Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 74 (2007) 208–214
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Synthesis of some polymerizable triazinylaminobenzotriazole stabilizers and benzanthrone dyes containing a stabilizer fragment

T.N. Konstantinova*, R.A. Lazarova

Organic Synthesis Department, University of Chemical Technology and Metallurgy, 8 Ohridsky Street, Sofia 1756, Bulgaria

Received 3 October 2005; received in revised form 20 January 2006; accepted 23 January 2006

Abstract

Four new monomer dyes, triazinylaminobenzanthrone derivatives, three of them containing a 2-hydroxybenzotriazole fragment, were synthesized. Two new polymerizable triazinylamino-benzotriazole stabilizers have been obtained as well. Two different synthetic routes for their synthesis have been experimented in order to find the better one. The course of the synthesis was monitored using a quantitative thin-layer chromatography (TLC). A benzanthrone dye, suitable for ‘‘one-step – in mass’’ coloration and stabilization of polymers, containing a tetramethylpiperidine (TMP) fragment, following a new approach, was synthesized. The compounds were characterized by TLC analysis, UV/vis, IR and ^{1}H NMR spectra. The ability of the derivatives to copolymerize with methylmethacrylate (MMA) was demonstrated, thus polymers with an intense color and fluorescence stable to solvents, were obtained. The quantity of the dye chemically bonded in polymer was estimated. A new approach for the synthesis of a benzanthrone dye containing a tetramethylpiperidine fragment suitable for ‘‘one-step’’ in mass coloration and stabilization of polymers was demonstrated.

Keywords: Polymerizable dyes; Triazinylamino-2-hydroxyphenylbenzotriazole stabilizers; One-step coloration and stabilization of PMMA

---

1. Introduction

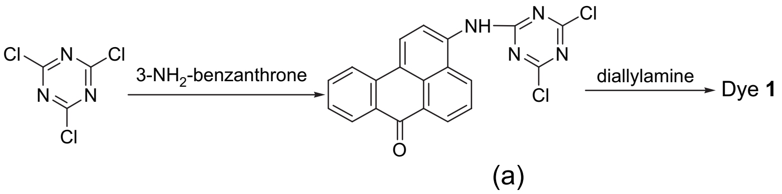
Benzanthrone dyes, due to their bright color, intense fluorescence and good thermostability, are widely used for coloration of polymers. In our previous papers, we have reported the synthesis of some polymerizable benzanthrone dyes and their application for obtaining self-colored polymers [1–4]. Along with coloration, the photo stability of the polymers is of great importance and current interest. Among different stabilizers used, 2-hydroxyphenylbenzotriazole (HBT) and 2,2,6,6-tetramethylpiperidine (TMP) derivatives are of interest [5]. Recently, the polymerizable stabilizers of different types were synthesized [6–10]. Their covalent bonding to the polymer chain provided stability towards solvents and a migration stabilizing effect, both improving their environmental behavior, which is of importance for application in food and cosmetics. We reported before the possibility for ‘‘one-step’’ coloration and stabilization of polymethylmethacrylate (PMMA) and polystyrene (PSt), using polymerizable benzanthrone [11] and naphthalimide [12,13] dyes containing a polymerizable group and a TMP fragment in the same molecule.

Bearing in mind these investigations, it was of interest to synthesize some new polymerizable triazinylaminobenzanthrone dyes containing an HBT fragment in their molecule and to compare their behavior to those of polymerizable stabilizers and dyes; to study more precisely the process of their synthesis, in order to find the most suitable conditions of the reaction. That was the aim of this study.

---

* Corresponding author. Tel.: +359 2 8163 208; fax: +359 2 68 1101.
E-mail address: konst@uctm.edu (T.N. Konstantinova).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.01.035

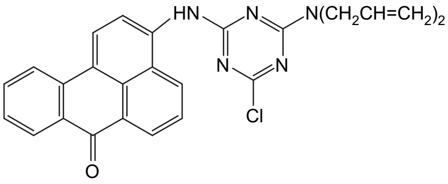


Scheme 1.

2. Results and discussion

2.1. Synthesis of 2-diallylamino-4-benzanthronoylamino-6-chloro-triazine (dye *1*)

Based on our experience of the synthesis of polymerizable triazinylaminobenzanthrone dyes [2], the synthesis of the dye with Formula 1 was of interest.



Formula 1.

