a flask fitted with a stirrer, a separation funnel and a reflux condenser 3.12 g disodium salt of Eosine B and 0.26 g 18-Crown-6 are dissolved in 90 ml DMSO. To this solution drop-wise 1 ml allylbromide dissolved in 10 ml DMSO was added. The mixture was heated at intensive stirring, while the process was monitored by TLC. Every 30 min, the reaction mixture was analyzed. Under these conditions, after 5 hours the reaction solution was poured out into water, the precipitate separated was filtered off, washed out with water up to neutral pH and was dried under vacuum at 30[°]C to constant weight. The product thus isolated was purified by column chromatography on aluminium oxide and the eluent system mentioned above. Data from the analysis of the dye are $R_f = 0.60$, m.p. 160-162[°]C, $\lambda_{max} = 530$ nm (ethanol); ¹H NMR spectra (DMSO, 250 MHz) δ ppm: 4,51 (t, 2H, CH₂-O), 4,53 (t, 2H, CH₂-O), 5,06 (t 2H, CH₂=CH), 5,14 (t, 2H, CH₂=CH), 5,60 (m, 1H, CH₂=CH), 5,70 (m, 1H, CH₂=CH), 7,00(d, 1H, ArH), 7,27 (d, 1H, ArH), 7,55 (m, 1H, ArH), 7,83 (m, 2H, ArH), 8,20 (dd, 1H, ArH).

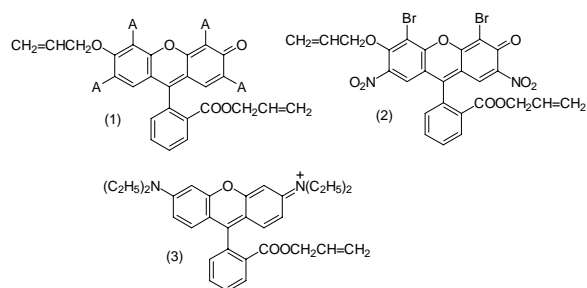
Copolymerization with acrylamide (ACA)

The polymerization was performed at 50[°]C for 4 and 7 h in ampules flushed with dry and pure nitrogen, according to a described procedure [16]. The

coloured polymers obtained are dissolved in water and reprecipitated with methanol (which is a good solvent for the dyes, but not for the polymer) several times until colourless filtrates were obtained. The polymers thus purified were dried under vacuum at 40[°]C up to constant weight and then analysed.

RESULTS AND DISCUSSION

The subject of the study were 5 dyes, derivatives of 9-phenylxanthene. They have the following general formulae:

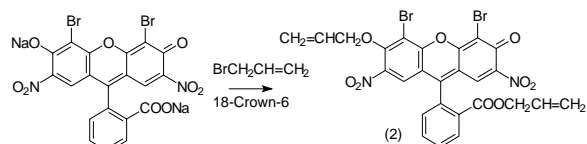


Formulae 1, 2 and 3

In formula (1) the meanings of A are: -H (dye 1.1); -Br (dye 1.2) and -I (dye 1.3).

Synthesis of monomer dye (2)

The synthesis of dye 2 which is an allylic ether-ester of Eosine B, could be presented by the following scheme:



Scheme 1

At room temperature and permanent stirring, 0.012 mol of allylbromide dissolved in DMSO, are added drop-wise to a mixture of 0.005 mol disodium salt of Eosine B and 20 mol % 18-Crown-6 in DMSO. The mixture was heated while the reaction was monitored by quantitative TLC. According to the procedure described in the Experimental section it was established that after the 1st hour of heating at 80[°]C, a new product was registered. After 2 hours its quantity attained 70 %

and did not increase for 2 more hours. Based on this, the process was assumed to be completed. The isolated product was purified by column chromatography and the pure product was characterized by the m.p. and R_f values and identified using $^1\text{N-NMR}$ and UV/Vis spectra. Data presented in the Experimental section completely confirm the dye (2) structure shown above.

Copolymerization of acrylamide with the monomer dyes

As mentioned, PACA is among the environmentally safe polymers used in foods and cosmetics. It is obtained easily by polymerization of ACA, in aqueous medium, the polymer being water-soluble as well. Following our idea, we carried out investigations to obtain copolymers of ACA with the monomer dyes with formulae 1, 2 and 3, which enable us to suggest them for application in polymer form. The copolymerization of ACA with these dyes was performed in an aqueous medium at two different concentration values 0.1 and 0.2 % of the ACA mass, of each of the respective dyes. These concentrations ensured a very saturated color and an intensive fluorescence of the mixture, that is why we did not consider it necessary to carry out experiments with higher concentrations. The polymerization was performed at temperature 50°C for 4 and 7 hours [16]. The polymers thus obtained, brightly coloured and of intensive fluorescence, were dissolved in water and were purified from unreacted monomers by several reprecipitations with methanol. The latter is a very good solvent of the dyes, but not of the polymer. After a 3-fold reprecipitation until a colourless filtrate was obtained, the polymers remained coloured. This was an indication that the dyes were chemically bound to the polymer i.e. for obtaining of copolymer. The colored polymers thus purified were dried at 40°C under vacuum to constant weight and then were analysed.

