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Synthesis and properties of new adducts of 2,2,6,6-tetramethylpiperidine and 2-hydroxyphenylbenzotriazole as polymer photostabilizers

Vladimir Bojinov[a],*, Ivo Grabchev[b]

[a] *Organic Synthesis Department, University of Chemical Technology and Metallurgy, 8 Kl. Ohridsky street, Sofia 1756, Bulgaria*
[b] *Institute of Polymers, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

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Abstract

The synthesis of new stabilizer type compounds (a combination between 2,2,6,6-tetramethylpiperidine and 2-hydroxyphenylbenzotriazole in one molecule) is reported. Three new polymerizable combined stabilizers as well as one unsaturated triazinyl-2,2,6,6-tetramethylpiperidine and three unsaturated triazinyl-2-hydroxyphenylbenzotriazoles as individual stabilizers were synthesized. Their copolymers and the terpolymers of the individual stabilizers with methyl methacrylate (MMA) were obtained. Chemical bonding of the stabilizers in the polymer was confirmed spectrophotometrically. The influence of these additives on the photostability of the copolymers was studied. The participation of the combined stabilizers in the polymerization did not affect considerably the rate of copolymerization, the molecular weight and polydispersity of the copolymers. A significant stabilizing effect against photodegradation was determined. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Photostability of the polymers is one of their most important properties. To solve the problem of polymer stabilization, a number of different stabilizers have successfully been applied. Among them, both 2-hydroxyphenylbenzotriazoles and hindered amines such as 2,2,6,6-tetramethylpiperidines are of a great interest due to their high photostabilizing efficiency [1]. These two groups differ in their action, although both are classed as photodegradation stabilizers. Hindered amine stabilizers are at present the most effective stabilizers for long-term stabilization of polyolefins, polystyrenes and polydienes and their copolymers and terpolymers [2–5]. The 2,2,6,6-tetramethylpiperidines are multifunctional stabilizers. They inhibit the processes of autoxidation by transformation of the parent amines to *N*-oxil radicals either by reaction with peroxy radicals or occasionally by reaction with singlet oxygen. The *N*-oxil radicals stop oxidative degradation by coupling of alkyl radicals [2–4]. In contrast to 2,2,6,6-tetramethylpiperidines, 2-hydroxyphenylbenzotriazoles prove to be UV-absorbers. They are transparent to visible light and are believed to dissipate the absorbed energy in a harmless manner, i.e. to convert the absorbed photon energy into heat without being chemically affected [6].

A combination of 2,2,6,6-tetramethylpiperidine and 2-hydroxyphenylbenzotriazole fragments through s-triazine ring in one molecule could result in a new stabilizer type of combined stabilizing effect. On the other hand, the introduction of polymerizable allyl group into the combined stabilizer molecule could provide of the latter capability of covalent bonding to the polymer chain by copolymerization with vinyl monomers. The covalent bonding to the polymer chain provides stability toward solvents and a migration stabilizing effect. In previous papers, we have reported on the synthesis and application of polymerizable triazinyl-2,2,6,6-tetramethylpiperidines as stabilizers for polymer materials [7,8]. Their influence on the rate of copolymerization and on the photostability of the styrene copolymers was studied. Recently, it has been demonstrated that photostability of poly(methyl methacrylate) (PMMA) was considerably improved by combination of 2,2,6,6-tetramethylpiperidine and UV-absorber fragments in one molecule [9,10].

It is worth synthesizing new adducts of hindered amine and 2-hydroxyphenylbenzotriazole which might have high stabilizing efficiency and an ability to polymerize with vinyl

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* Corresponding author. Tel.: +359-2-6254359.
E-mail address: vlbojin@uctm.edu (V. Bojinov).

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monomers. The present work reports on the synthesis of three new polymerizable photostabilizers, a combination of 2-hydroxyphenylbenzotriazole and 2,2,6,6-tetramethylpiperidine fragments in one molecule, and investigation of the influence of the synthesized adducts on the photostability of their copolymers with methyl methacrylate (MMA).

2. Experimental

2.1. Materials

The 2,2,6,6-tetramethylpiperidine **1a**, *o*-aminophenol, 2-amino-4-chlorophenol, 2-amino-4-nitrophenol, *m*-phenylenediamine, allyl alcohol, cyanuric chloride and tetrabutylammonium bromide (TBAB) (Fluka products), p.a. grade, were used without purification. The 2-(2,2,6,6-tetramethylpiperidin-1-yl)-4,6-dichloro-1,3,5-triazine **1b** and 2-(2,2,6,6-tetramethylpiperidin-1-yl)-4-allyloxy-6-chloro-1,3,5-triazine **2** were synthesized and purified as before [7,11]. The 2-hydroxyphenylbenzotriazoles **3a–c** were synthesized modifying previously described procedure [12]. Commercial MMA was used after distillation under reduced pressure in a nitrogen (99.9%) atmosphere. Dibenzoyl peroxide (DBP, Fluka) recrystallized from chloroform was used as an initiator of the free radical copolymerization. Used solvents were of p.a. or spectrophotometric grade.

