

On The Copolymerization of Styrene and Methyl Methacrylate with Some Monomeric Benzanthrone-Derivative Dyes

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Received 14 August 1996; accepted 6 December 1996

ABSTRACT: The copolymerization of styrene and methyl methacrylate with two monomeric fluorescent dyes, benzanthrone derivatives, have been investigated. The most suitable parameters of the process were determined. The copolymers obtained had an intensive stable to solvent color and fluorescence, due to the chemical bonding of the dye to the polymer's chain. It was established that between 85 and 95% of the dye reacted in the process. The course of the copolymerization was investigated by gel permeation chromatography, and the influence of the dyes on the molecular weight and polydispersity of the polymers was determined. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 91–97, 1997

Key words: monomeric benzanthrone dyes; styrene and methyl methacrylate copolymers

INTRODUCTION

The synthesis of copolymers of the traditional monomers with monomeric dyes and pigments is a possible way to obtain polymeric materials with color resistance to solvents and with definite properties like photo- and thermostability and fluorescence. Benzanthrone derivatives, because of their intensive fluorescence and stability,¹ are well known as fluorescent dyes or pigments, applied for polymeric materials.

In our earlier articles, the synthesis of some benzanthrone dyes, capable of copolymerizing

with styrene (St) and acrylonitrile, was reported.² We investigated the photochemical properties of the dyes and their polymers with St³ and their influence on the copolymerization process.⁴ It was found that some of these monomeric dyes acted as stabilizers for the polymer's photodegradation, while the others accelerated the process.³

With these results in mind, it was of interest to investigate the ability of some of the above-mentioned dyes to copolymerize with methyl methacrylate (MMA), a monomer produced in Bulgaria and widely applied together with St, to obtain a threefold copolymer. Therefore, to investigate the copolymerization of St, MMA, and two of the benzanthrone dyes, containing an allyloxy group and to determine the most appropriate parameters of the process and the influence of the

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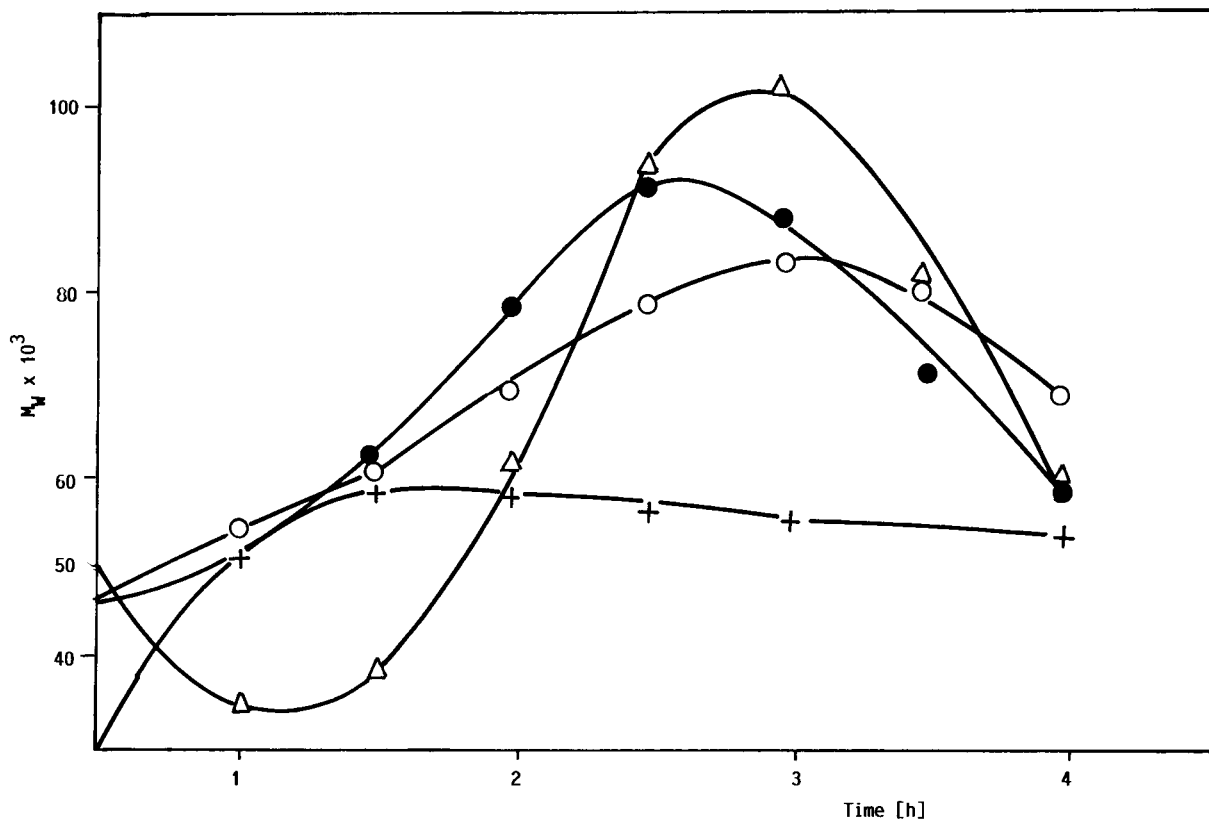