Investigation of the properties of the copolymers obtained

- The absorption UV/Vis spectra of all colored copolymers purified by the method described above, dissolved in

formamide (concentration $2.10^{-2}\text{ g. ml}^{-1}$) were recorded and compared with those of the pure dyes in the same solvent (concentration $2.10^{-4}\text{ g. ml}^{-1}$). Neither hypso-, nor bathochromic shift in the dye absorption maxima were established, thus showing that the basic chromophore did not change neither during the polymerization, nor as a result of their incorporating in the polymer chain. These results advised us to determine colorimetrically the quantity of the dye chemically bound using the method of the standard calibration curve. The data obtained are presented in Table 1. Considering these results one can see that the percentage of the dye chemically bound in the copolymer, except for the dye (2), is satisfactory. Taking into account the fact that during the reprecipitation of the polymers, lower-molecular mass fractions were removed as well, the real quantity of the dye reacted is higher and exceeds 50 %. Thanks to the high color strength of the chromophores, the reprecipitated polymers were very intensely colored with bright fluorescence, and this intensity would be sufficient for the practice. The relatively lower activity (15

Table 1. Data for the chemically bonded in the copolymer dye [%] depending on the time of polymerization [h] and its initial concentration [wt %].

Copolymer with dye №	$\lambda_{\text{max}}^{\text{abs}}$ [nm]	Time of polymerization [h]	Chemically bounded dye at 0.1 wt %	Chemically bounded dye at 0.2 wt %
1.1	460	4	43	62
		7	56	74
1.2	534	4	43	63
		7	57	80
1.3	542	4	47	54
		7	52	65
2	538	4	15	23
		7	22	28
3	570	4	72	43
		7	68	43

Table 2. Data for the $[\eta]$ and M_w of the copolymers of ACA with dyes.

Copolymer with Dye N	$[\eta]$ for copolymer with 0.1 wt.% Dye		$M_w \cdot 10^{-3}$ for copolymer with 0.1 wt.% Dye		$[\eta]$ for copolymer with 0.2 wt.% Dye		$M_w \cdot 10^{-3}$ for copolymer with 0.2 wt.% Dye	
	4 h	7 h	4 h	7 h	4 h	7 h	4 h	7 h
1.1	1.39	1.61	103.8	130.5	1.71	1.85	142.4	161.2
	1.68	1.80	139.2	154.2	2.0	2.1	182.2	201.3
1.3	1.23	1.70	86.3	141.0	1.32	2.04	96.8	185.5
	1.82	1.96	156.6	174.9	2.02	2.07	188.2	190.0
2	1.45	1.61	110.3	130.1	1.88	2.0	163.7	180.0
	1.45	1.74	122.6	146.0	-	-	-	-
Without dye	1.45	1.74	122.6	146.0	-	-	-	-
	1.45	1.74	122.6	146.0	-	-	-	-

to 25 % bound dye) of dye 2, could be due eventually to the steric hinderence. More accurate conclusions however, would be possible after future studies. By increasing the time of copolymerization, increasing of the quantity of dye chemically bound was observed. This would provide the possibility for obtaining copolymers with higher dye content when increasing of the time of the process.

• The intrinsic viscosity $[\eta]$ of all reprecipitated colored copolymers were determined [16,17]. The same measurements were performed for PACA, obtained under the same conditions, but without a dye. The obtained results are presented in Table 2. One can see that at an initial concentration of 0.1 % of dye, participation of the dyes in the copolymerization process does not affect the molecular mass of the copolymer.

CONCLUSIONS

As a result of the investigations carried out it may be concluded that all the derivatives of 9-phenylxantene are capable to copolymerize with ACA. This ensured obtaining of intensely colored polymers, with bright fluorescence which could be applied in a more tolerant polymer form for coloring of foods and cosmetics. The potential increase of their light resistance, following from the analogy of their copolymers with methylmethacrylate (MMA) [11], will improve further their ecological behavior and make them more suitable for application.

Acknowledgements

The authors would like to thank the Science & Research Programme of the University of the Chemical Technology and Metallurgy for the financial support (Project 10130).

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