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On the Copolymerization of Styrene and Acrylonitrile with 1,8-Naphthalimide Derivatives (Optical Brightening Agents)

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Abstract: The polymerization of styrene and acrylonitrile in the presence of two unsaturated optical brightening agents (OBs), 1,8-naphthalimide derivatives, has been investigated. It was found that the monomeric optical brighteners took part in the polymerization and were covalently bound in the polymer chain. The influence of the monomeric OBs on the rate of the process and on some of the properties of the copolymers thus obtained, such as molecular weight and thermostability, was established.

Key words: polymerizable naphthalimide derivatives, optical brightening agents, copolymers of styrene or acrylonitrile.

INTRODUCTION

Bleaching of polymeric materials is important for their applications. Optical brightening agents (OBs) have rapidly found wide use. Materials treated with these agents attain a shining whiteness which cannot be achieved by other bleaching methods.¹ Bleaching of polymers is usually achieved by blending or surface treatment of the materials with OBs. In both cases, the OBs migrate with time and the whiteness of the polymer decreases.

The chemical bleaching of polymers, using monomeric OBs able to take part in polymerization or polycondensation, is interesting and promising. This results

in incorporation of OB into the polymeric molecule, thus providing resistance to wet treatment and solvents.

In our earlier papers, the synthesis of some monomeric triazinyl stilbene OBs and their ability to copolymerize with styrene and acrylonitrile has been reported.^{2,3} The whiteness of the copolymers thus obtained was resistant to wet treatment and to solvents, owing to the covalent bonding of the brightener to the polymer.

1,8-Naphthalimide derivatives are well known as dyes for polymers with good properties.⁴ In our previous publications^{5,6} we reported the synthesis and properties of some polymerizable 4-alkylamino-*N*-allyl-1,8-naphthalimide derivatives, which had an intense fluorescence and good photostability. Their copolymers with styrene also had an intense fluorescence.⁷

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When the alkylamino group in the fourth position of a naphthalimide molecule is replaced with an alkoxy residue, the derivatives obtained have an intense fluorescence in the near UV range and thus are suitable as optical brightening agents.¹

It was thus of interest to synthesize polymerizable 4-alkoxy-1,8-naphthalimide derivatives and to investigate the possibility of obtaining polymers with a good retention of brightness.

The synthesis of 4-alkoxy-*N*-allyl-1,8-naphthalimide derivatives, investigation of their properties and their ability to copolymerize with styrene and acrylonitrile, was the object of the present work.

EXPERIMENTAL

Materials

Optical brighteners, naphthalimide derivatives, were synthesized by a method described before,⁸ where a solution of 0.01 mol of 4-bromo-*N*-allyl-1,8-naphthalimide in 50 ml methanol or ethanol was refluxed in the presence of 0.01 mol of KOH for 4 h. The process was controlled by thin-layer chromatography (TLC) and the final products were filtered off with very good yields after pouring the liquor into water. The resulting pale-yellow crystals were dried in vacuum at 40°C. They were characterized and identified by melting point (m.p.) R_f , elemental analysis and UV/vis., IR and ¹H nuclear magnetic resonance (NMR) spectra.⁸

Data for the products were as follows. No. **1a**: m.p. = 119–120°C, R_f = 0.54 on silica gel plates (Fluka F₆₀ 254, 20 × 20 cm, 0.02 mm) and the system *n*-heptane–acetone (1 : 1, v/v), $\lambda_{\text{max}}^{\text{abs}}$ = 366 nm (in CHCl₃). No. **1b**: m.p. = 131–133°C, R_f = 0.50 (in the same system), $\lambda_{\text{max}}^{\text{abs}}$ = 370 nm (in CHCl₃).

Styrene (Nephtochim-BG), boiling point (b.p.) 144–145°C, was redistilled and dried. Acrylonitrile (AN) (Fluka), b.p. = 75–77°C, was redistilled and dried. Dibenzoylperoxide (DBP) (C.Erba) was 99.9% recrystallized. CH₃OH and C₂H₅OH-p.a., dimethylformamide (DMF) and CHCl₃ were spectroscopic grade.

Analysis

Spectrophotometric investigations were carried out on a UV/vis. spectrophotometer (Hewlett-Packard 8452-A) with solutions in DMF (concentration 1×10^{-4} g ml⁻¹ for OB and 4×10^{-2} g ml⁻¹ for the polymers).