Firstly, the synthesis of the dye was performed following Scheme 1.

According to the scheme, 0.01 mol of 3-aminobenzanthrone reacted with 0.01 mol of cyanuric chloride (CC) in boiling nitrobenzene [2]. After 2 h under these conditions the product (**a**) with 82% yield was isolated. In the next step of the reaction, 0.01 mol of (**a**) was dissolved in DMF and 0.012 mol of diallylamine was added. The mixture was heated at 120 °C while the process was monitored by the quantitative TLC procedure described in Section 3. After 1 h under these conditions a new product was registered. At the end of the second hour when the conversion ratio of the starting product (**a**) reached ≈90%, the process was completed. The final product (dye **1**) was isolated, purified by column chromatography and analyzed. The data for R_f, m.p., λ_{max}, IR and ^{1}H NMR spectra confirmed the aimed structure.

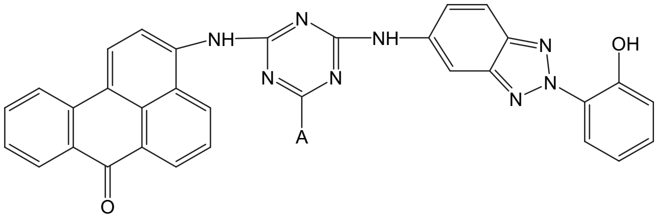
We experimented another reaction route presented by Scheme 2.

Following this scheme, firstly 2-diallylimino-4,6-dichlorotriazine (**b**) by a method described before, at 0–5 °C for 1 h was obtained [14]. In the next step of the synthesis, 0.01 mol of products (**b$_1$** or **b$_2$**) dissolved in DMF reacted with 0.01 mol of 3-aminobenzanthrone at 120 °C in the presence of triethylamine. The process was monitored by quantitative TLC. After 90 min under these conditions, ≈98% conversion of product (**b**) was registered. The dye **1** was isolated, dried under vacuum till constant weight, purified and analyzed. The data of R_f, m.p., UV/vis, IR and ^{1}H NMR spectra are presented in Section 3 and Table 1.

Comparing the two methods, presented by Schemes 1 and 2, we concluded that the second method is more acceptable because of the lower reaction temperature, higher yields and purity of the final product, achieved for shorter reaction time.

2.2. Synthesis of polymerizable triazinylaminobenzanthrone dyes containing a 2-hydroxyphenylbenzotriazole (HBT) fragment (dyes **2–5**)

Having in mind our experience in the synthesis of polymerizable hydroxyphenylbenzotriazole stabilizers and benzanthrone dyes, it was of interest to synthesize some dyes containing an HBT moiety. These dyes can be presented by the general Formula 2, where meanings of A are as follows: dye **2** A = $-$Cl; dye **3** A = $-NHCH_2CH{=}CH_2$; dye **4** A = $-N(CH_2CH{=}CH_2)_2$; dye **5** A = $-OCH_2CH{=}CH_2$.

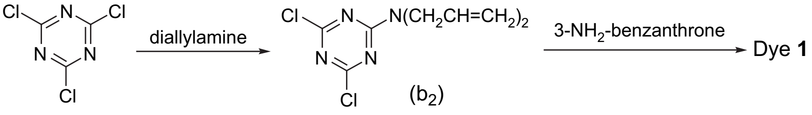


Formula 2.

The synthesis of the dyes was achieved following Scheme 3.

2.2.1. Synthesis of dye **2**

According to this scheme, firstly the dye **2** was synthesized. Product (**a**) (0.01 mol) obtained by Scheme 1 was dissolved in DMSO and to this solution at 25 °C 0.01 mol



Scheme 2.

Table 1
Characteristic data for the dyes **1**–**5** and THBT compounds **1** and **2**

Compounds (*N*)	m.p. (°C)	R_f	λ_{max} of absorption (nm)
Dye **1**	140–142	0.67[a]	428[d]
Dye **2**	>250	0.68[b]	414[d]
Dye **3**	203–205	0.55[b]	444[d]
Dye **4**	188–190	0.52[b]	442[d]
Dye **5**	176–178	0.43[b]	424[d]
THBT compound **1**	154–156	0.63[c]	336[e]
THBT compound **2**	128–130	0.75[c]	335[e]

[a] Eluent system: *n*-heptane–acetone (1:1, v/v).

[b] Eluent system: *n*-heptane–ethylacetate–acetone (2:2:1, v/v).

