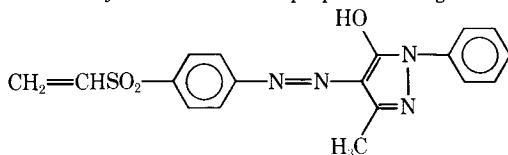


On the Polymerization of Styrene in the Presence of Vinyl Sulfone Dyes

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Synopsis

An azo dye derived from vinyl sulfone has been prepared having the following formula:



A study has been made of the copolymerization of styrene with the above dye in the presence of benzoyl peroxide as an initiator. The colored polymers thus obtained preserve their shade even after repeated precipitation, because the dye is directly bound to the polymer chain. The polymerization has been studied in the temperature interval of 60–80°C, and the activation energy of the process has been determined. The effect of the amount of dye on the polymerization process has been investigated, and the proportion of dye chemically bound to the polymer has been determined spectrophotometrically. The effect of the dye on the molecular weight, corresponding on $[\eta]$ and the polydispersity of the colored polymers, has also been studied.

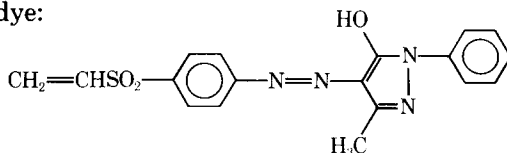
INTRODUCTION

In an earlier paper,¹ the authors reported on the polycondensation of ethylene glycol and dimethyl terephthalate in the presence of triazine dyes resulting in a colored polyethylene-glycol terephthalate. Persistently colored polymers were also obtained by copolymerization of styrene with some triazine dyes.² In the first case, the dyes carry —OH or —COOH groups which take part in the polycondensation, while in the latter case, it is the unsaturated groups which participate in the polymerization.

The vinyl sulfone dyes are a rather reactive class of compounds which are used for dyeing of textiles. The vinyl sulfone moiety has been shown to be able to enter to copolymerization with certain vinyl monomers,³ so that this class of dyes could be useful in the synthesis of colored polymers.

It was interesting to study the copolymerization of styrene with some vinyl sulfone dyes in order to establish the effect of the dye on the polymerization process as well as on some properties of the colored polymers thus obtained.

The present paper deals with the polymerization of styrene in the presence of the following dye:



This dye has been used as a model compound since it has the simplest possible structure and contains no other groups that might affect the process under study.

EXPERIMENTAL

Materials. Acetanilide (DDR) p.a.; chlorosulfonic acid 99% (DDR); ethylenechlorohydrine, p.a. (DDR); 1-phenyl-3-methylpyrazolone-5, 97% (Schhardt); dioxane, bp 95–103°C (Fluka); styrene, bp 144–145°C (Fluka), made free of inhibitors and redistilled; dibenzoyl peroxide 99.2% (Chemapol); N,N-dimethylformamide, bp 152–154°C (Merk); alumina for chromatography, activity II according to Brockman (Hungary); *n*-butanol, bp 117–118°C (Hungary).

Equipment. The synthesis of the dyes is carried out in a three-necked flask mounted with a thermometer, a stirrer, and a reflux condenser. The polymerization is done in a sealed ampoule flushed in advance with nitrogen of 99.99% purity, placed in a thermostated bath. A Perkin-Elmer spectrophotometer and a FEK-M (USSR) colorimeter were also used.

Synthesis of the Dye. The dye was prepared in the equipment described above by a method analogous to the one described in the literature⁴ starting with 33.8 g acetanilide, 82.5 ml chlorosulfonic acid, 17.4 ml ethylenechlorohydrin, and 13.3 g pyrazolone. The orange-yellow product was cleaned up on an alumina column and eluted with dioxane. It was characterized by elemental analysis and infrared spectrum.

ANAL. Calcd for $C_{18}H_{16}N_4O_3$: N, 15.21%. Found: N, 14.95%.