2.2. Methods

The ^{1}H NMR spectra were recorded on JEOL JNM-PS spectrometer, operating at 100 MHz in acetone d_6 (chemical shifts are given as δ in ppm). Electronic spectra were recorded on a Hewlett-Packard 8452A spectrophotometer with 2 nm resolution, at room temperature in chloroform. Elemental analysis data were obtained on Perkin-Elmer 240 automatic analyzer. The reaction course and purity of the final products were followed by TLC on silica gel (Fluka $F_{60}254$ 20×20, 0.2 mm), using as eluant *n*-hexane/ethyl acetate/methanol = 7:2:1. The melting points were determined by means of a Kofler melting point microscope. The polymer molecular weights were determined on a GPC Waters 244 apparatus equipped with a combination of 100 and 1000 Å, linear ultrastyragel columns; the solvent was THF at a flow rate of 1.0 ml min^{-1} at 45 °C. Both differential refractive index and UV-visible absorption detectors were used. Polystyrene calibration was used for all molecular weight calculations.

2.3. Synthesis of stabilizers

2.3.1. General procedure for the synthesis of combined 2,2,6,6-tetramethylpiperidine—2-hydroxyphenylbenzotriazole derivatives (*5a–c*)

To a solution of 2-(2′-hydroxy-5′-Zphenyl)-5-aminobenzotriazole **3a–c** (0.01 mol) and (1.5 g, 0.01 mol) of sodium acetate in 40 ml of glacial acetic acid a solution of 2-(2,2,6,6-tetramethylpiperidin-1-yl)-4-allyloxy-6-chloro-1,3,5-triazine **2** (3.1 g, 0.01 mol) in 20 ml of glacial acetic acid was added dropwise at room temperature for 30 min. The resulting mixture was stirred for an hour at 120 °C and then after cooling, poured into 60 ml of water. The crude precipitated product was filtered and dried. Two-fold recrystallization from chlorobenzene afforded pure target compound **5a–c** as white needles.

*2.3.1.1. 2-(2,2,6,6-Tetramethylpiperidin-1-yl)-4-[2-(2′-hydroxyphenyl)benzotriazole-5-imino]-6-allyloxy-1,3,5-triazine **5a**.* The ^{1}H NMR (acetone d_6, 100 MHz) ppm: 8.62 (br.s, 1H, OH); 7.94 (m, 1H, 7-ArH); 7.54 (m, 3H, 4-ArH, 4′-ArH and 6′-ArH); 7.02 (m, 3H, 6-ArH, 3′-ArH and 5′-ArH); 6.16 (br.s, 1H, NH); 5.90 (m, 1H, CH=); 5.22 (m, 2H, $=CH_2$); 4.78 (m, 2H, OCH_2); 1.82 (m, 6H, 3 × piperidine CH_2); 1.54 (s, 12H, 2 × piperidine $C(CH_3)_2$). Analysis: calculated for $C_{27}H_{32}N_8O_2$—C 64.80, H 6.40, N 22.40%; found—C 64.93, H 6.34, N 22.31%.

*2.3.1.2. 2-(2,2,6,6-Tetramethylpiperidin-1-yl)-4-[2-(2′-hydroxy-5′-chlorophenyl)benzotriazole-5-imino]-6-allyloxy-1,3,5-triazine **5b**.* The ^{1}H NMR (acetone d_6, 100 MHz) ppm: 8.74 (br.s, 1H, OH); 7.98 (m, 1H, 7-ArH); 7.62 (m, 4H, 4-ArH, 3′-ArH, 4′-ArH and 6′-ArH); 7.08 (m, 1H, 6-ArH); 6.10 (br.s, 1H, NH); 5.92 (m, 1H, CH=); 5.28 (m, 2H, $=CH_2$); 4.86 (m, 2H, OCH_2); 1.78 (m, 6H, 3 × piperidine CH_2); 1.50 (s, 12H, 2 × piperidine $C(CH_3)_2$). Analysis: calculated for $C_{27}H_{31}ClN_8O_2$—C 60.62, H 5.80, N 20.95%; found—C 60.78, H 5.88, N 21.04%.