[c] Eluent system: *n*-heptane–acetone (3:2, v/v).

[d] Solvent: DMF.

[e] Solvent: acetone.

of amino-HBT (**c**) was added. The mixture was heated at 60 °C while the reaction was monitored applying a quantitative TLC procedure. After 2 h under these conditions, almost 100% conversion of the starting products (**a**) and (**c**) was registered. The dye **2** thus obtained was isolated and analyzed. It was identified and characterized by TLC, m.p., UV/vis, IR and ^{1}H NMR spectra. Dye **2** was further used for the synthesis of dyes **3**–**5**.

2.2.2. Synthesis of dye 3

Allylamine (0.01 mol) was added dropwise at room temperature to a solution of 0.01 mol of dye **2** in DMSO and the mixture was heated at 100 °C. The course of the synthesis was monitored by quantitative TLC. After 3 h, over 98% conversion of the dye **2** to dye **3** was registered. The dye **3** was isolated, purified by column chromatography and analyzed by the above-mentioned methods, which confirmed the desired structure.

2.2.3. Synthesis of dye 4

The synthesis of dye **4** was performed following the same procedure of reaction of 0.01 mol of dye **2** with 0.01 mol of diallylamine in DMSO solution at 100 °C. After 4 h under these conditions, over 98% conversion of the dye **2** to dye **4** was registered. The product was isolated, purified and analyzed by TLC, m.p., UV/vis, IR and ^{1}H NMR spectra, which confirmed the aimed structure.

2.2.4. Synthesis of dye 5

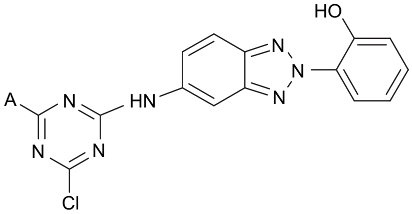
Natriumallylalcoholate (0.01 mol) at 20–25 °C was added to a solution of 0.01 mol of dye **2** in DMSO. The mixture was heated at 80 °C and the course of the reaction was followed using the quantitative TLC procedure (the eluent system: *n*-heptane–ethylacetate–acetone 2:2:1, v/v). After 2 h under these conditions over 99% conversion of dye **2** was registered and the dye was isolated, purified and analyzed by the above-mentioned methods, which confirmed the desired structure of dye **5**.

As a result of the investigation, four novel dyes were synthesized (characteristic data are presented in Table 1 and Section 3). One of them (dye **2**) contained an HBT fragment and will be suitable for "one-step in mass" coloration and stabilization of polymers. The others, containing one or two unsaturated group(s) could be applied for "one-step" chemical coloration and stabilization of polymers. The application of the dyes, their copolymerization with MMA and their influence on the photo stability of the polymers, will be a subject of our future study.

2.3. Synthesis of polymerizable triazinylaminobenzotriazole derivatives

In our previous papers, we have reported the synthesis of some polymerizable triazinylaminobenzotriazole derivatives, containing an allyloxy group in their molecule and their copolymerization with styrene and MMA [7,8]. We decided to synthesize another two polymerizable triazinylaminobenzotriazole derivatives containing allylamine and diallylamine groups, which enable us to compare more precisely their behavior and the most suitable compound to be chosen.

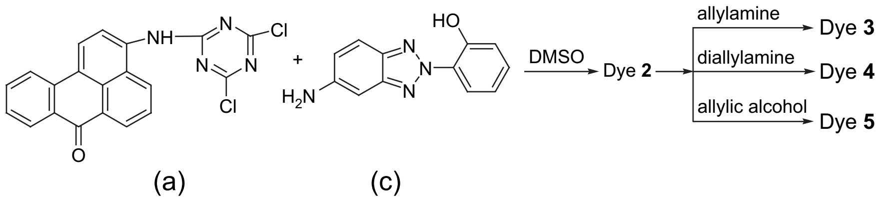
The compounds under present study can be presented by the general Formula 3, where meanings of A are as follows: A = $-NHCH_2CH{=}CH_2$ for compound **1** and A = $-N(CH_2CH{=}CH_2)_2$ for compound **2**.



Formula 3.

The synthesis of these compounds can be presented by Scheme 4.