The molecular weights of polystyrene were measured using gel permeation chromatography (GPC) equipment (Waters 441) in tetrahydrofuran (THF) at 30°C. Values of the limiting viscosity number $[\eta]$ for polyacrylonitrile derivatives were determined by mea-

suring the specific viscosity of DMF solutions (0.5 wt%) at 25°C in an 'Ubbelohde AV-1' viscometer.

The thermal analysis of the OBs and their copolymers was accomplished on a Derivatograph 'MOM-Q' (Hungary) in stationary air in the temperature range 20–500°C and with a heating rate of 10°C min⁻¹.

Thin-layer chromatography (TLC) was performed on silica gel (Fluka F₆₀ 254, plates 20 × 20 cm, 0.2 mm), using a Linomat IV and Scanner II (Camag).

Polymerization

Polymerization with styrene in bulk. In an ampoule flushed with dry and pure N₂, 10 g of purified styrene, 0.01 g (or 0.02 or 0.03 g) of the corresponding OB and 0.1 g of DBP were mixed. The ampoule was sealed and heated in a thermostat for 8 h at 80°C. The solid, transparent polymers thus obtained, which had intense fluorescence, were dissolved in CHCl₃ and precipitated with ethanol (four to five times), until a filtrate free of OB was obtained. The precipitated polymers were dried *in vacuo* at 30°C to constant weight. Yield 80–85%.

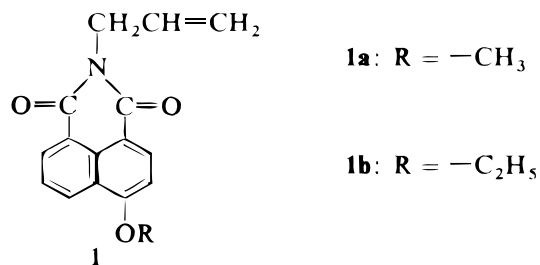
Dilatometric investigations were carried out at 80°C in a dilatometer with 7 ml volume and capillary of diameter 1.088 mm, in the presence of 1 wt% of DBP with respect to the monomeric mixture. The concentration of OB relative to styrene was varied from 0.1 to 0.3 wt% in different experiments.

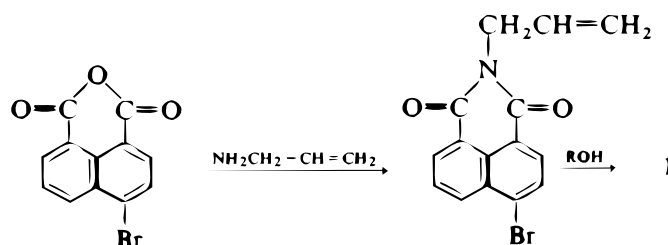
Polymerization with acrylonitrile. Polymerization in an ampoule was carried out with solutions of the monomeric mixture (AN and OB) in DMF (20 vol%) in the presence of 1 wt% of DBP at 70°C. The concentration of the OB relative to AN was varied as above. After 8 h, the polymers obtained were purified by precipitation with ethanol to remove unreacted monomers and were dried *in vacuo* at 30°C to constant weight.

Dilatometric investigations were performed in a dilatometer with a volume of 5 ml and diameter of 0.642 mm, in DMF (20 vol%) solution in the presence of 1 wt% DBP relative to the monomeric mixture, at 70°C.

RESULTS AND DISCUSSION

The optical brighteners which were investigated have the general formula **1**:





Scheme 1

The route employed in their synthesis is presented by Scheme 1, according to the method described before.⁸

The synthesis was followed by TLC and after 4 h the methoxy- or ethoxy-derivative was isolated with good yield ($\approx 90\%$). The pale-yellow products thus obtained were characterized and identified by m.p., R_f , elemental analysis and UV/vis., IR and ^1H NMR spectra. They had an intense blue-violet fluorescence in organic solvent ($\lambda_{\text{max}}^{\text{abs}} = 360\text{--}370\text{ nm}$).

In comparison with the 4-alkylamino-*N*-allyl-1,8-naphthalimide derivatives synthesized before,^{5,7} a shift was observed in the absorption λ_{max} of the compounds of 50–60 nm from the visible to the near-UV range, the so called ‘hypsochromic shift’.⁹ The intense blue-violet fluorescence and disappearance of the colour made the compounds suitable as optical brighteners.