Figure 1 Dependence of M_w for the copolymer of St-MMA-benzanthrone dye **1a** on time (h) with different concentrations of the dyes: (●) 0%, (△) 0.1%, (○) 0.2%, and (+) 0.3%.

colored monomers on the properties of the polymers thus obtained were the objects of this work.

EXPERIMENTAL

Materials

Dyes were synthesized and purified by a method previously described.²⁻⁴ St (Nephtochim-BG) and MMA (Agrochim-BG) were purified and distilled under vacuum in a nitrogen atmosphere. Dibenzoylperoxide (DBP; Fluka) was recrystallized from CHCl_3 (99.9%).

Methods

In an ampule flushed with pure and dry nitrogen, containing 5 g of purified St and MMA (1 : 1), 0.1

wt % of the corresponding dye, calculated to the total amount of St, MMA, and DBP (1.25 wt % against the monomers) was dissolved. The ampule was sealed and heated in a thermostat at $120 \pm 0.1^\circ\text{C}$. After 0.5 h, every 15 min, the mixture from the ampule was dissolved in 12 mL of toluene and the polymer was isolated by precipitation with methanol. Yields were between 60 and 90%, depending on the time. With the same conditions, polymers, containing 0.2 and 0.3 wt % of the corresponding dye, were obtained. The polymers were purified by fourfold to fivefold reprecipitation with methanol to remove the unreacted monomers and dried under vacuum at 30°C to constant weight. The polymers thus prepared were analyzed by gel permeation chromatography (GPC) ("Waters" equipment), where pump M-510, Injector U-6K, and differential refractometer M-410 as a detector were used. The analyses were performed on three columns ("UltraStyragel"; 100 and 500 Å and a