Infrared spectral data: $\nu_{>SO_2} = 1335\text{--}1310\text{ cm}^{-1}$, $1160\text{--}1130\text{ cm}^{-1}$; $\nu_{OH} = 1850\text{--}3000\text{ cm}^{-1}$; $\nu_{CH=CH_2} = 920\text{ cm}^{-1}$; and absorption bands at 1600, 1580, and 1500 cm^{-1} , typical for benzene in conjugated system.

Polymerization of Styrene. Bulk polymerization was carried out in sealed ampoules flushed with pure nitrogen. Two per cent of dibenzoyl peroxide (on total monomer) were added as initiator, and the ampoule was held 8 hr at 80°C. The dye was added at a rate of 0.1 wt-% calculated on the styrene. The polymers were washed with ethanol and dried to constant weight. This procedure was used in a series of experiments by varying the temperature, time of polymerization, and concentration of the dye in the starting mixture.

Preparation of Polymers for Analysis. The polymers obtained above were dissolved in N,N-dimethylformamide (DMF) and precipitated by the addition of *n*-butanol, which is a good solvent for the dye. This operation was repeated seven times until a colorless filtrate was obtained. The precipitated polymers were dried under vacuum.

Spectrophotometric Measurements. The relationship $D_c\text{-}\lambda$ in the visible region of the spectrum was recorded at a concentration of 2×10^{-4} g/ml for the dye and at 8×10^{-2} g/ml for the precipitated polymers. The concentration of the dye in the polymers was determined on a FEK-M colorimeter (green filter) by the method of standard calibration.

Molecular Weights. The $[\eta]$ values of the colored polymers were deter-

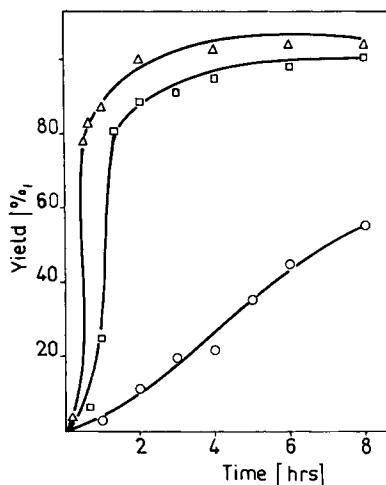


Fig. 1. Relationship between conversion rate (polymer yield in %) and time (hr) with 0.1 wt-% dye at (O) 60°C; (□) 70°C; (Δ) 80°C.

mined by measuring the viscosity of the toluene solutions (0.4–0.5 wt-%) at 25°C.

Polydispersity. The polydispersity of the colored polymers, as well as that of the colorless ones obtained under identical conditions, was determined by fractional precipitation via the addition of *n*-butanol to 0.1 wt-% solutions in toluene.

RESULTS AND DISCUSSION

Yellow-colored polymers were obtained as a result of the copolymerization of styrene with the vinyl sulfonic dye. They preserve their color after repeated sevenfold precipitation, which is an indication that the dye is bound to the polymer chain. This is borne out by the appearance of absorption bands at $1335\text{--}1310\text{ cm}^{-1}$ and $1160\text{--}1130\text{ cm}^{-1}$ (characteristic of the $>\text{SO}_2$ group) and the absence of maxima at 920 cm^{-1} (typical of an end double bond) in the infrared spectra of the repeatedly precipitated colored polymers.

By studying the reaction at 60°, 70°, and 80°C with the addition of 0.1 wt-% of dye, a plot was obtained of conversion rate versus time, which is shown in Figure 1. On the basis of this relationship and the Arrhenius equation, the activation energy of the process was calculated to be 23.7 kcal/mole. Several authors⁵ have reported a value of 21.3 ± 5 kcal/mole for the activation energy of the homopolymerization of styrene under the same conditions. On the basis of this, it can be assumed that the participation of the dye in the polymerization does not affect the activation energy of the process.