*2.3.1.3. 2-(2,2,6,6-Tetramethylpiperidin-1-yl)-4-[2-(2′-hydroxy-5′-nitrophenyl)benzotriazole-5-imino]-6-allyloxy-1,3,5-triazine **5c**.* The ^{1}H NMR (acetone d_6, 100 MHz) ppm: 8.82 (br.s, 1H, OH); 8.34 (m, 2H, 4′-ArH and 6′-ArH); 7.88 (m, 2H, 7-ArH and 3′-ArH); 7.62 (m, 1H, 4-ArH); 7.08 (m, 1H, 6-ArH); 6.18 (br.s, 1H, NH); 5.96 (m, 1H, CH=); 5.30 (m, 2H, $=CH_2$); 4.90 (m, 2H, OCH_2); 1.84 (m, 6H, 3 × piperidine CH_2); 1.52 (s, 12H, 2 × piperidine $C(CH_3)_2$). Analysis: calculated for $C_{27}H_{31}N_9O_4$—C 59.45, H 5.69, N 23.12%; found—C 59.59, H 5.64, N 23.21%.

2.3.2. General procedure for the synthesis of allyloxytriazinylbenzotriazoles (*4a–c*)

Cyanuric chloride (1.85 g, 0.01 mol) dissolved in dichloromethane (15 ml) was added dropwise to a mixture of allyl alcohol (0.58 g, 0.01 mol) dichloromethane solution (15 ml), 50% hydrous sodium hydroxide solution (10 ml) and TBAB (0.32 g, 0.001 mol) under vigorous stirring. The resulting mixture was stirred for 15 min at 10 °C and then diluted in 20 ml of water. Organic layer was separated, washed with water, dried over anhydrous sodium sulphate and evaporated in vacuum to give pure allyloxy-s-triazine in quantitative yield.

To a solution of 2-(2′-hydroxy-5′-Zphenyl)-5-aminobenzotriazole **3a**–**c** (0.01 mol) in 40 ml of glacial acetic acid 1.5 g (0.01 mol) of sodium acetate and allyloxy-s-triazine above obtained were added at room temperature. The resulting mixture was stirred for an hour at 80 °C and then after cooling, poured into 40 ml of water. The crude precipitated product was filtered and dried. Two-fold recrystallization from chlorobenzene gave pure desired product **4a–c** as white needles.

*2.3.2.1. 2-[2-(2′-Hydroxyphenyl)benzotriazole-5-imino]-4-allyloxy-6-chloro-1,3,5-triazine **4a**.* The ^{1}H NMR (acetone d$_6$, 100 MHz) ppm: 8.68 (br.s, 1H, OH); 7.96 (m, 1H, 7-ArH); 7.56 (m, 3H, 4-ArH, 4′-ArH and 6′-ArH); 7.16 (m, 3H, 6-ArH, 3′-ArH and 5′-ArH); 6.14 (br.s, 1H, NH); 5.92 (m, 1H, CH=); 5.22 (m, 2H, =CH$_2$); 4.86 (m, 2H, OCH$_2$). Analysis: calculated for $C_{18}H_{14}ClN_7O_2$—C 54.61, H 3.54, N 24.78%; found—C 54.73, H 3.49, N 24.70%.

*2.3.2.2. 2-[2-(2′-Hydroxy-5′-chlorophenyl)benzotriazole-5-imino]-4-allyloxy-6-chloro-1,3,5-triazine **4b**.* The ^{1}H NMR (acetone d$_6$, 100 MHz) ppm: 8.76 (br.s, 1H, OH); 8.02 (m, 1H, 7-ArH); 7.66 (m, 4H, 4-ArH, 3′-ArH, 4′-ArH and 6′-ArH); 7.02 (m, 1H, 6-ArH); 6.08 (br.s, 1H, NH); 5.94.(m, 1H, CH=); 5.24 (m, 2H, =CH$_2$); 4.92 (m, 2H, OCH$_2$). Analysis: calculated for $C_{18}H_{13}C_{l2}N_7O_2$—C 50.23, H 3.02, N 22.79%; found—C 50.35, H 3.08, N 22.91%.

*2.3.2.3. 2-[2-(2′-Hydroxy-5′-nitrophenyl)benzotriazole-5-imino]-4-allyloxy-6-chloro-1,3,5-triazine **4c**.* The ^{1}H NMR (acetone d$_6$, 100 MHz) ppm: 8.84 (br.s, 1H, OH); 8.38 (m, 2H, 4′-ArH and 6′-ArH); 7.88 (m, 2H, 7-ArH and 3′-ArH); 7.52 (m, 1H, 4-ArH); 6.98 (m, 1H, 6-ArH); 6.16 (br.s, 1H, NH); 5.98 (m, 1H, CH=); 5.26 (m, 2H, =CH$_2$); 5.02 (m, 2H, OCH$_2$). Analysis: calculated for $C_{18}H_{13}ClN_8O_4$—C 49.04, H 2.95, N 25.42%; found—C 49.17, H 3.02, N 25.53%.