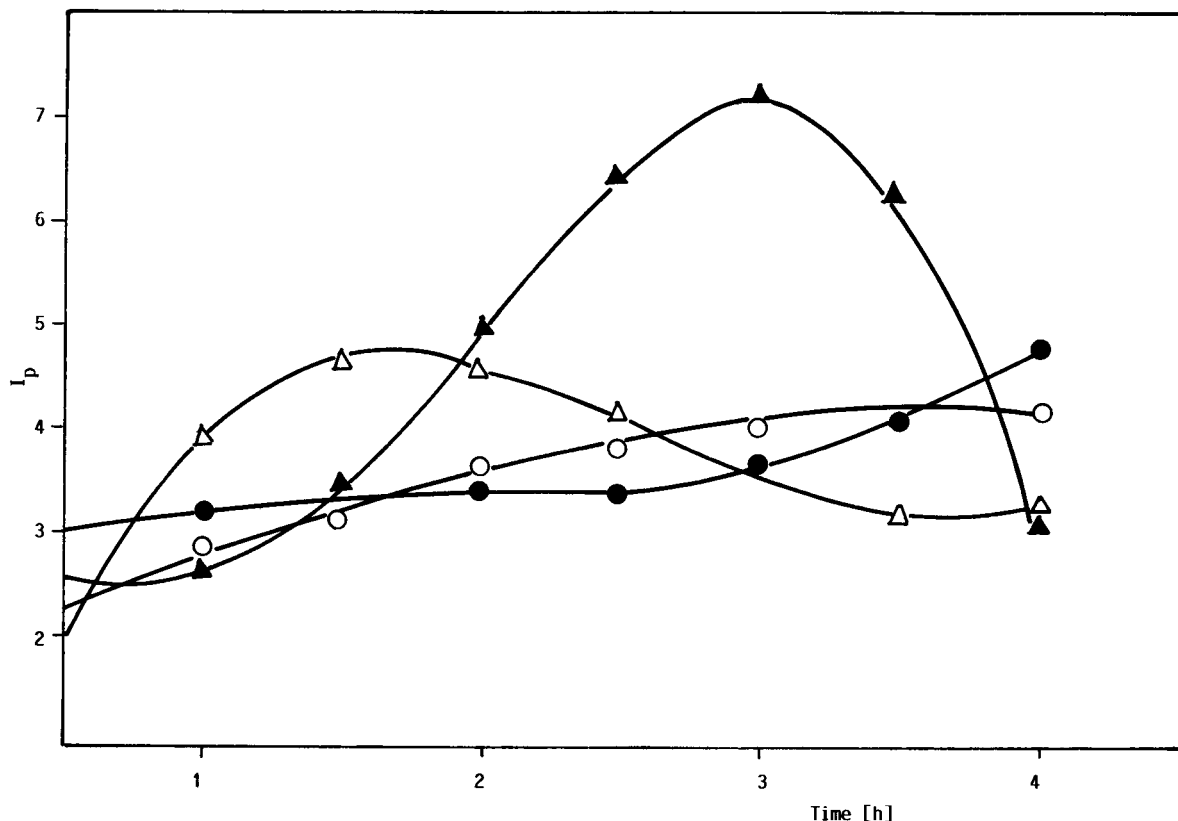


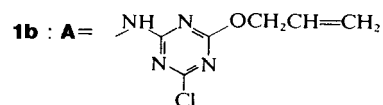
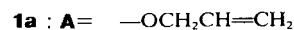
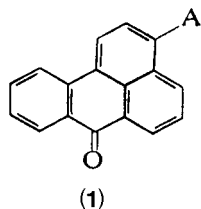
Figure 2 Dependence of polydispersity (I_p) of the copolymers of St-MMA-benzanthrone dye **1a** on the time of polymerization (h) with different concentrations of the dye: (●) 0%, (▲) 0.1%, (○) 0.2%, and (△) 0.3%.

linear one), with tetrahydrofuran (THF) as eluent at 45°C and a flow velocity of 1 mL/min.

The quantity of the unreacted dye was determined by high-performance liquid chromatography (HPLC) ("Waters" equipment, Detector M-991 with the data station), using the method of the external standard⁵ at λ_{\max} of the corresponding chromophore between 190 and 500 nm. Column "Lichrosorb" RP-18, an eluent mixture of acetonitrile : water (86 : 14), was used under a flow velocity of 1 mL/min. On the basis of these data, the percentage of chemically bonded polymer dye was calculated.

RESULTS AND DISCUSSION

The monomeric dyes used in this work have the general formula **1**, where **A** is as follows:



The synthesis of the dyes was previously reported.⁴ On the basis of this series of preliminary experiments, the parameters of the copolymerization were determined, where polymers with the most appropriate molecular weight and polydispersity were obtained: temperature, 120°C; ratio of St : MMA, 1 : 1; and concentration of initiator DBP against the total amount of monomers, 1.25 wt %. In these experiments, we obtained colored polymers with three different concentrations of the dyes, 0.1, 0.2, and 0.3 wt %, against the mixture of St and MMA, in order to investigate the influence of the dye on the properties