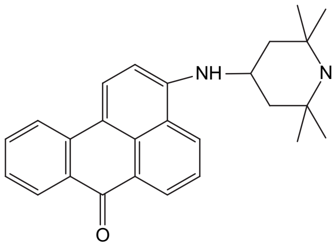
According to the scheme, firstly CC reacted with allylamine (or diallylamine) by a method described before [14]. The resulting compounds ($\mathbf{b_1}$ or $\mathbf{b_2}$) further reacted with equimolecular quantity of amino-HBT (**c**) at 25 °C (acetone solution) while adjusting the pH to 7.5 (adding 50% NaOH aqueous solution). The reaction was followed by quantitative TLC (the eluent system: *n*-heptane–acetone 3:2, v/v). The process was completed in 60 min, when the quantity of the corresponding compounds **1** and **2** reached ≈76 and 68%, respectively. The new compounds were isolated after partial evaporation of acetone under reduced pressure and pouring the mixture into water. Furthermore, they were purified by column chromatography on Al_2O_3 using an eluent system *n*-heptane–acetone (3:1, v/v). They were analyzed by TLC, m.p., UV/vis, IR and ^{1}H NMR spectra and their data are given in Section 3 and Table 1.



Scheme 3.

2.4. Synthesis of 3-(TMP-ylamino-)-benzanthrone (dye **6**)

Another possibility for "one-step" coloration and stabilization of polymers is when the stabilizer was bonded directly to the chromophore. We reported before the synthesis of two polymerizable naphthalimide dyes [12,13] containing a TMP fragment in their molecule and another six dyes suitable for "in mass" coloration and stabilization of polymers [15]. In a paper published recently, the synthesis of a benzanthrone derivative containing a TMP moiety directly bonded to the chromophore (Formula 4) was described [16].



Formula 4.

The authors of the above-cited paper performed the synthesis by a substitution of the nitro group in the 3-nitrobenzanthrone with 2,2,6,6-tetramethylpiperidin-4-ylamine in DMF solution at 80 °C for 8 h. Based on our experience in the synthesis of various benzanthrone dyes, it was of interest to study the synthesis of the above-mentioned dye, using 3-bromobenzanthrone as a starting compound. Therefore, we experimented the synthesis of dye **6** following Scheme 5.

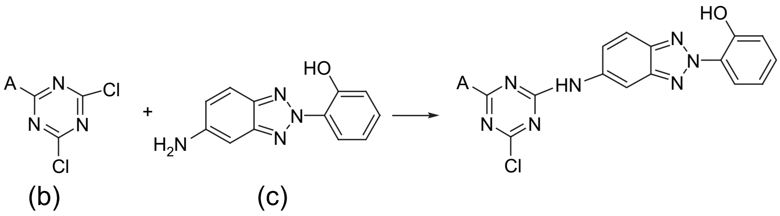
According to the scheme, 0.01 mol of 3-bromobenzanthrone was dissolved in DMF and to this solution 0.01 mol of 2,2,6,6-tetramethylpiperidin-4-ylamine and equimolecular quantity of triethylamine at 20–25 °C were added. Using the quantitative TLC (the eluent system: *n*-heptane–toluene–acetone 2:2:1, v/v), the process was monitored. The formation of a new product was registered at temperature over 50 °C. After heating of the mixture at 120 °C for 5 h, ≈75% conversion of the starting 3-bromobenzanthrone was registered. The product was isolated, purified by column chromatography and analyzed. Its characteristics (R_f, λ_{max} and ^1H NMR spectra) corresponded to those described in Ref. [16]. Based on the results obtained, we could summarize some advantages of the synthesis thus performed – shorter reaction time and higher conversion rate, which are of importance for the purity of the dye.

2.5. Spectrophotometric measurements

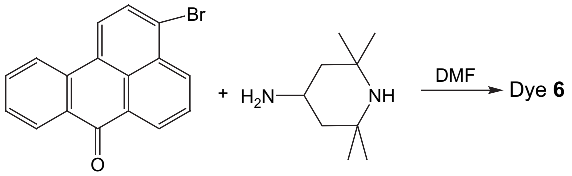
The absorption spectra of all dyes were recorded in a range of solvents with increasing polarity. The data are presented in Table 2. On the basis of these data, we can see that for dyes **1**–**5** neither blue nor red shift was observed which indicated that $n \rightarrow \pi^*$ charge transfer transition is most probable for these dyes, while for dye **6** probably this transfer is $\pi \rightarrow \pi^*$. These results are in accordance with the data published before for the similar dyes [2].