*2.3.3. General procedure for the synthesis of 2-(2′-hydroxy-5′-Zphenyl)-5-aminobenzotriazole derivatives (**3a–c**)*

A solution of 5.45 g (0.05 mol) of *o*-aminophenol (2-amino-4-chlorophenol or 2-amino-4-nitrophenol, respectively) in 25 ml of water and 9 ml of concentrated hydrochloric acid was diazotized at 0 °C in the presence of 0.2 g of cuprous sulphate with a solution of sodium nitrite (3.5 g, 0.05 mol) in 7 ml of water. The solution of the diazonium chloride was added to a solution (5 °C) of *m*-phenylenediamine (5.4 g, 0.05 mol) in 100 ml of water and 5 ml of concentrated hydrochloric acid. To the resulting mixture a solution of sodium acetate (34 g, 0.4 mol) was added over a period of 2 h with stirring at 5 °C. After 2 h stirring at room temperature to the reaction mixture 17 ml of 25% aqueous ammonium hydroxide solution were added (pH 8) and the dark-red azo compound was isolated by filtration, washed with water, and then dissolved in methanol (160 ml). Cuprous sulphate (30 g) in 70 ml of water and 120 ml of 25% aqueous ammonium hydroxide solution were added with stirring to the solution of the azo compound. After 2 h refluxing the suspension was filtered and the residue was stirred with 100 ml of 5N hydrochloric acid for an hour. To the resulting acid mixture 50 ml of water and 26 ml of 25% aqueous ammonium hydroxide solution were added (pH 8). The crude precipitated product was isolated by filtration, washed with water and dried. Three-fold recrystallization from ethanol–water (50:50 vol.%) afforded the 2-(2′-hydroxy-5′-Zphenyl)-5-aminobenzotriazole **3a–c** as colorless needles.

*2.3.3.1. 2-(2′-Hydroxyphenyl)-5-aminobenzotriazole **3a**.* The ^{1}H NMR (acetone d$_6$, 100 MHz) ppm: 8.64 (br.s, 1H, OH); 7.92 (m, 1H, 7-ArH); 7.52.(m, 3H, 4-ArH, 4′-ArH and 6′-ArH); 6.98 (m, 3H, 6-ArH, 3′-ArH and 5′-ArH); 5.96 (br.s, 2H, NH$_2$). Analysis: calculated for $C_{12}H_{10}N_4O$—C 63.72, H 4.42, N 24.78%; found—C 63.58, H 4.35, N 24.69%.

*2.3.3.2. 2-(2′-Hydroxy-5′-chlorophenyl)-5-aminobenzotriazole **3b**.* The ^{1}H NMR (acetone d$_6$, 100 MHz) ppm: 8.72 (br.s, 1H, OH); 7.96 (m, 1H, 7-ArH); 7.62 (m, 4H, 4-ArH, 3′-ArH, 4′-ArH and 6′-ArH); 6.98 (m, 1H, 6-ArH); 5.82 (br.s, 2H, NH$_2$). Analysis: calculated for $C_{12}H_9ClN_4O$—C 55.28, H 3.45, N 21.50%; found—C 55.40, H 3.51, N 21.43%.

*2.3.3.3. 2-(2′-Hydroxy-5′-nitrophenyl)-5-aminobenzotriazole **3c**.* The ^{1}H NMR (acetone d$_6$, 100 MHz) ppm: 8.86 (br.s, 1H, OH); 8.38 (m, 2H, 4′-ArH and 6′-ArH); 7.86 (m, 2H, 7-ArH and 3′-ArH); 7.58 (m, 1H, 4-ArH); 6.96 (m, 1H, 6-ArH); 5.94 (br.s, 2H, NH$_2$). Analysis: calculated for $C_{12}H_9N_5O_3$—C 53.14, H 3.32, N 25.83%; found—C 53.05, H 3.38, N 25.72%.

2.4. Synthesis of polymers

The free-radical copolymerization and terpolymerization of the monomeric stabilizers **2**, **4a–c** and **5a–c** with MMA was carried out in ampoules previously purged with pure dry nitrogen [13]. The processes of copolymerization and terpolymerization of MMA were conducted at 70 °C in the presence of 1.0 wt.% each of DBP and corresponding monomeric stabilizer (**2**, **4a–c** or **5a–c**) as well as a mixture of stabilizers **2** and **4a–c** (each with a concentration of 0.5 wt.%). After 10 h transparent, solid and colorless polymers were obtained. The side-chain copolymers thus obtained were purified by five-fold precipitation with ethanol from chloroform. This process was controlled by TLC until filtrates were free of stabilizers **2**, **4a–c** or **5a–c**. The precipitated copolymers and terpolymers were repeatedly washed with ethanol, recovered by filtration and dried in vacuum to constant weight. All measurements for the characterization and investigation were carried out with precipitated polymers.