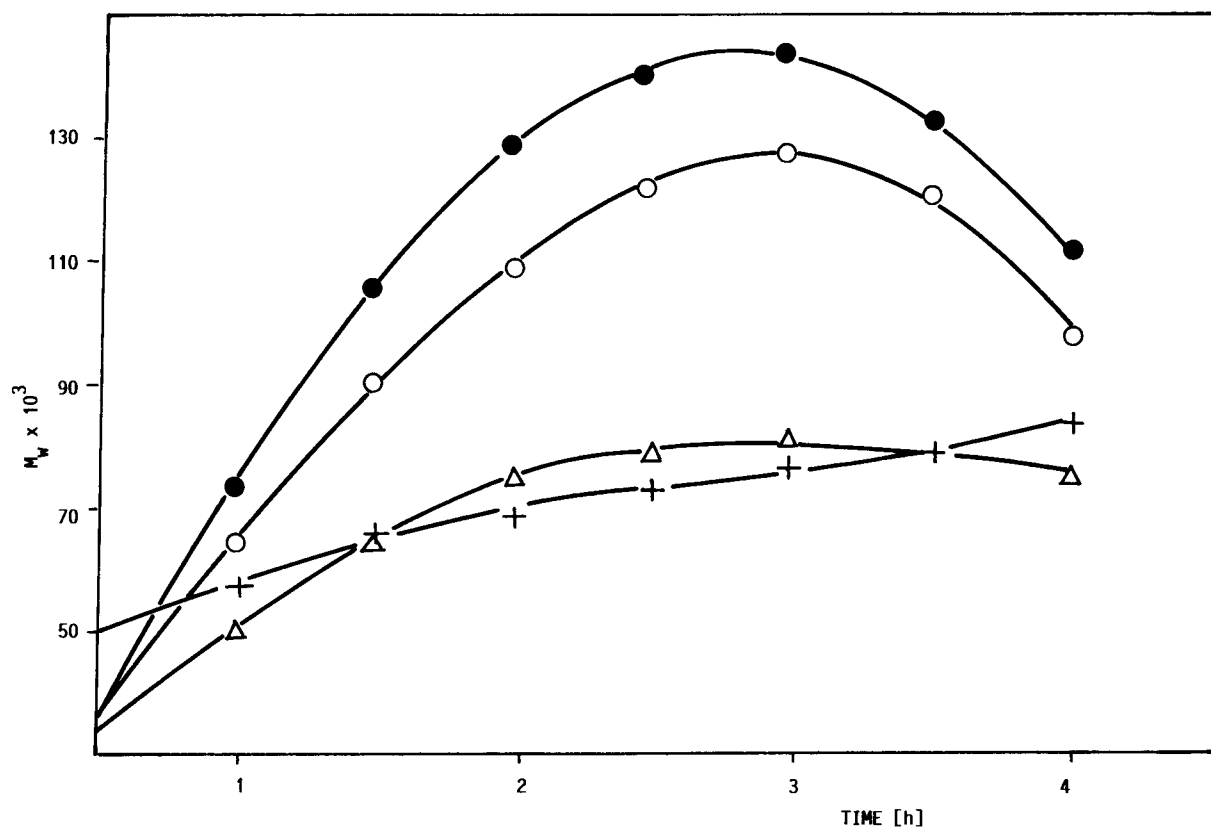


Figure 3 Dependence of M_w for the copolymer of St-MMA-benzanthrone dye **1b** on time (h) with different concentrations of the dye: (+) 0%, (●) 0.1%, (○) 0.2%, and (Δ) 0.3%.

of the polymers. These values of concentration are more than enough to obtain polymers with an intensive color and bright fluorescence and assured good solubility of the dyes in the monomeric mixture. On the other hand, higher concentrations for luminophores are not recommended because of the possibility for quenching the fluorescence.¹

In all cases, transparent yellowish-orange-colored polymers with an intensive fluorescence were obtained. They preserve their color and fluorescence after fourfold to fivefold precipitation by methanol (a good solvent for the dyes), which was an indication that the dye was bound to the polymer chain. This conclusion was also confirmed by GPC analysis. Absorption ultraviolet/vis spectra for the reprecipitated polymers showed the same λ_{\max} as the parent dyes, which was an indication that no change in the chromophoric system occurred, either during the poly-

merization or as a result of its bonding into the polymer chain.

Investigations on the Influence of the Dyes on the Properties of the Polymers

Polymers with three different concentrations of the corresponding dye, 0.1, 0.2, and 0.3 wt % (in terms of the St-MMA mixture), were obtained in order to study their influence on the molecular weight and polydispersity of the copolymers. The data obtained by GPC analysis are presented in Figures 1–4.

Figure 1, showing the course of copolymerization with dye **1a**, demonstrates that increasing the dye's concentration led to obtaining polymers with lower values of M_w , without significant change of their polydispersity (Figure 2), compared with those of polystyrene without dye. On