2.6. Copolymerization with methylmethacrylate

To study the ability of dyes **1** and **3**–**5** and the HBT compounds **1** and **2** to copolymerize with MMA the experiments for copolymerization were performed. Experiments on bulk copolymerization of all derivatives (0.1 wt% against MMA) with MMA at 70 °C were carried out. In all the cases solid, transparent polymers were obtained. They were brightly colored with an intense fluorescence. All polymers obtained were subjected to reprecipitation from chloroform by methanol, which was a good solvent for the dyes to remove the unreacted monomers. This operation was repeated 4–5 times until no color or fluorescence in the filtrates under UV light was observed. The colored polymers retained their color after this operation, which indicated that the dyes were chemically bound to the polymer chain. UV/vis spectra of the purified



Scheme 4.



Scheme 5.

polymers were compared to those of the pure monomer compounds. In their spectra, neither batho- nor hypsochromic shift was observed (no change of λ_{max}). This was an indication that there were no changes in the basic chromophore during the polymerization or as a result of its bonding to the polymer chain. Furthermore, by the method of the standard calibration curve the percentage of the chemically bonded dye or stabilizer was calculated. The data obtained were between 44–45% for the stabilizers and 42–58% for the dyes. One can see from these data that the percentage of the chemically bonded compounds is not very high. Nevertheless, bearing in mind that the data are referred to reprecipitated polymers and that during the reprecipitation not only the unreacted monomers, but also a part of the lower molecular fractions containing bound dye or stabilizer were removed, the content can be considered satisfactory. The more profound investigations of the polymerization process in order to find the most suitable conditions for copolymerization will be the subject of our future study.

3. Experimental

3.1. Materials, equipment and analysis

3-Aminobenzanthrone and 2-(2′-hydroxyphenyl)-5-aminobenzotriazole (HBT) were synthesized by methods described before [2,4]. 4-Amino-2,2,6,6-tetramethylpiperidine was a Fluka product. All solvents were of p.a. or analytical grade. Allylamine, diallylamine, allyl alcohol (Fluka) and cyanuric chloride (CC) (Merck) were used without purification. All melting points were uncorrected (Kofler melting point microscope). IR spectra were recorded on a Specord 71 IR Spectrophotometer using KBr pellets, and UV/vis absorption spectra were recorded in DMF solution (concentration 1×10^{-4} g ml^{-1}) on a Hewlett Packard 8452A UV/Vis Spectrophotometer. ^{1}H NMR spectra were recorded on Bruker equipment, operating at 250 MHz in DMSO (chemical shifts are given as δ in ppm).

Table 2
Spectrophotometric data (λ_{max} of absorption, nm) for the dyes **1**–**6** in different solvents

Dyes	Methanol	DMF	Acetone	Chloroform
1	430	428	426	426
2	416	414	414	414
3	446	444	442	440
4	444	442	440	438
5	424	424	422	422
6	510	498	486	470

The quantitative TLC measurements were performed using aluminum-backed ready-to-use plates (20 cm × 20 cm) precoated with 0.2 mm layer of aluminum oxide 60F$_{254}$ (Merck, Germany), a Camag (Switzerland) TLC system, comprising of Linomat IV device for sample application, a Scanner II equipped with a SP 4290 Integrator. For the quantitative TLC analysis samples (1 μl) of standard solutions (2.4×10^{-4} g ml^{-1}) of the dyes in DMF were applied to the chromatographic plates by means of the Linomat IV spotting device, equipped with a Hamilton microsyringe. The chromatograms were developed with the appropriate mobile phases, the spots were scanned by the Scanner II (densitometer) and the data for the area (%) of each spot were recorded.