By varying the amount of dye added at 80°C from 0.1 wt-% to 0.4 wt-% (in terms of monomers mixture), it was established that in this range of concentration the dye has no effect on the course (correspondingly the rate) of the process (Table I). Moreover, a concentration of 0.1 wt-% is sufficient for obtaining an intensive color.

It was established by means of spectrophotometric measurements that no changes occur in the chromophore group of the dye molecule, neither during

TABLE I
Relationship between Initial Concentration of the Dye on the Conversion Rate

Concentration of dye, %	0.1	0.2	0.3	0.4	0.0
Conversion rate, %	93.8	92.6	91.5	90.5	94.3

TABLE II
Relationship between the Initial Dye Concentration on Molecular Weight

Concentration of dye, %	0	0.1	0.2	0.3	0.4
$[\eta]$, 100 ml/g	0.321	0.316	0.305	0.298	0.287

the process nor as a result of the inclusion of the dye in the polymer chain. This finding was used to determine the content of chemically bound dye in the repeatedly precipitated polymer by the method of the standard calibration curve. From the plot of the per cent chemically bound dye versus time of polymerization, shown on Figure 2, it can be seen that, by the end of the polymerization period (8 hr), about 85% of the dye is incorporated in the chain. By increasing the initial concentration of the dye, this proportion goes up to 93%. One should bear in mind that these results are for repeatedly precipitated polymers. If account is taken of the fact that precipitation removes, along with the unreacted dye, also part of the chemically bound dye to low molecular weight fractions, it becomes obvious that the percentage is actually higher and quite adequate for an intensive coloring.

The study of the effect of the dye on the molecular weight (correspondingly the $[\eta]$), revealed that by increasing the initial concentration of the dye, a certain lowering of the molecular weight is taking place (Table II).

Figure 3 demonstrates that the incorporation of the dye in the polymer chain does not affect significantly the polydispersity of the colored polymer, a parameter which is important in the processing of the polymer.

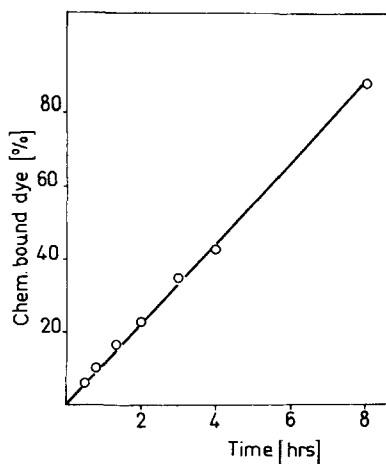


Fig. 2. Relationship between proportion of dye chemically bound to polymer (%) and time of polymerization (hr) with an initial concentration of dye, 0.1 wt-%.

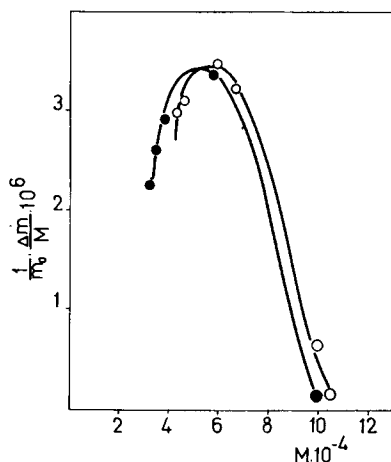


Fig. 3. Differential distribution curves: (○) colorless polystyrene; (●) colored polystyrene; 0.1 wt-% dye, 8 hr, at 80°C.

In summary, the following conclusions can be drawn: The vinyl sulfone dye of the present study is suitable for the synthesis of colored polymers. The minimum concentration for obtaining an intensively colored polymer is 0.1 wt-% (calculated on a styrene base). Higher concentration of the dye does not affect significantly the course of the polymerization process. More than 85% of the dye added to the mixture reacts and is incorporated in the polymer chain. This does not change the activation energy of the process and does not affect the polydispersity of the product.

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