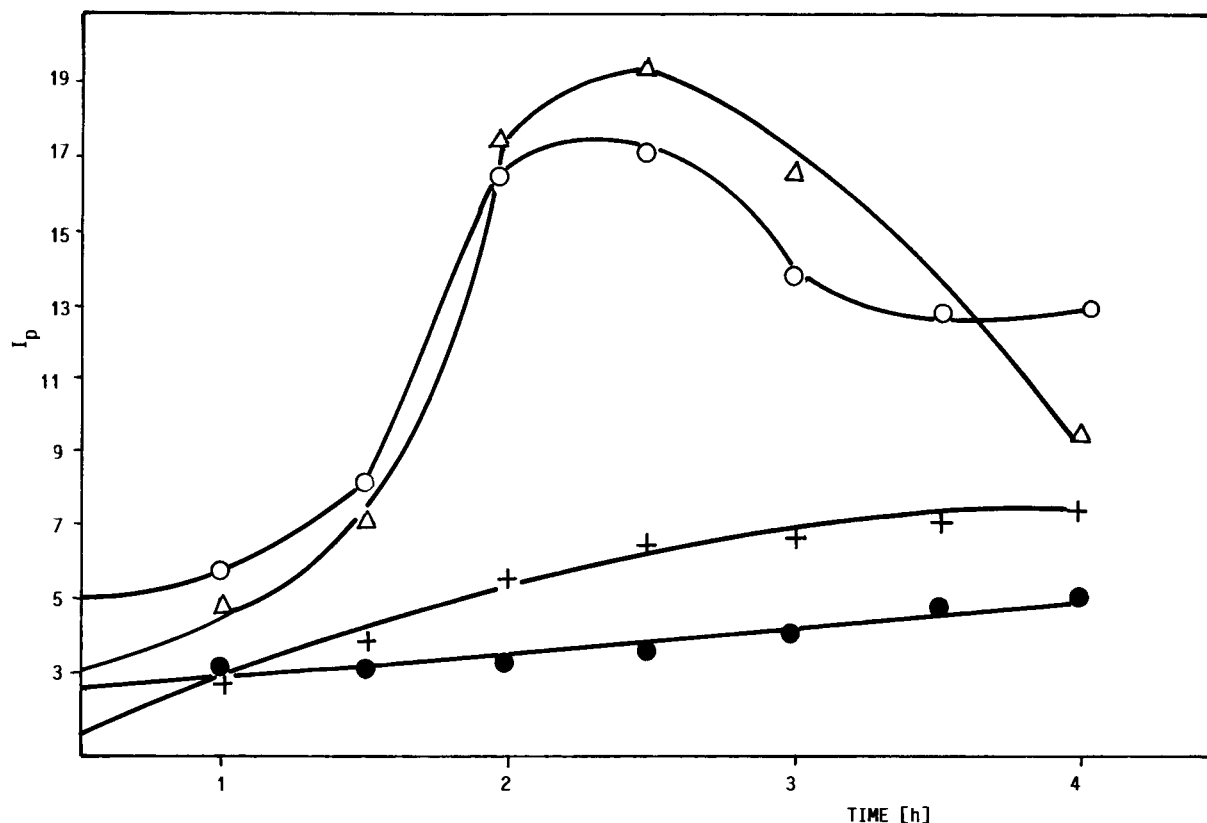


Figure 4 Dependence of polydispersity (I_p) of the copolymers of St-MMA-benzanthrone dye **1b** on the time of polymerization (h) with different concentrations of the dye: (●) 0%, (△) 0.1%, (○) 0.2%, and (+) 0.3%.

the basis of these results, we can assume that dye **1a** decelerated the growing of the polymer chain, probably because of the stability of the dye's radical. The values of M_w for the polymers obtained with the lowest concentration (0.1 wt %) of the dye were close to or even higher than those for the polymer without dye, but with significantly higher values of polydispersity. One very likely explanation of this phenomenon is that probably some processes of recombination took place. This explanation was based on the fact that M_n values stayed approximately constant during the course of the process, while M_w values were increasing. This hypothesis should be supported by additional investigations, which are the object of our future work.

Investigations on the course of polymerization with dye **1b** are presented in Figures 3 and 4. The values for M_w of the polymers (Fig. 3) and their polydispersity (Fig. 4) increased in proportion in-

verse to the initial concentration of the dye. We can note here the difference between the influence of two dyes, **1a** and **1b**. Obviously, the fact that in dye **1b** the polymerizable group was isolated from the chromophoric system through a triazine ring is important for the activity of the dye's radical. This suggestion was also confirmed by the data for the chemically bonded polymer dye (Figs. 5 and 6).