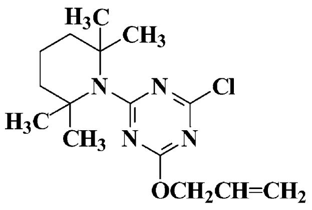
2.5. Photodegradation of the copolymers

The solid polymeric films were irradiated in SUNTEST CPS equipment (Heraeus, Germany), supplied with an air-cooled xenon lamp (Hanau, 1.1 kW, 765 W m^{-2}). The photodegradation was followed by the changes of the molecular weight using GPC. The polymeric films of poly(MMA-co-stabilizer), poly(MMA-ter-stabilizers) and PMMA were of 60 μm thickness.

3. Results and discussion

The aim of the present study can be expressed in two ways: (1) to obtain copolymers and terpolymers of MMA with polymerizable stabilizers which differ from each other in their action; (2) to obtain copolymers of MMA with monomers in whose molecules two types of stabilizers are combined.

Following aim (1), based on our earlier investigations [7,8], we choose the polymerizable hindered piperidine type stabilizer **2** (Formula 1), which inhibit the processes of autoxidation [2–4].



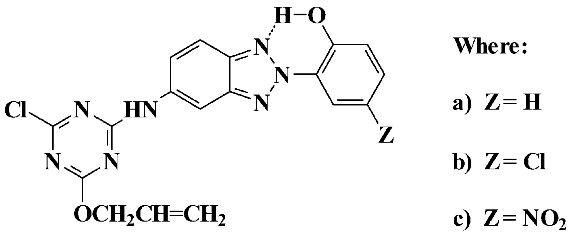
2

Formula 1

The compound **2** was synthesized as before [7].

Among the other types of stabilizers, we synthesized polymerizable 2-hydroxyphenylbenzotriazole stabilizers **4a–c** (Formula 2) known to be UV-absorbers [6].

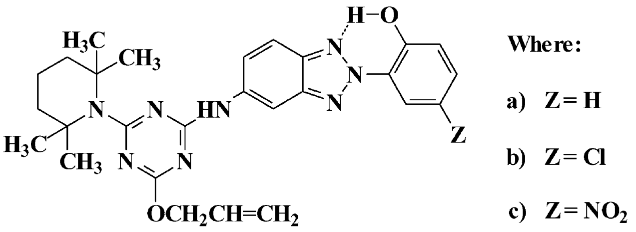
These compounds were obtained by modifying procedures described before [10,12,14].



4a-c

Formula 2

In order to follow aim (2), we synthesized polymerizable adducts **5a–c** of hindered piperidine with 2-hydroxyphenylbenzotriazole in which the different stabilizer fragments are combined through the s-triazine ring into one molecule (Formula 3).



5a-c

Formula 3

3.1. Synthesis of stabilizers

The combined stabilizers **5a–c** were synthesized following Scheme 1.

Initially, 2,2,6,6-tetramethylpiperidine **1a** was converted into 2-(2,2,6,6-tetramethylpiperidin-1-yl)-4,6-dichloro-1,3,5-triazine **1b** by method described before [11].

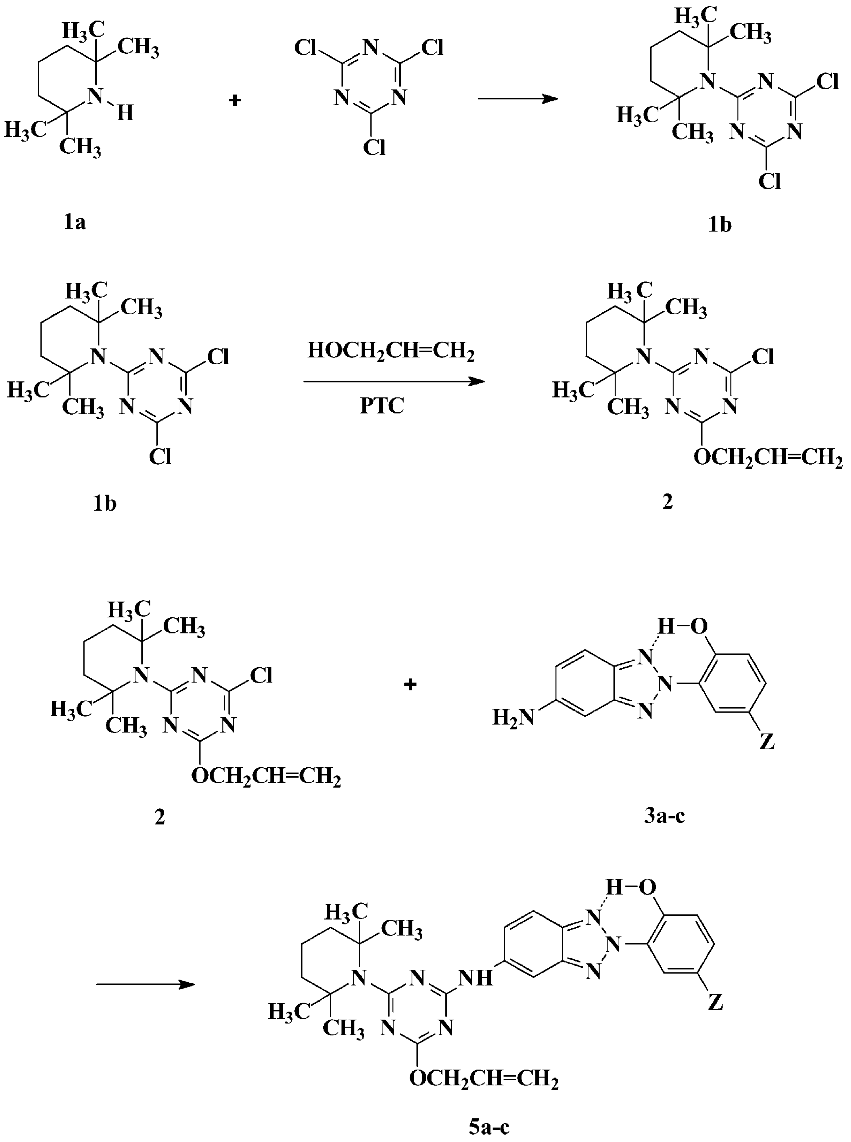
The polymerizable piperidine **2** was synthesized in quantitative yield by nucleophilic substitution of the second chlorine atom of the intermediate **1b** with allyl alcohol under phase transfer catalysis (PTC) conditions as previously described [7]. The reaction was carried out in 50% hydrous sodium hydroxide solution/water-immiscible organic solvent two-phase system at room temperature in the presence of a quaternary ammonium salt. The selection of favorable PTC conditions was very important for the synthesis results. Both the correct choice of the two-phase system type and the solubility of the initial and final products in the water-immiscible organic solvents governed this selection.