3.2. Synthesis of the dyes

3.2.1. Synthesis of dye **1** (Formula 1)

- *Method 1* (Scheme 1): 3 g of 3-aminobenzanthrone reacted with 1.2 g of CC, as it was previously described [2]. 2-(Aminobenzanthron-3-yl)-4,6-dichloro-1,3,5-triazine (**a**) (3.9 g) thus obtained, was dissolved in 50 ml of DMF and to this solution 1.2 ml of diallylamine and 1.4 ml of triethylamine were added. The reaction mixture was heated at 120 °C. At every 30 min, samples from the solution were taken and analyzed by the quantitative TLC using an eluent system *n*-heptane–acetone (1:1, v/v). After 2 h the reaction was completed and the solution was poured into water. The product thus precipitated was filtered off, dried under vacuum at 40 °C, purified by column chromatography on Al_2O_3 and analyzed. Analytical data: $R_f = 0.67$; m.p. = 140–142 °C; λ_{max} [DMF] = 428 nm; IR [KBr], ν (cm^{-1}): 3380 (NH), 1695 (C=O), 1650 (C=C), 1580 (C=N), 795 (C–Cl); ^{1}H NMR spectra ppm δ: 4.07–4.39 (m, 4H, $2 \times CH_2N$), 5.13–5.24 (m, 4H, $2 \times CH_2{=}$), 5.69–5.89 (m, 2H, $2 \times CH{=}$), 7.55–9.22 (m, 9H, ArH and 1H, NH).
- *Method 2* (Scheme 2): 2.4 g of 2-diallylamino-4,6-dichloro-1,3,5-triazine [14] and 2.45 g of 3-aminobenzanthrone were dissolved in 50 ml of DMF and heated at 120 °C in the presence of 1.4 ml of triethylamine. Using a quantitative TLC analysis (the above eluent system) after 90 min the reaction was completed. Then the solution was poured into water and the compound thus obtained was filtered off, dried, purified and analyzed. The data for R_f, m.p., λ_{max}, IR and ^{1}H NMR spectra were the same as for the compound obtained according to Method 1.

3.2.2. Synthesis of dye **2** (Scheme 3)

The compound (**a**) (3.9 g) was dissolved in 50 ml of DMSO and to this solution 2.26 g of 2-(2′-hydroxyphenyl)-5-aminobenzotriazole was added. The solution was heated at 60 °C (quantitative TLC control in system *n*-heptane–ethylacetate–acetone 2:2:1, v/v). After 2 h, when the reaction was completed, the product was isolated after pouring the mixture into water and was dried under vacuum at 40 °C. Analytical data: $R_f = 0.68$; m.p. > 250 °C; λ_{max} [DMF] = 414 nm; IR [KBr], ν (cm^{-1}): 3400 (OH), 3300 (NH), 1675 (C=O), 1585 (C=N), 725 (C–Cl); ^1H NMR spectra ppm [DMSO] δ: 6.92–9.17 (m, 16H, ArH, benzanthrone and HBT; 2H, 2 × NH), 10.65 (br s 1H, OH).

3.2.3. Synthesis of dye **3**

The solution of 5.8 g of dye **2** and 0.8 ml of allylamine in 50 ml of DMSO were heated at 100 °C. The course of the process was monitored by quantitative TLC using an eluent system *n*-heptane–ethylacetate–acetone (2:2:1, v/v). After 3 h, the reaction was completed and the compound was isolated by the above-mentioned procedure, filtered, dried under vacuum at 40 °C, purified by column chromatography and analyzed. Analytical data: $R_f = 0.55$; m.p. = 203–205 °C; λ_{max} [DMF] = 444 nm; IR spectra [KBr], ν (cm^{-1}): 3400 (OH), 3250 (NH), 1680 (C=O), 1650 (C=C), 1580 (C=N); ^1H NMR spectra ppm [DMSO] δ: 4.15–4.43 (m, 2H, CH_2N), 5.09–5.28 (m, 2H, $=CH_2$), 5.78–6.06 (m, 2H, CH=), 6.68–9.26 (m, 16H, ArH, benzanthrone and HBT; 3H, 3 × NH), 10.67 (1H, OH).

3.2.4. Synthesis of dye **4**

It was obtained following the same procedure. Analytical data: $R_f = 0.52$; m.p. = 188–190 °C; λ_{max} [DMF] = 442 nm; IR spectra [KBr], ν (cm^{-1}): 3400 (OH), 3280 (NH), 1675 (C=O), 1645 (C=C), 1580 (C=N); ^1H NMR spectra ppm [DMSO] δ: 4.02–4.32 (m, 4H, 2 × CH_2N), 4.88–5.22 (m, 4H, 2 × CH_2=), 5.76–6.00 (m, 2H, 2 × CH=), 6.72–8.98 (m, 16H, ArH, benzanthrone and HBT; 2H, 2 × NH), 10.52 (br s 1H, OH).

