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New two- and three-cationic polymethine dyes. Synthesis, properties and application

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ABSTRACT

Three new two- and three-cationic monochromophoric polymethine dyes based on the 2-methylbenzothiazole were synthesized and applied as visible light initiators for acrylic monomer polymerization. In the photoinitiating system, the polymethine dye cation acts as an electron acceptor whereas borate anion is an electron donor.

The actual photoinitiators can only operate in a restricted part of the visible light region; as a consequence, a several photoinitiators are usually necessary to harvest all the emitted visible photons. In the present paper, new dyes based on a donor-π-acceptor structure (2-methylbenzothiazole derivatives) are incorporated into visible light sensitive photoinitiating systems of triacrylate polymerization. They exhibit an unusual and remarkable broad absorption lying from the blue to the red. When employed in the presence of organoborate salts, these dyes can efficiently initiate the radical photopolymerization of acrylates under exposure at 514 nm.

1. Introduction

Visible light induced photopolymerization reactions occur in the presence of a colored molecule incorporated into an absorbing photoinitiating systems PIS and being able to act as a photoinitiator PI or a photosensitizer PS [1–3].

Free radical polymerization can be easily achieved both under high and low intensity light sources. Many dyes incorporated in mono- and multi-component photoinitiating systems have been already proposed [1,2].

Improving the performance attained or meeting new or promising possibilities of applications requires a continuous search for new structures.

Looking at the literature, it is quite amazing; despite the fact that more than 50 years of research have led to the possible use of a huge number of photoinitiators, photosensitizers and photoinitiating systems, the most recent analysis of the current work in this area shows tremendous and successful efforts deployed by numerous groups for innovative proposals of new dye structures as exemplified by the recent introduction of colored substituted ketones, modified organometallic derivatives, various series of dyes, light harvesting compounds or multicolor photoinitiators [1,4–52]. Nevertheless, there is still a place for the continuous disclosure of new photoinitiating systems (PIS). Following our work in this area [17,53] we now explore the possibility of using new molecules, *N*-methylpicolinium ester derivatives, that could exhibit a broad visible absorption and act as photosensitizers for free radical polymerization operating in the visible light region. New sensitizers have symmetrical (thiacarbocyanine dye), and unsymmetrical (hemicyanine dyes) structure. As known, the hemicyanine dye molecules consist of unsymmetrically substituted D-π-A arrangements bearing electron donor (D) and electron acceptor (A) functionalities at each end of planar conjugated spacer.

The push–pull effect which results from the intramolecular donor/acceptor interaction and a favorable orientation of the charge delocalization in the axis of the chromophore is characterized by a strong absorption band detected in the visible region (named intramolecular charge transfer band ICT) [1]. While the structure of the third type of dye under study is symmetrical and it belongs to carbocyanine dyes. Many different carbocyanine dyes have been studied as photosensitizers in the visible light photoinitiating systems for the radical polymerization of acrylates [12,15–19]. Commonly, an organoborate salt was used as a co-initiator is such systems. On the other hand, many types of compounds have been added to such photoinitiating systems in order to improve the photoinitiating efficiency, for example: *N*-alkoxypyridinium salts [15,54], 1,3,5-triazine derivatives or *N*-

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methylpicolinium ester derivatives [12,16]. In our previous papers [12,17], it was shown that *N*-methylpicolinium derivatives can act as an efficient second co-initiator for free radical polymerization induced by cyanine dye, a popular photosensitizer. The second co-initiator strongly affects the rates of cyanine/borate-induced polymerization. It was found that the second electron transfer process from the dye-based radical to the *N*-methylpicolinium derivative enhances the rate of photopolymerization. Generally, by a combination of *N*-methylpicolinium derivative and cyanine borate salt, two radicals can be generated per one absorbed photon, thus enhancing the overall efficiency of polymerization.

Our actual search for new initiating systems for visible light prompts us to develop new dyes based on the D-π-A structure. They are based on the difunctional structures where the benzothiazole moiety is linked to *N*-alkyl methylpicolinium ester group through a carbon–carbon bond. Therefore, present paper is focused on the synthesis and application of the visible light bifunctional two-component photoinitiating systems composed of sensitizer with pyridin-4-ylmethyl 2-phenylacetate and pyridin-4-ylmethyl 2,2-diphenylacetate groups attached to a nitrogen atom in a heterocyclic ring (Dyes **NS1**, **NS2**, **S2**) and borate salts as the co-initiators (**B2**, **B3**, **B4**, **B5**) in the photopolymerization reaction of triacrylate (TMPTA) (Scheme 1).

2. Experimental section

2.1. Materials

The substrates used for the synthesis of dyes (2-methylbenzothiazole, 4-pirydylcarbinol, diiodopropane, *N*,*N*′-dicycloheksacarbodiimide, diphenylacetic acid, *p*-(*N*,*N*-dimethylamino) benzaldehyde, triethyl orthoformate), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and 1-methyl-2-pyrrolidinone (MP) were purchased from Aldrich (Poland) and were used without further purification.