However, the PTC method was not suitable for replacement of s-triazine chlorine atom with the amino group of the 2-hydroxyphenylbenzotriazoles **3a–c** [15]. That is why, the final reaction (Scheme 1) of monomer **2** with 2-(2′-hydroxy-5′-Zphenyl)-5-aminobenzotriazoles **3a–c** for obtaining the target stabilizers **5a–c** was conducted in glacial acetic acid medium.

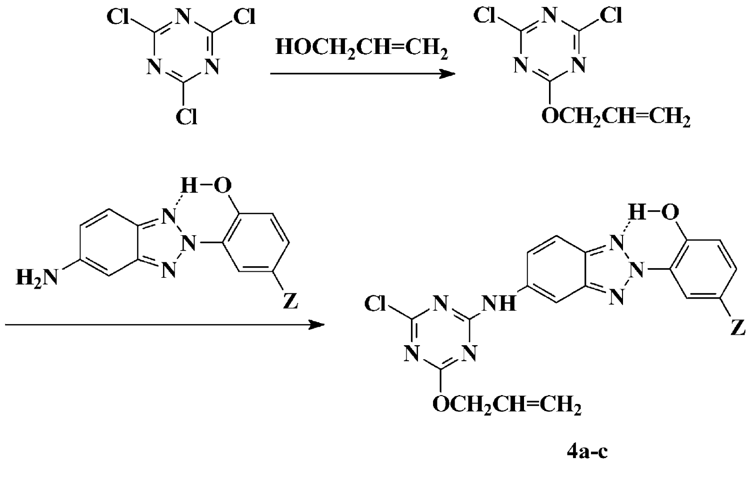
In contrast to the synthesis of monomer **2**, in the synthesis of monomers **4a–c** the allyloxy group was introduced in the s-triazine ring under PTC conditions before 2-hydroxyphenylbenzotriazole fragment. This was necessary because of the possibility for a substitution of the benzotriazole hydroxyl group under PTC conditions, which was the reason for changing the way of monomers **4a–c** synthesis (Scheme 2).

First, the allyloxy-1,3,5-triazine was synthesized under PTC conditions with the use of a concentrated water phase [14] and then treated with compounds **3a–c** in glacial acetic acid medium.

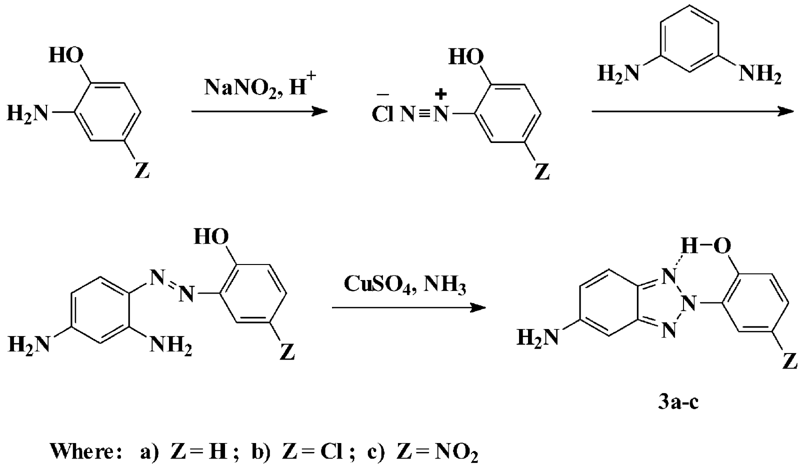
The intermediate benzotriazoles **3a–c** were synthesized modifying procedures described before [12] (Scheme 3).