3.2.5. Synthesis of dye **5**

Dye **2**(5.8 g) was dissolved in 50 ml of DMSO and to this solution 0.8 g of Na allylalcoholate was added. The mixture was heated at 80 °C (TLC control using an eluent system *n*-heptane–ethylacetate–acetone (2:2:1, v/v). After 2 h, the reaction mixture was poured into water, the product was filtered, washed with water until neutral pH, dried and analyzed. Analytical data: $R_f = 0.43$; m.p. = 176–178 °C; λ_{max} [DMF] = 424 nm; IR spectra [KBr], ν (cm^{-1}): 3410 (OH), 3320 (NH), 1670 (C=O), 1650 (C=C), 1580 (C=N), 1250 (C–O–C); ^1H NMR spectra ppm [DMSO] δ: 4.58–4.78 (m, 2H, CH_2O), 5.18–5.46 (m, 2H, CH_2=), 5.78–6.10 (m, 1H, CH=), 6.92–9.16 (m, 16H, ArH–benzanthrone and HBT; 2H, NH), 10.54 (br s 1H, OH).

3.2.6. Synthesis of polymerizable TBT compounds

- *Compound **1***: 2.05 g of 2-allylamino-4,6-dichloro-*s*-triazine and 2.26 g of amino-HBT were dissolved in 100 ml of acetone and stirred at 25 °C in the presence of NaOH (50% aqueous solution), according to a method described before [7]. The reaction was monitored by quantitative TLC using an eluent system *n*-heptane–acetone (3:2, v/v). After 1 h, when the conversion rate was 76%, the acetone was partially evaporated and the mixture was poured into water. The new product was filtered off, washed several times until neutral pH and dried at 40 °C under reduced pressure. It was purified by column chromatography and analyzed. Analytical data: $R_f = 0.63$; m.p. = 154–156 °C; λ_{max} [acetone] = 336 nm; IR spectra [KBr], ν (cm^{-1}): 3400 (OH), 3300 (NH), 3090 ($=CH_2$), 3010 (CH_{Ar}), 1645 (C=C); ^1H NMR spectra ppm [DMSO] δ: 3.75–3.93 (m, 2H, CH_2N), 4.08 (s, 2H, 2 × NH), 4.94–5.28 (m, 2H, $=CH_2$), 5.61–5.66 (m, 1H, CH=), 7.19–8.07 (m, 7H, ArH), 11.16 (1H, OH).
- *Compound **2***: the synthesis was performed following the same procedure from 2-diallylamino-4,6-dichloro-1,3,5,-triazine (**b_2**) and 2.3 g of amino-HBT for 1 h and the conversion rate was 68%. Analytical data: $R_f = 0.75$; m.p. = 128–130 °C; λ_{max} [acetone] = 335 nm; IR spectra [KBr], ν (cm^{-1}): 3450 (OH), 3300 (NH), 3085 ($=CH_2$), 3010 (CH_{Ar}), 1645 (C=C); ^1H NMR spectra ppm [$CDCl_3$] δ: 3.76–4.03 (m, 4H, 2 × CH_2N), 4.19 (s, 1H, NH), 4.94–5.18 (m, 4H, 2 × CH_2=), 5.58 (m, 2H, 2 × CH=), 7.19–8.23 (m, 7H, ArH), 11.20 (br s 1H, OH).

3.2.7. Synthesis of 3-(TMP-ylamino-)-benzanthrone (dye **6**)

2,2,6,6-Tetramethylpiperidin-4-ylamine (TMP amine, 1.7 ml) was added dropwise at 25 °C to a solution of 3.1 g of 3-bromobenzanthrone in 50 ml of DMF. The mixture was gradually heated to reflux. The process was monitored using the quantitative TLC procedure, described before (the eluent system: *n*-heptane–toluene–acetone 2:2:1, v/v). After 5 h under these conditions, when ≈63% conversion of the starting 3-aminobenzanthrone was registered, the reaction mixture was cooled, poured into water, the product was filtered off and dried under vacuum. It was purified by column chromatography on Al_2O_3 using the solvent system mentioned above and then analyzed. Analytical data: R_f (*n*-heptane–acetone 1:1, v/v) = 0.34; m.p. = 196–197 °C; λ_{max} [DMF] = 498 nm.

