

On the Copolymerization of Styrene with Some Dyes that are Naphthalimide Derivatives

T. KONSTANTINOVA* and I. GRABCHEV

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

SYNOPSIS

The copolymerization of styrene with eight polymerizable fluorescent dyes, naphthalimide derivatives, was investigated. Their effect on the polymerization rate was established. It was found that the chemical structure of the dye influences the copolymerization process.

© 1996 John Wiley & Sons, Inc.

INTRODUCTION

The copolymerization of different traditional monomers with comonomers, which are colored compounds, is not only a method for obtaining so-called self-colored polymers, with a resistance to wet treatment and solvent color, but also a very interesting possibility for the modification of polymers. By copolymerization with the appropriate polymerizable organic compounds, different polymeric materials can be obtained with the desired properties, like fluorescence, photo- and thermostability, and/or sensitivity, solubility, biological activity, etc.

For many years we have synthesized polymerizable dyes and pigments and investigated their copolymerization with some monomers, like styrene¹⁻³ and acrylonitrile,⁴ as well as their influence on the polymerization process and on some of the properties of the copolymers thus obtained. Luminophores are of particular interest due to the bright and nice hues achieved. Among the various classical luminophores, derivatives of naphthalimide are of special interest. They are successfully applied for mass coloration of different polymers.⁵

In our previous articles we reported the synthesis of a group of polymerizable naphthalimide derivatives and their principal ability to copolymerize with styrene and acrylonitrile, obtaining copolymers with an intensive color and fluorescence.⁶⁻⁸ This pre-

sented a possibility not only to receive polymers with resistance to solvent color but also to modify the macromolecule with a fluorescent compound as a marker, which is very useful in some biological investigations. Recently, these possibilities have become of special interest.

Bearing in mind the aforementioned and the results of our previous investigations, it was of interest to find more detail on the influence of the chemical structure of the polymerizable naphthalimide dyes on the process of their copolymerization with styrene, which would enable us to propose one or another structure for application. This was the object of the present work.

EXPERIMENTAL

Materials

Styrene (Nephtochim-Bulgaria) was purified, re-distilled under vacuum and N₂, and dried. Dyes were synthesized and purified by a method previously described.⁶ Dibenzoylperoxide (DBP) (Fluka) 99.6% was recrystallized from CHCl₃. Nitrogen (99.99%) was dry.

Polymerization

Dilatometric investigations were carried out in a dilatometer (5 mL), preliminary flushed with dry oxygen-free nitrogen, with capillary diameter 0.642 mm in the presence of 0.1 wt % of the corresponding dye,

* To whom correspondence should be addressed.

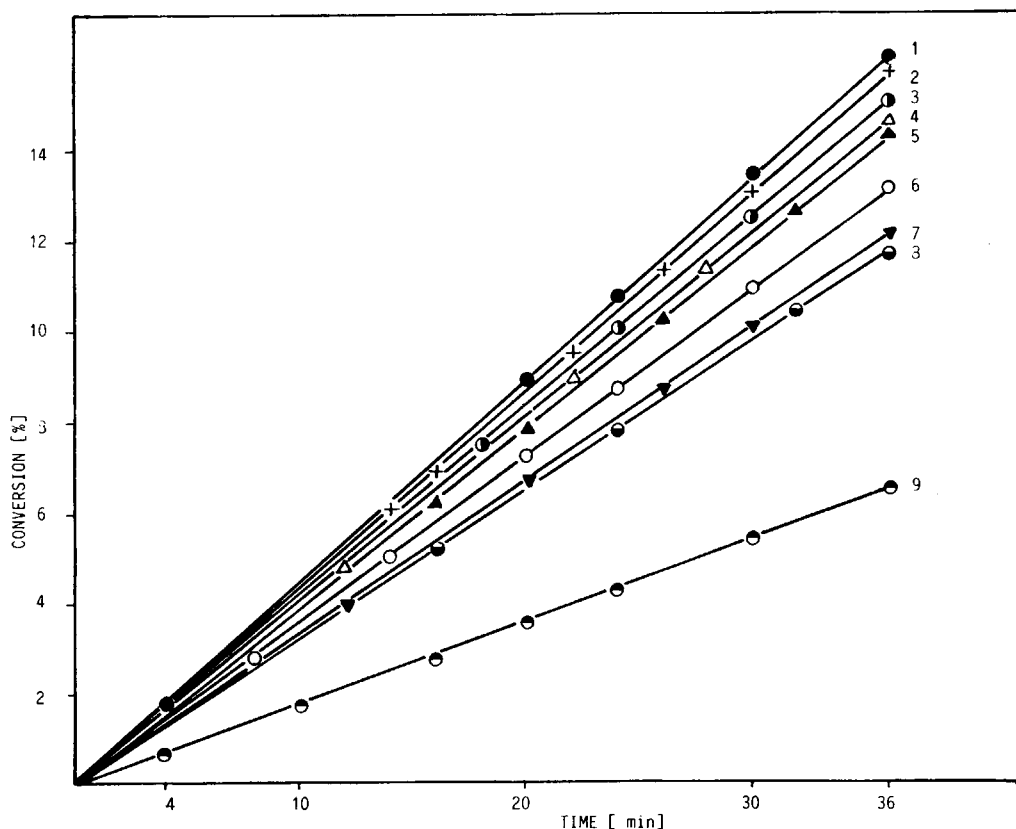


Figure 1 Relationship between conversion (polymer yield) (%) and time of copolymerization (min) of styrene with different dyes: (1) **2**; (2) **3**; (3) **4**; (4) **7**; (5) **8**; (6) without dye; (7) **6**; (8) **5**; (9) **1**.

against styrene and 1 wt % of DBP, toward the monomeric mixture at 80°C ($\pm 0.5^\circ\text{C}$).