Polymerization investigations

It was of interest to establish the ability of the OBs to copolymerize with monomers such as styrene and acrylonitrile, because these monomers and their polymers and copolymers are produced and widely applied in Bulgaria.

The polymerization of styrene was effected in bulk, and that of AN in DMF solution, both in the presence

of DBP (1 wt% against monomers). It is under these conditions that the polymers are produced in industry. The concentration of the OBs against the corresponding monomer was varied between 0.1 and 0.3 wt%. In all cases, after 8 h, polymers with an intense blue-violet fluorescence were obtained. After their multiple precipitation by ethanol, which is a good solvent for the monomeric OB but not for the polymers, the covalent bonding of OB in polymer molecules was established using TLC, spectrophotometric (UV/vis.) and GPC techniques.

The absorption UV/vis. spectra of the precipitated polymers had the same λ_{max} as the monomeric OB, showing that the basic chromophore of the brightener did not change, either during the polymerization, or as a result of its bonding to the polymer chain.

Colorimetrically, using a standard calibration curve, it was determined that 40–90% of the initial amount of the particular OB was incorporated into the macromolecule (see Tables 1 and 2). Considering that these results were for repeatedly precipitated polymers, where part of the reacted OB bonded to lower molecular fractions was removed during the process, these values can be considered to be satisfactory.

The copolymers of styrene were investigated by GPC and the results are presented in Table 1. It can be seen from the data that the participation of the OB in the

TABLE 1. Polymerization rate, molecular weights and quantity of chemically bound OB for the copolymers of styrene and different concentrations of monomeric OB with formula 1

OB	Initial conc. (%)	Rate ($\text{mol l}^{-1} \text{s}^{-1}$)	$\bar{M}_w \times 10^3$	$\bar{M}_n \times 10^3$	$[\eta]$ (ml g^{-1})	Chem. bound OB (%)
1a	0.1	5.56	48.9	9.9	4.8	41
1a	0.2	5.92	51.5	8.2	5.1	64
1a	0.3	6.39	62.6	10.2	6.2	66
1b	0.1	5.73	30.5	4.3	3.1	41
1b	0.2	6.07	53.2	7.6	5.3	55
1b	0.3	6.65	77.9	7.5	7.7	65
Without OB		5.28	27.9	4.4	2.7	—

TABLE 2. Polymerization rate, limiting viscosity numbers and quantity of chemically bound OB for copolymers of AN and different concentrations of monomeric OB with formula 1

OB	Initial conc. (%)	Rate ($\text{mol l}^{-1} \text{s}^{-1}$)	$[\eta]$ (ml g^{-1})	Chemically bound OB (%)
1a	0.1	4.27	1.17	75
1a	0.2	4.06	1.10	73
1a	0.3	3.80	0.90	70
1b	0.1	4.19	1.22	90
1b	0.2	3.84	1.15	87
1b	0.3	3.59	1.10	86
Without OB		4.53	1.34	—

polymerization of styrene resulted in polymers with higher molecular weights compared with those of polystyrene alone obtained under the same conditions. On the basis of the data for the molecular weight and percentage of chemically bound OB, the concentration of 0.1 wt% OB is not suitable, because the incorporation of the OB in the polymer is unsatisfactory (40%). A concentration of 0.3% is the most suitable of those tried.

The limiting viscosity numbers $[\eta]$ of the polyacrylonitrile polymers were determined and are presented in

Table 2. The data show that the participation of monomeric OB in the copolymerization with AN leads to a decrease in this value.

In both cases (copolymerization with styrene and AN) the influence of the monomeric OB depended on its concentration related to that of the other monomer.

These results stimulated an investigation of the influence of the monomeric OB on the rate of the polymerization. Dilatometric investigations were carried out with three different ratios of the monomers OB and