3.3. Polymerization of MMA

MMA (10 g), 0.1 wt% of the corresponding monomer dyes **1** and **3–5** and 0.5 wt% of azo-bis-*iso*-butyronitrile (ABIN) were mixed in an ampoule, flushed with dry and pure nitrogen. The ampoules were sealed and heated at 70 °C for 8 h. The transparent colored polymers with yellow fluorescence were obtained. They were dissolved in chloroform and were three-fold precipitated with methanol, which is a good solvent for the monomers but not for polymer. The polymers thus treated were dried under vacuum at 30 °C till constant weight and further analyzed.

The polymerization of MMA with the compounds **1** and **2** was performed according to the same procedure. The polymers obtained were purified as it was described above by five-fold precipitation with methanol.

4. Conclusions

As a result of the present study, seven novel compounds, five of them triazinylaminobenzanthrone dyes and two of them monomer triazinyl-HBT derivatives, were synthesized and characterized. Six of these compounds had one or two unsaturated (allylic) group(s). Their ability to copolymerize with MMA was determined, which made these derivatives suitable for "one-step" coloration and stabilization of polymeric or/ and textile materials.

Acknowledgment

The authors would like to thank the Science and Research Program at the University for the financial support.

References

[1] Konstantinova T. Synthesis of some benzanthrone derivatives for use as dyes for polymeric materials. Dyes Pigments 1988;10:63–7.

[2] Konstantinova T, Meallier P, Konstantinov Hr, Staneva D. Synthesis and photochemical properties of triazinylaminobenzanthrone derivatives as dyes for polymeric materials. Polym Degrad Stab 1995;48:161–6.

[3] Konstantinova T, Konstantinov Hr, Kaneva T, Spirieva A. On the synthesis and properties of copolymers of some benzanthrone derivatives with methylmethacrylate. Polym Degrad Stab 1998;62:323–6.

[4] Bojinov V, Konstantinova T. A new method for the synthesis of 3-alkoxybenzanthrones as luminophore dyes for polymers. Dyes Pigments 1996;32(3):151–7.

[5] Jellinek H, editor. Aspects of degradation and stabilization of polymers. Amsterdam: Elsevier; 1978. p. 195–218.

[6] Shuhaibar K, Rasoul F, Pasch H, Mobasher A. Synthesis and characterization of polymers containing naphthyl-2*H*-benzotriazoles. 1. Monomer synthesis and characterization. Angew Makromol Chem 1991;193: 147–58.

[7] Konstantinova T, Bogdanova A, Stanimirov S, Konstantinov Hr. Synthesis and application of UV stabilizers for polymeric materials based on triazinylaminobenzotriazole. Polym Degrad Stab 1994;43:187–93.

[8] Konstantinova T, Konstantinov Hr, Avramov L. Synthesis and properties of copolymers of triazinylaminobenzotriazole stabilizers with methylmethacrylate. Polym Degrad Stab 1999;64:235–7.

[9] Bojinov V, Konstantinova T, Konstantinov Hr. Synthesis and application of triazinyl-2,2,6,6-tetramethyl-piperidine derivatives as stabilizers for polymeric materials. Angew Makromol Chem 1998;260:17–20.

[10] Bojinov V. Synthesis and properties of adducts of a hindered amine and 2-hydroxyphenylbenzotriazole as novel polymer stabilizer. Photochem Photobiol Sci 2002;1(5):340–6.

[11] Bojinov V, Konstantinova T. On the possibility of "one-step" colouration and stabilization of polystyrene. Polym Degrad Stab 2000; 68:295–8.

[12] Bojinov V, Konstantinova T. Synthesis of polymerizable 1,8-naphthalimide dyes containing hindered amine fragment. Dyes Pigments 2002;54:239–45.

[13] Konstantinova T, Lazarova R, Bojinov V. On the photostability of some naphthalimide dyes and their copolymers with methyl methacrylate. Polym Degrad Stab 2003;82:115–8.

[14] Konstantinova T. Synthesis of unsaturated amino and alkoxy derivatives of 1,3,5-triazine and their copolymers. Compt rendus de l ' Acad Bulg des Sci 1988;41(10):69–71.

[15] Konstantinova T, Lazarova R, Venkova A, Vassileva V. On the synthesis and photostability of some new naphthalimide dyes. Polym Degrad Stab 2004;84:405–9.

[16] Bojinov V, Grabchev I. Synthesis and photophysical investigation of novel combined benzo[*de*]anthracen-7-one/2,2,6,6-tetramethylpiperidines as fluorescent stabilizers for polymer materials. Polym Degrad Stab 2004;85:789–97.