2.2. Synthesis of different photoinitiators

The investigated dyes (**NS1**, **NS2** and **S2**) shown in Scheme 1 were prepared in multistep reactions presented in Scheme 2.

Generally, dyes (**NS1**, **NS2**, **S2**) were prepared by Knoevenagel condensation of the appropriate 2-methylbenzothiazole quaternary salt with the corresponding aldehyde and triethyl orthoformate, respectively.

The synthesis of pyridin-4-ylmethyl 2,2-diphenylacetate was carried out based on the method described by Sunderarajan [55].

n-Butyltriphenylborate tetramethylammonium salt (**B2**), *sec*-butyltriphenylborate tetramethylammonium salt (**B3**), *tert*-butyltriphenylborate tetramethylammonium salt (**B4**), tetrakis (*n*-butylborate) tetramethylammonium salt (**B5**) were synthesized based on the method described by Damico [56].

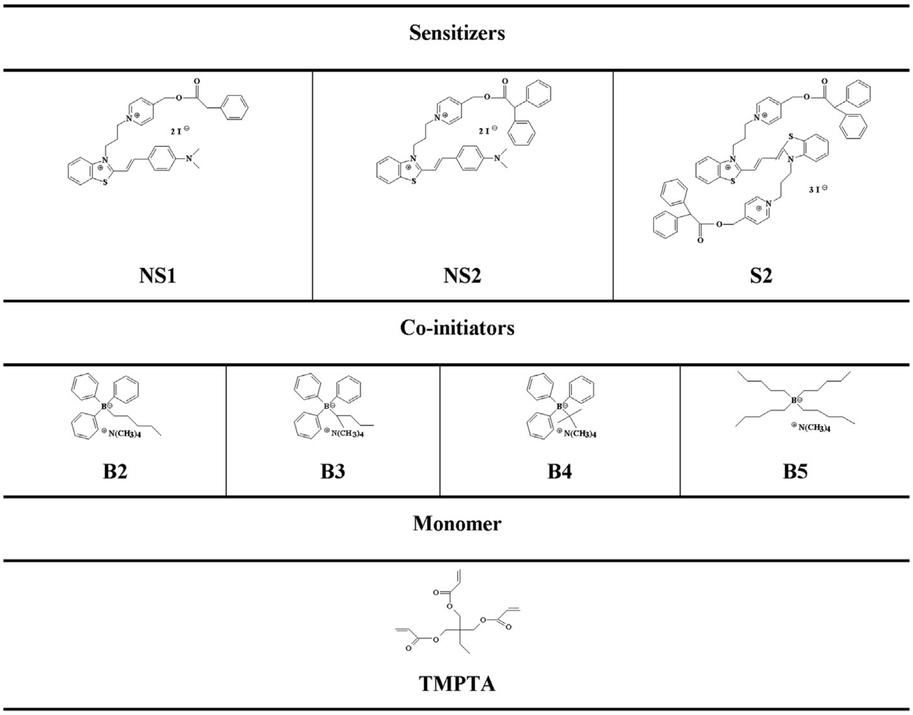
All compounds were prepared with analytical purity (>98%) which was checked by proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopy, IR spectroscopy and elemental analysis. The spectra obtained were the evidence that the reaction products were of the desired structure.

2.2.1. Synthesis of pyridin-4-ylmethyl 2,2-diphenylacetate

3.4 g (16.4 mmol) of *N*,*N*′-dicyclohexylcarbodiimide (DCC) was added to a solution of 3.84 g (16.4 mmol) of diphenylacetic acid and 1.67 g (14.8 mmol) of 4-pyridylcarbinol in 50 mL of dichloromethane. The reaction mixture was stirred at room temperature for about 24 h. The urea precipitate was filtered off, and the filtrate was washed with (2 × 25 mL) $NaHCO_3$ and (2 × 25 mL) water. The organic layer were collected and dried over $MgSO_4$, and the solvent was evaporated yielding required compound [56].

Yield: 3 g, (58.8%), m.p. 59–61 °C.

^{1}H NMR (DMSO-d_6), δ (ppm): 5.22 (s, 2H, $-CH_2$); 5.36 (s, 1H, $-CH$); 7.20–7.23 (d, $J = 6$ Hz, 2H, Ar); 7.23–7.35 (m, 10H, Ar); 8.49–8.52 (d, $J = 6$ Hz, 2H, Ar). ^{13}C NMR (DMSO-d_6), δ (ppm): 39.5; 47.50; 55.59; 64.37; 121.07; 128.44; 138.63; 144.78; 149.53; 171.54.



Scheme 1. Structures of sensitizers, co-initiators and monomer.