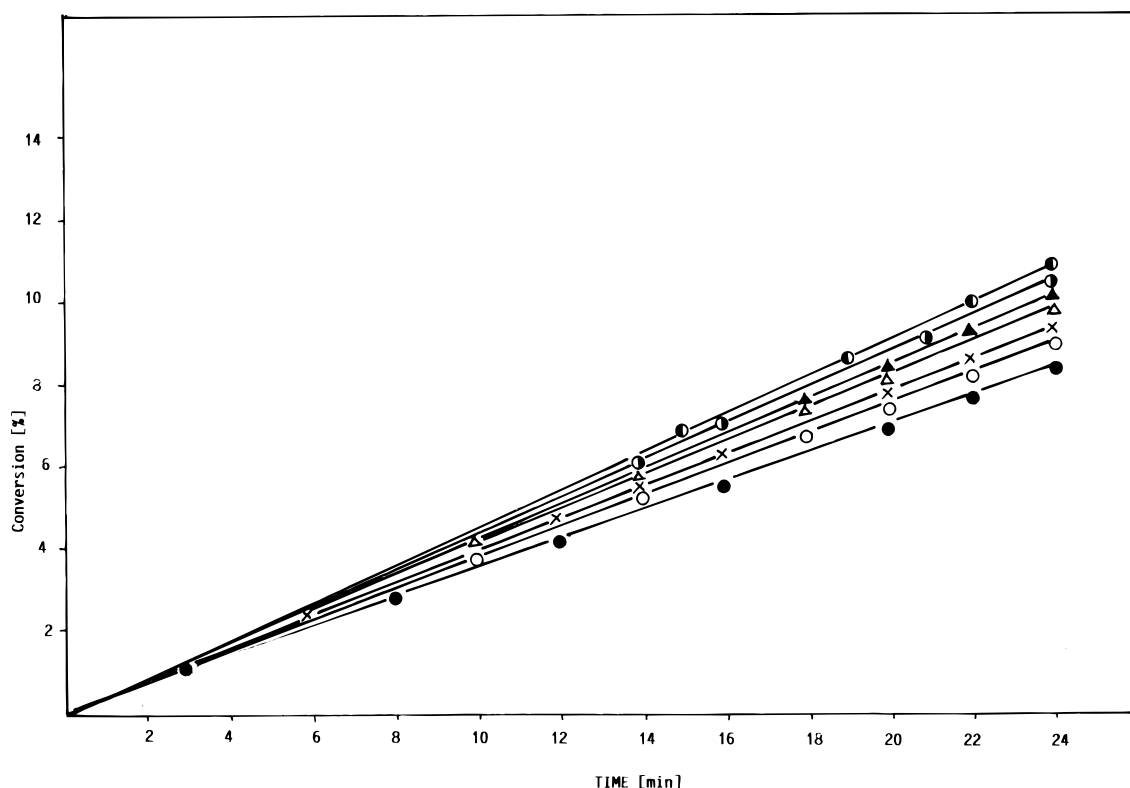


Fig. 1. Relationship between conversion (%) and polymerization time (min) for the bulk polymerization of styrene at 80°C and 1 wt% of DBP in the presence of OB: ○, 1a, 0.1 wt%; ×, 1b, 0.1 wt%; △, 1a, 0.2 wt%; ▲, 1b, 0.2 wt%; ●, 1a, 0.3 wt%; ○, 1b, 0.3 wt%; ●, without OB.