Scheme 1. Synthesis of combined 2,2,6,6-tetramethylpiperidine–2-hydroxyphenylbenzotriazole stabilizers **5a–c**.



Scheme 2. Synthesis of monomeric 2-hydroxyphenylbenzotriazole stabilizers **4a–c**.



Scheme 3. Synthesis of intermediate 2-hydroxyphenylbenzotriazoles **3a–c**.

First, *o*-aminophenol (2-amino-4-chlorophenol or 2-amino-4-nitrophenol, respectively) was diazotized. The diazonium salt was coupled with *m*-phenylenediamine in acid medium and the dye obtained was oxidative cyclized with $CuSO_4$/25% NH_3 in weakly alkaline medium, giving semiproduct 2-(2′-hydroxy-5′-Zphenyl)-5-aminobenzotriazole **3a–c**.

All reactions were monitored by TLC on silica gel and the synthesized products **3a–c**, **4a–c** and **5a–c** were characterized (Table 1) and identified by their melting points, TLC R_f values, elemental analyses, UV-visible and ^{1}H NMR spectra.

3.2. Polymerization of methyl methacrylate

3.2.1. Kinetics of polymerization

In order to study the influence of the synthesized monomeric stabilizers on the rate of copolymerization and terpolymerization, the free-radical polymerization of MMA in the presence of 1.0 wt.% of the corresponding monomeric stabilizer (**2**, **4a–c** or **5a–c**) as well as a mixture of stabilizers **2** and **4a–c** (each with the concentration of 0.5 wt.%) was investigated kinetically. The polymer yields were 69–81 wt.% for poly(MMA-co-stabilizer **2**, **4** or **5**), 56–58 wt.% for poly(MMA-ter-stabilizeres ***2*** + ***4***) and 88 wt.% for PMMA. The polymerization rates R_p were determined from the time–yield curves (Table 2). It can be seen that stabilizers **2**, **4a–c** and **5a–c** did not affect the polymerization rate significantly, especially stabilizers **2** and **4a–c**. In the case of terpolymerization, the retardation effect was stronger.

3.2.2. Evidence for a chemical bond between PMMA and the stabilizers

The presence of a covalent bond between the monomeric stabilizer units and the polymer chain has been proved by GPC and by TLC technics. In the GPC chromatograms only one peak was observed for copolymers and terpolymers containing stabilizers, its retention time being different from that of the PMMA.

The unprecipitated copolymers (they comprise also some amount of unreacted stabilizers), precipitated copolymers and terpolymers, monomeric stabilizers and mixtures of a homopolymer with the stabilizers were studied by TLC. After the chromatography development, it was established that the stabilizers in the mechanical mixtures (a mechanical blend of homopolymer and stabilizer) moved at the

Table 1
Yields and characteristic data obtained for benzotriazoles **3a–c**, monomers **4a–c** and combined stabilizers **5a–c**

Compound	Yield (%)	M_p (°C)	R_f	λ_{max} (nm)	lg ε
3a	74	212–215	0.62	364	4.238
3b	71	165–167	0.68	370	4.226
3c	69	187–189	0.69	378	4.218
4a	89	127–129	0.49	342	4.138
4b	86	99–101	0.53	346	4.114
4c	84	112–114	0.56	354	4.068
5a	81	192–194	0.25	332	4.126
5b	78	164–166	0.28	338	4.132
5c	79	177–179	0.31	344	4.096

Table 2
Copolymerization rates R_p of MMA with stabilizers **2**, **4a–c** and **5a–c**

Polymer	Yield (%)	R_p (mmol l^{-1} s^{-1})
Poly(MMA-co-stabilizer **2**)	81	2.11
Poly(MMA-co-stabilizer **4a**)	76	1.98
Poly(MMA-co-stabilizer **4b**)	74	1.93
Poly(MMA-co-stabilizer **4c**)	75	1.96
Poly(MMA-co-stabilizer **5a**)	70	1.83
Poly(MMA-co-stabilizer **5b**)	69	1.80
Poly(MMA-co-stabilizer **5c**)	69	1.80
Poly(MMA-ter-stabilizers **2** + **4a**)	58	1.51
Poly(MMA-ter-stabilizers **2** + **4b**)	56	1.46
Poly(MMA-ter-stabilizers **2** + **4c**)	57	1.49
Poly(methyl methacrylate)	88	2.30