It was of interest to compare these results with those obtained previously. Our investigations with the same monomeric dyes with St⁴ showed that they both accelerated the process of polymerization of St and their copolymers with higher molecular weight were obtained in comparison to the polystyrene without dye. When the third comonomer like MMA was involved, this effect was observed only for dye **1b**, where the polymerizable group was isolated from the chromophore system.

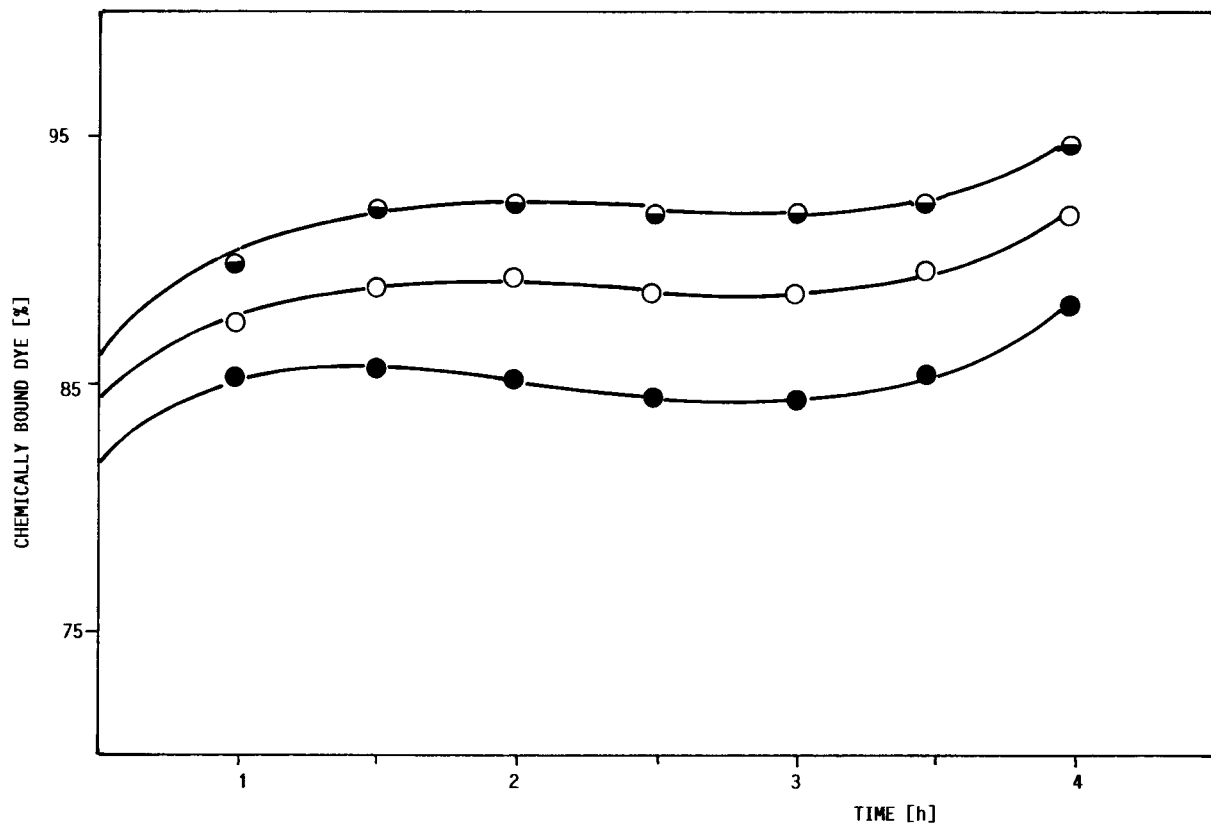


Figure 5 Dependence of the chemically bound dye **1a** on the time of polymerization (h) with different concentrations of the dye in monomeric mixture: (●) 0.1%, (○) 0.2%, and (●) 0.3%.

