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The Polycondensation of Dimethyl Terephthalate and Ethylene Glycol in the Presence of Dye Derivatives of 1,3,5-*sym*-Triazine

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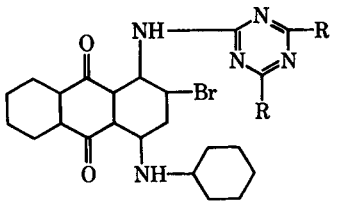
Synopsis

Two new triazine-based dyes have been prepared with the following general formula:



in which R = —$HNCH_2CH_2OH$ or —$NHCH_2COOH$. As a result of the presence of suitable functional groups, these compounds can be incorporated in the polycondensation process which gives colored polyethylene glycol terephthalates (PEGT). By means of a spectrophotometric investigation, it has been demonstrated that the dye does not change its structure under high temperature or its incorporation in the polymer chain. A colorimetric study has been made of the dye content of the polymer as related to the quantity initially taken for the reaction. It has been shown that the inclusion of the dye in the polycondensation process does not affect notably the molecular weight, melting point, and the polydispersion of the polymers. Intensive coloration can be obtained with very low concentrations of the dye, 0.1–0.5%. By comparing the infrared spectra of the polymer and the pure dyes, the dyes have been demonstrated to be bound to the polymer molecule. Since the dye is part of the basic chain of PEGT, the polymers retain their color after repeated reprecipitation. The proposed method can be used for the preparation of saturated polyesters of divers properties and persistent colors.

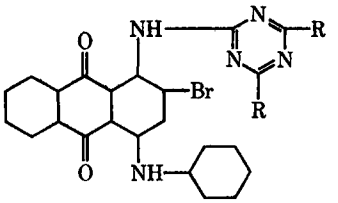
INTRODUCTION

The method used at present for dyeing synthetic polymer materials have many drawbacks. Recently, techniques have been proposed which combine the processes of synthesis and dyeing. The colors thus obtained are very fast in respect to wet treatment owing to the chemical bond between the dye and the polymer. In order to be able to take part in such type of dyeing, the dye should contain suitable functional groups. Various dyes have been suggested for the coloration of polymer resins. These dyes con-

tain vinyl,[1] acryloyl,[2] vinylsulfonic,[3] and other unsaturated groups[4] capable of taking part in copolymerization. For the dyeing of polycondensation resins, the dyes are required to contain at least two hydroxyl, amino, or carboxyl groups which can take part in the polycondensation or can block the endgoups of the chain.[5,6]

The saturated polyesters are considered to be one of the most difficult to dye because of the compactness of their molecule. Therefore, particular importance is attached to studies on the dyeing of these materials by one of the above-mentioned chemical methods. The first stage in this direction is the synthesis of proper dyes. The latter should, on the one hand, contain two hydroxyl or carboxyl groups each in order to participate in the polycondensation process and, on the other hand, should be thermostable enough not be degraded or changed during the process.

Dyes that will meet those requirements are some anthraquinone derivatives of triazine with the general formula in which R = —$HNCH_2CH_2OH$



or —$HNCH_2COOH$.

The purpose of the present work is to synthetize suitable dyes of this series and to study the process of copolycondensation of dimethyl terephthalate and ethylene glycol in their presence.

EXPERIMENTAL

Materials

1-Amino-2-bromo-4-anilineanthraquinone, mp 227°C; cyanuric chloride, mp 146–147°C (Fluka); aminoacetic acid, p.a. (Hungary); ethanolamine, bp 68–70°C (Fluka); dioxane, bp 95–103°C (Fluka); dimethyl terephthalate, 97% (BDH); ethylene glycol, bp 197°C (Chemapol); $Zn(OOC \cdot CH_3)_2$ (Analar); antimonous oxide, Sb_2O_3, 99% (BDH); alumina, for chromatography, grade II according to Brockmann (Hungary), were used.

Equipment

Synthesis of the dyes was carried out in a three-neck round-bottom flask, provided with a seal, mechanical agitator, thermometer, and reflux condenser. The synthesis of PEGT was performed in three-neck flask mounted with a contact thermometer, a capillary tube connected to a source of dry and oxygen-free CO_2 for flushing the system, and a distillation condenser with a receiver.

Also used were a photoelectric colorimeter FEK-M (USSR), spectrophotometer SFD-2 (USSR), and a laboratory pH meter SP-2 (Bulgaria).

Procedures

Synthesis of Dyes. (a) 2-(2′-Bromo-4′-aniline-1′-anthraquinonylamino)-4,6-dioxyethylamino-1,3,5-*sym*-triazine: 5.44 g of 2-(2′-bromo-4′-aniline-1′-anthraquinonylamino)-4,6-dichloro-1,3,5-*sym*-triazine (I), prepared by a published method,[7] is dissolved in 50 ml dioxane and the solution is added in portions to a water–ice mixture, and placed in the flask described under equipment. Ethanolamine, 5.4 g, is added to the fine suspension and the whole mixture is refluxed for 1 hr. The pH of the reaction mixture by the end of the reaction should be 8.5. The mixture is cooled, filtered, and the precipitate is washed with water until the washings are free from chloride ion and dried under vacuum. Yield is 75%. The blue-violet product thus obtained, after purification on alumina (Brockmann grade II) using tetrahydrofuran as solvent and eluent, shows a mp 131°C. Analysis: calcd. for $C_{27}H_{24}BrN_7O_4$: N, 16.60%. Found: N, 16.40%.