RESULTS AND DISCUSSION

The copolymerization of styrene with the following dyes, presented with the general formula **I**, was investigated where A is as delineated:

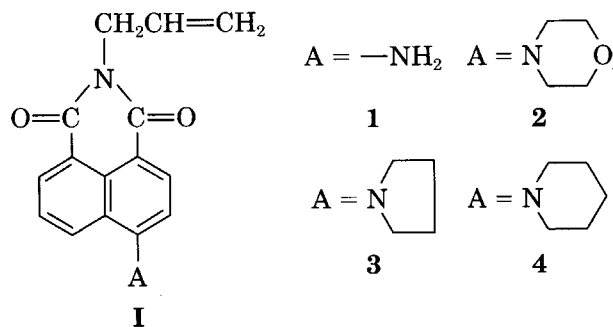


Table I Rate of Copolymerization of Styrene with Different Dyes

Dye No.	Polymerization Rate $\times 10^4$ (mol/L s)
1	2.7
2	6.1
3	6.0
4	5.8
Without dye	5.3
5	4.9
6	5.0
7	5.7
8	5.6

A = $-\text{NHCH}_3$ (**5**), A = $-\text{NHC}_2\text{H}_5$ (**6**), A = $-\text{N}(\text{CH}_3)_2$ (**7**), and A = $-\text{N}(\text{C}_2\text{H}_5)_2$ (**8**). All of them have a yellowish-orange color and bright fluorescence.

The dyes' copolymerization with styrene was investigated dilatometrically. The results obtained are plotted in Figure 1 and compared with those for the homopolystyrene. On the basis of these data, the polymerization rates were calculated (Table 1) and the relationship of these results from the character of the dye was obtained. It can be assumed as follows:

1. Participation of the monomeric dyes **2–4**, **7**, and **8** in the copolymerization process accelerated it in comparison to those of pure styrene. These observations coincided with the results of our previous investigations on the copolymerization of styrene with other polymerizable luminophores—benzanthrone³ and stilbene⁹ derivatives. The likely explanation of the behavior of these compounds could be that all of them had an intensive fluorescence in or near the UV/vis region (340–500 nm), and this transfer of energy probably accelerated the process.
2. Dyes **1**, **5** and **6** had better spectral characteristics (high intensity of absorption and fluorescence, quantum yields ≈ 0.9 – 1) than others. Their participation in copolymerization with styrene decreased the rate of the process. This influence is the most significant for dye **1**, containing a primary amino group, which was attended with a strong hypsochromic effect, resulting in a change from orange to yellow color. That is why (because of the results observed here) it would not be suitable for polymerization. The other two derivatives, **5** and **6**, containing secondary amino groups ($-\text{NHCH}_3$, $-\text{NHC}_2\text{H}_5$, respectively) decreased the polymerization, but not so significantly, without any hypsochromic effect.

On the basis of these results, we can assume that naphthalimide derivatives, containing a primary amino group, as the A residue in the general formula **I**, will not be suitable for polymerization. These dyes, in which molecule A were secondary amines' residue

and in which very good fluorescent characteristics were combined with not very significant influence on the polymerization rate, will be preferred for modification or obtaining of self-colored polymers.

Our future more detailed investigations on these processes will probably illumine the mechanism of that behavior and, we hope, will be of theoretical and practical use as well.

The authors would like to thank the Bulgarian Foundation for Scientific Research for its financial support.

REFERENCES

1. T. Konstantinova, A. Draganov, and Hr. Konstantinov, *Die Angew. Makromol. Chemie*, **50**, 1 (1976).
2. T. Konstantinova and A. Draganov, *J. Appl. Polym. Sci.*, **20**, 351 (1976).
3. T. Konstantinova and J. Bojadgieva, *Die Angew. Makromol. Chemie*, **205**, 91 (1993).
4. T. Konstantinova, *Die Angew. Makromol. Chemie*, **64**, 205 (1977).
5. A. T. Peters and M. J. Bide, *Dyes & Pigments*, **6**, 349 (1985).
6. T. Konstantinova, P. Meallier, and I. Grabchev, *Dyes & Pigments*, **22**, 191 (1993).
7. I. Grabchev, P. Meallier, T. Konstantinova, and M. Popova, *Dyes & Pigments*, **28**, 41 (1995).
8. I. Grabchev, S. Guittonneau, T. Konstantinova, and P. Meallier, *Bull. Soc. Chimie France*, **131**, 828 (1994).
9. T. Konstantinova and I. Grabchev, *Die Angew. Makromol. Chemie*, **196**, 107 (1992).

Received November 24, 1993

Accepted February 16, 1996