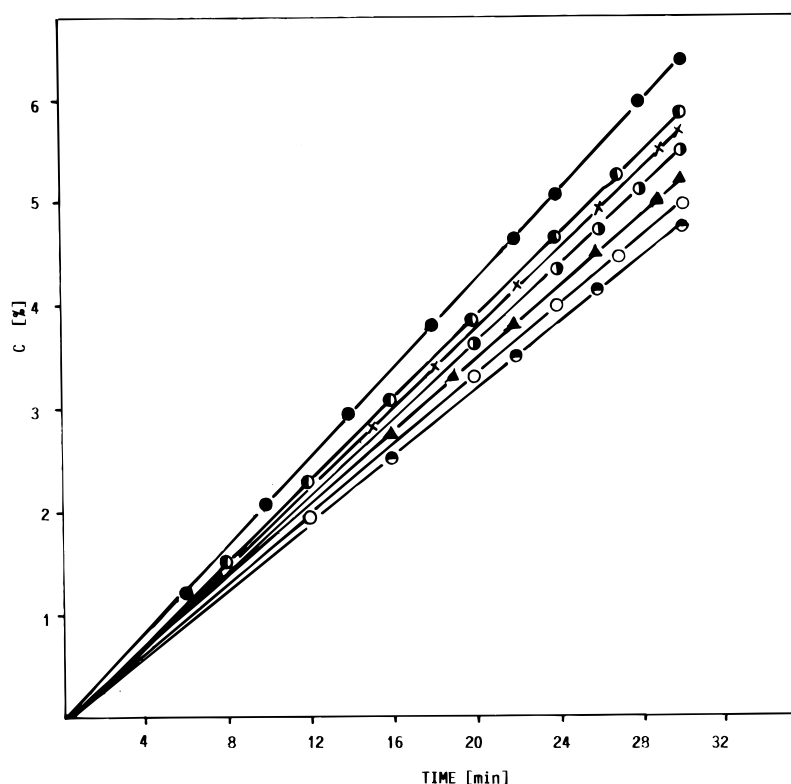


Fig. 2. Relationship between conversion (%) and polymerization time (min) for the polymerization of AN in DMF solution (20 vol%) at 70°C and 1 wt% of DBP in the presence of OB: ●, **1a**, 0.1 wt%; ×, **1b**, 0.1 wt%; ●, **1a**, 0.2 wt%; ▲, **1b**, 0.2 wt%; ○, **1a**, 0.3 wt%; ●, **1b**, 0.3 wt%; ●, without OB.

styrene or AN (concentrations between 0.1 and 0.3% of OB are usually applied to obtain brightening).

On the basis of statistical data the relationship between the percentage conversion and polymerization time for styrene (Fig. 1) was determined. This shows that the rate of polymerization of styrene increased in the presence of OB in the order: $w^{1b} 0.3\% > w^{1a} 0.3\% > w^{1b} 0.2\% > w^{1a} 0.2\% > w^{1b} 0.1\% > w^{1a} 0.1\% > w^{st}$. The polymerization rates for the process were calculated and their values are shown in Table 1.

One probable explanation of these results is that the polymerizable allylamine group, because of the influence of the chromophoric system and especially of two neighbouring CO groups with their electron-accepting effect, produced a more active radical in comparison with that derived from styrene, and hence copolymers with higher \bar{M}_n and \bar{M}_w were obtained (Table 1).

Results of the copolymerization of OB with AN are presented in Fig. 2 and the values for the rate in Table 2. It can be seen that, in this case, participation of the monomeric OB retarded the process. This influence depended again on the concentration of OB. For polyacrylonitrile (PAN) polymers, 0.1 wt% of OB is the most suitable, with 75 and 90% of the OB being bound into the polymer, without significant effect on the molecular weight or the rate of the process.

A likely explanation of this different influence of OB on the polymerization of styrene and AN is

undoubtedly connected with differences in the nature of the basic monomers and the position of the allylamine monomer between them. However, copolymerization of AN was carried out in DMF solution, where the processes of solvation exert an influence as well. The role of the solvent in the process is the object of future investigations.

The thermal analysis of the monomeric OBs showed that their thermo-oxidative destruction began above 280°C, with about 6% loss up to 300°C. The analysis of their copolymers with styrene and AN showed that the participation of the brighteners in the polymer chains exerted no effect on the process of degradation and the curves for the copolymers were identical with those of the homopolymers (polystyrene and PAN).

CONCLUSIONS

On the basis of the results it can be assumed that the polymerizable naphthalimide derivatives investigated are suitable for obtaining copolymers with styrene and AN, which provide whiteness that is resistant to wet treatment and to solvents.

REFERENCES

- 1 Anliker, R. (ed.), *Fluorescent Whitening Agents*. G. Thieme Ver., Stuttgart, 1975, p. 15.

- 2 Konstantinova, T. & Grabchev, I., *Angew. Makromol. Chemie*, **196** (1992) 441.
- 3 Konstantinova, T. & Grabchev, I., *Compt. Rendus de l'Acad. Bulg. Sci.*, **44**: 10 (1991) 59.
- 4 Peters, A. T. & Bide, M. J., *Dyes Pigments*, **6** (1985) 349.
- 5 Konstantinova, T., Meallier, P. & Grabchev, I., *Dyes Pigments*, **22** (1993) 191.
- 6 Grabchev, I., Guittonneau, S., Konstantinova, T. & Meallier, P., *Bull. Soc. Chim. France*, **131** (1994) 828.
- 7 Grabchev, I., Meallier, P., Konstantinova, T. & Popova, M., *Dyes Pigments*, **28** (1995) 41.
- 8 Konstantinova, T. & Grabchev, I., *Bulgarian Authorsertificate*, No. 51120 (1990).
- 9 Zollinger, H., *Color Chemistry*, VCH Verlag, Weinheim, 1987, p. 12.