(b) 2-(2′-Bromo-4′-aniline-1′-anthraquinonylamino)-4,6-dicarboxymethylamino-1,3,5-*sym*-triazine: The compound was prepared from 5.44 g of (I) and 2.3 g of aminoacetic acid by the method described under (a). During the reaction, 0.4 g sodium hydroxide dissolved in water is added to the mixture so as to obtain a pH of 8.5 by the end of the reaction. The product is violet in color and has a mp of 270°C. Yield is 84%. Analysis: calcd. for $C_{27}H_{20}BrN_7O_6$: N, 15.86%. Found, N 15.63%.

Synthesis of Polyethylene Glycol Terephthalate. The setup described under equipment has been used to prepare saturated polyesters in the presence of solvents.[8] For that purpose, 16.2 g dimethyl terephthalate is mixed with 16.2 g ethylene glycol, 0.013 g zinc acetate, and 0.01 g Sb_2O_3 in 45 ml ditolylmethane. The condensation is carried out with 0.1%, 0.2%, and 0.5% of the dye, respectively. The duration of the reaction is 7 hr.

Preparation of the Resins for Analysis. To remove the unreacted dye and other products, the reaction mixture is first washed with ethanol, which dissolves the dye until the washings are colorless. Next, the polymer is precipitated 3–4 times from a tricresol solution by the addition of ethanol. The colored product thus obtained is dried at 70°C under reduced pressure and is analyzed.

Determination of λ_{max} of Dyes and Polymers. The relationship between D_c and λ_{max} for the two dyes (at a concentration of 4.10^{-2} g/l.) and the prepared colored polymers (at a concentration of 8.10^{-2} g/l.) was measured on a spectrophotometer SFD-2 (Fig. 1). The same procedure was used to determine the spectra of the pure dyes heated under the same conditions as applied in the polycondensation reaction.

Determination of Amount of Chemically Bound Dye. The determinations were carried out by a photoelectric colorimeter FEK-M. Standard calibration curves of the pure dye were plotted in advance (Fig. 2); tri-

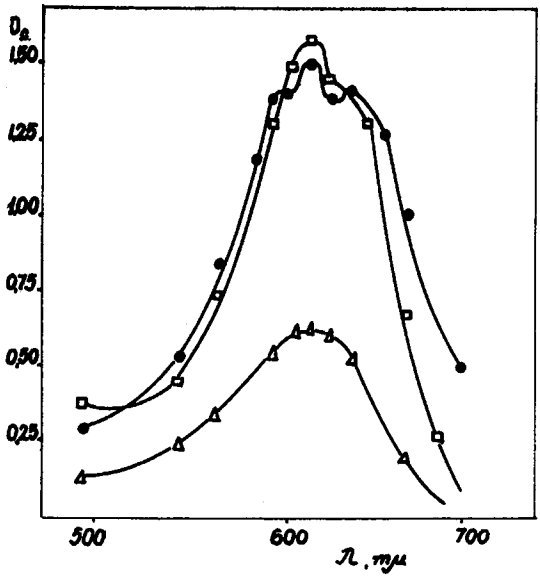


Fig. 1. Absorption spectra for dye (a) and colored PEGT (solution in tricresol): (□) pure dye (a), concentration 4.10^{-2} g/l.; (●) pure dye (a), heated, concentration 4.10^{-2} g/l.; (△) colored PEGT, concentration 8.10^{-2} g/l.

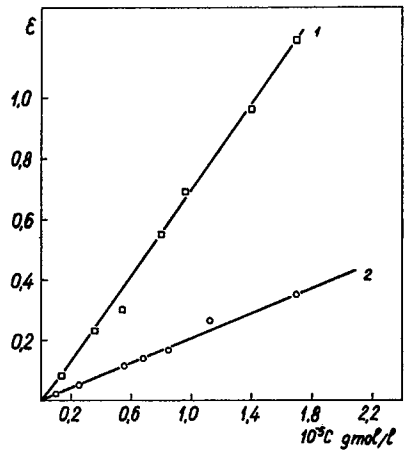


Fig. 2. Standard calibration curves for dyes in tricresol: (□) dye (a), concentration 1.7×10^{-5} gmole/l. in red filter; (○) dye (b), concentration 3.4×10^{-5} gmole/l. in red filter.

cresol solutions of the polymer containing fixed quantities of the product, 2 g/25 ml, are prepared, their optical density measured, and the corresponding concentrations are read off the calibration curve of the dye. The results of different colored polymers are shown in Table I.