Investigations on the Participation of the Dyes in the Polymerization Process

It was of interest to study the kinetics of the dyes' participation in the polymerization and to determine the quantity of their bonding in the polymer molecule. In order to do this, we studied, by HPLC analysis, the polymers obtained with three concentrations of the corresponding dye, using the method of the external standard.⁵ Data from these HPLC analyses for dye **1a** are presented in Figure 5 and for dye **1b** in Figure 6. One can see from the figures that both dyes reacted actively at the very beginning of the process and thus reached the maximum of participation (85–90%) for 1 h. The activity of dye **1b** is higher than that of **1a**. This behavior is similar to that observed with some polymerizable azo dyes and anthraquinonic dyes, investigated by us previously.^{6,7}

CONCLUSIONS

The possibility of obtaining a triplicate copolymer of St, MMA, and two benzanthrone dyes, containing an allyloxy polymerizable group, was shown. The most suitable ratio between monomers was found to be St : MMA : dye = 1 : 1 : $0.35 \cdot 10^{-3}$ mol/mol, where the copolymers with high molecular weight and not very high polydispersity have been obtained. The monomeric dyes, benzanthrone derivatives, participated actively in polymerization, and more than 85–90% of them were incorporated in the polymer chain. When the polymerizable group is isolated from the chromophoric system, the activity of the monomeric dye is higher. The mechanism of their copolymerization and influence on the rate of the process are the objects of our future investigations.

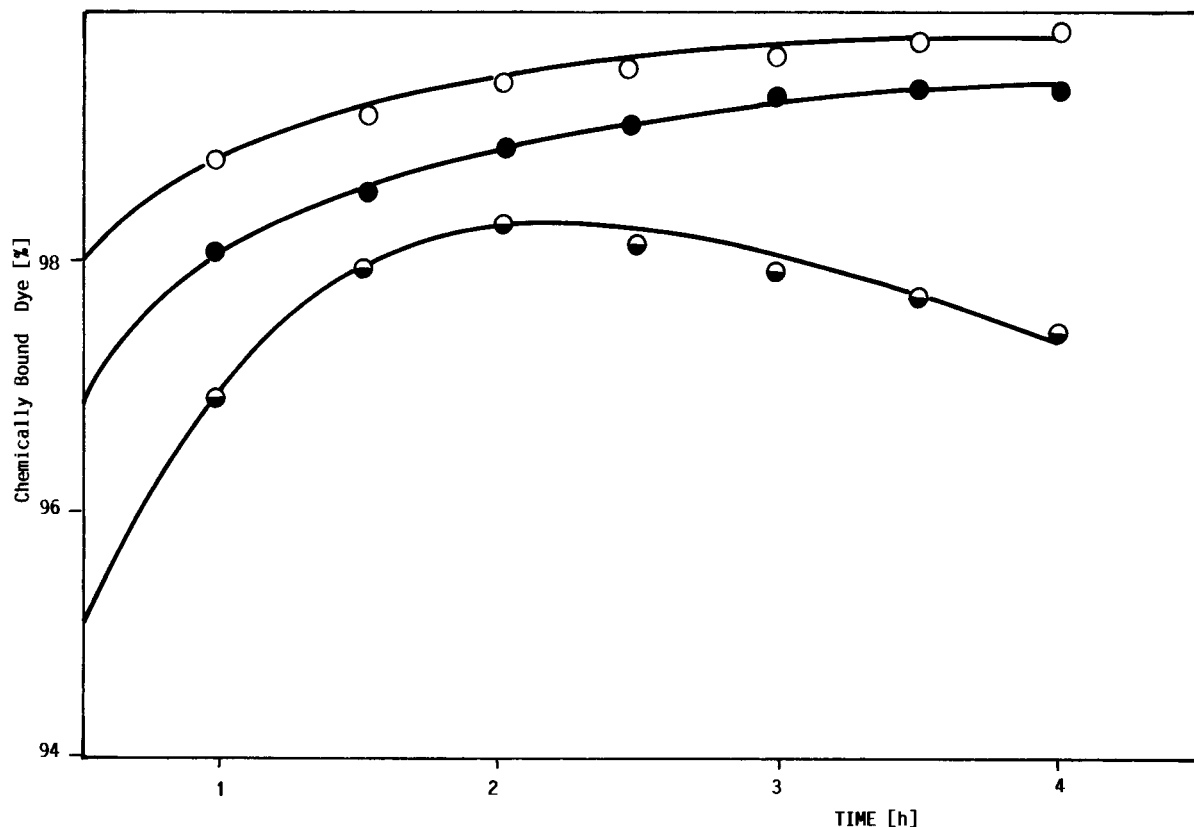


Figure 6 Dependence of the chemically bound dye **1b** on the time of polymerization (h) with different concentrations of the dye in monomeric mixture: (○) 0.1%, (●) 0.2%, and (◐) 0.3%.

The authors thank Bulgarian Foundation "Scientific Research" for some financial support of these investigations.

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