Determination of Molecular Weight and Polydispersion. The specific viscosity (η_{sp}) of a 0.5% solution of the corresponding colored polymer i$_n$

tricresol was determined in a Oswald capillary viscosimeter at 20°C. Table II summarizes the results of these measurements.

The polydispersion of the polymers was determined by fractional precipitation of the polymer from a 0.1% tricersol solution by the addition of

TABLE I
Dependence of Amount of Chemically Bound Dye on its Beginning Concentration in the Mixture

Sample No.	Dye 1		Dye 2	
	Used, %	Found, %	Used, %	Found, %
1	0.125	0.016	0.10	0.125
2	0.250	0.018	0.25	0.380
3	0.500	0.048	0.50	0.680

TABLE II
Dependence of Molecular Weight (resp. η_{sp}) on the Amount of Chemically Bound Dye

Dye no.	Found dye, %	η_{sp}
1	0.016	0.1550
	0.018	0.1401
	0.048	0.1296
2	0.125	0.1363
	0.380	0.1270
	0.680	0.1188

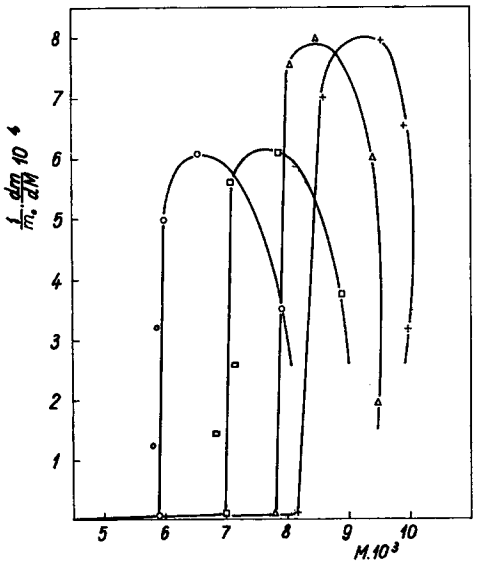


Fig. 3. Differential distribution curves for colored PEGT (from 0.1% tricresol solution): (O) dye (b), concentration in reaction mixture 0.5%; (□) dye (b), concentration in reaction mixture 0.25%; (Δ) dye (a), concentration in reaction mixture 0.5%; (+) dye (a), concentration in reaction mixture 0.25%.

ethanol. From the four to five fractions thus obtained, a differential distribution curve is plotted (Fig. 3).

Determination of Melting Temperature. The melting temperature of the polymers was determined in a Koffler apparatus. The polyesters prepared with dye no. 1 have a melting temperature of 253–5°C, and those with dye no. 2, 250–2°C.

RESULTS AND DISCUSSION

The first part of the experiments covers the preparation of triazine derivative dyes containing two hydroxyl or two carboxyl groups. It should be noted that these compounds are new and no references to them exist in the literature. They are characterized by their melting point, elemental analysis, and infrared spectra. The study of their incorporation in the polycondensation process of the polyethylene glycol terephthalate established the following features:

The polymers retain their color after repeated extraction and reprecipitation, which confirms the fact that the dyes are incorporated into the macromolecular chain. The dyes do not themselves change during the polycondensation, as shown in Figure 1. Also their incorporation into the polymer chain does not cause any changes since the polymer has λ_{max} in the same field of absorption. These findings offer sufficient ground for measuring the concentration of the chemically bound dye by the method of the calibration curve. Calibration lines of the two dyes prepared in advance (Fig. 2) allow reading off the concentration of the chemically bound dye in the polymer. As is shown in Table I, an increase in the quantity of the dye in the reaction mixture results in an increase in the concentration of polymer-bound dye. It has been established that increasing the time of polycondensation up to 24 hr does not change the concentration of the dye in the polymer, and that maximum bonding occurs up to the 7th hour. The incorporation of the dye does not affect appreciably the molecular weight (the η_{sp}) of the polymer. This is to be expected taking into consideration the low concentration of the dye. Figure 3 demonstrates that the incorporation of the dye in the polymer does not increase the polydispersion of the colored polyesters, which is of particular importance for the application of the fiber.

The dye concentration affects the melting point of the polymers as much as it affects their molecular weights. In that sense the melting points of the polymers fall slightly with increase in concentration of the dyes. There is no substantial difference between the melting points of the original and the colored polymers, which once again is important for their processing.

The infrared spectra of the prepared polyesters were compared with the infrared spectra of the pure dyes. The absorption band at 1640 cm^{-1} (characteristic of a =CO group as part of a conjugated double bond system) in the spectrum of the polyester is confirmation of the incorporation of the dye in the polymer chain.

On the basis of the above studies, it can be concluded that the newly prepared triazine derivatives can be used in the synthesis of colored polyethylene glycol terephthalates. Intensive coloration can be obtained with as low as 0.1–0.5% of the dye in the reaction mixture. The colors thus obtained are resistant to wet treatment, because the dye is incorporated into the polymer chain. The study demonstrates that the dye does not appreciably affect molecular weight, melting point, and polydispersion of the polymers, all of which are important factors in the practical application of the materials.

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