Table 3
Molecular characteristics of MMA copolymers and terpolymers

Polymer	Before irradiation			After irradiation			
	$(M_n)o \times 10^5$	$(M_w)o \times 10^5$	$(M_w)o/(M_n)o$	$M_n \times 10^5$	$M_w \times 10^5$	M_w/M_n	A
Poly(MMA-co-stabilizers **2**)	1.15	2.21	1.9	0.90	1.83	2.0	0.28
Poly(MMA-co-stabilizers **4a**)	1.06	2.11	2.0	0.86	1.82	2.1	0.23
Poly(MMA-co-stabilizers **4b**)	1.01	2.06	2.0	0.84	1.79	2.1	0.20
Poly(MMA-co-stabilizers **4c**)	0.99	2.01	2.0	0.83	1.76	2.1	0.19
Poly(MMA-co-stabilizers **5a**)	0.93	1.98	2.1	0.86	1.86	2.2	0.08
Poly(MMA-co-stabilizers **5b**)	0.88	1.87	2.1	0.83	1.85	2.2	0.06
Poly(MMA-co-stabilizers **5c**)	0.85	1.83	2.1	0.81	1.82	2.2	0.05
Poly(MMA-ter-stabilizers **2** + **4a**)	0.79	2.03	2.6	0.69	1.96	2.8	0.15
Poly(MMA-ter-stabilizers **2** + **4b**)	0.76	2.02	2.7	0.67	1.94	2.9	0.13
Poly(MMA-ter-stabilizers **2** + **4c**)	0.74	1.98	2.7	0.66	1.89	2.9	0.02
Poly(methyl methacrylate)	1.29	2.37	1.9	0.65	1.93	3.0	0.98

same speed as the monomeric stabilizers did and had the same values of retention factor R_f (Table 1), while the stabilizers in the copolymers and terpolymers, where they should be chemically bound, remained at the start together with the polymer ($R_f = 0$). This indicates the different absorbencies of bound and unbound stabilizers and qualitatively confirms the binding of the stabilizers to the polymer chain [16,17].

The stabilizers influence upon the molecular weight and polydispersity of the polymers was of great interest. The molecular characteristics of the copolymers and terpolymers, determined by GPC, are listed in Table 3. The molecular weight and molecular weight distribution confirmed the formation of high molecular weight polymers. The polymers weight-average and number-average molecular weights are $(M_w)o = (1.83–02.21) \times 10^5$ and $(M_n)o = (0.74–1.15) \times 10^5$, respectively, and those of PMMA are $(M_w)o = 2.37 \times 10^5$ and $(M_n)o = 1.29 \times 10^5$. The polydispersity is in the range of 1.9–2.7 for PMMA based copolymers and terpolymers and 1.9 for PMMA. The polydispersity for the terpolymers is higher (2.6–2.7), compared to the copolymers with stabilizers **2**, **4a**–**c** and **5a**–**c**.

3.2.3. *UV-visible spectroscopy*

Absorption UV-visible spectra of the precipitated polymers were compared with those of the corresponding pure monomeric stabilizers **2**, **4a–c** and **5a–c**. Neither bathochromic nor hypsochromic shifts were observed, which was an indication that there were no changes in the basic chromophore during the polymerization or as a result of its bonding to the polymer chain. That is why, the percentage of the chemically bonded stabilizers (**2**, **4a–c** and **5a–c**) into the polymer chain was determined spectrophotometrically using the method of the calibration curve (Table 4).

As it is seen from Table 4, the content of chemically bonded stabilizers **5a–c** is relatively smaller (70–74%) probably because of the lower activity of the polymerizable group in these compounds or it is bonded mainly in lower molecular weight fractions, which were removed during the precipitation. The reason for such behavior may be the large steric volume of the combined stabilizer molecule. In contrast to compounds **5a–c**, the content of the chemically bonded monomer **2** is higher (89%) in respect to the other monomers, which can be explained in a similar way, i.e. by the smaller steric volume of the piperidine monomers.

Table 4
Spectrophotometric data for copolymers and terpolymers of MMA with stabilizers **2**, **4a**–**c** and **5a**–**c**

Stabilizer	Stabilizer feed		Chemically bonded stabilizer	
	(wt.%)	(mol%)	(%)	(mol) $\times 10^{-3}$
2	1	0.322	89	2.63
4a	1	0.253	81	2.10
4b	1	0.232	82	1.88
4c	1	0.227	83	1.82
5a	1	0.200	70	1.43
5b	1	0.187	72	1.29
5c	1	0.183	74	1.28
2 + **4a**	0.5 + 0.5	0.161 + 0.126 = 0.287	69 + 61	1.11 + 0.77 = 1.88
2 + **4b**	0.5 + 0.5	0.161 + 0.116 = 0.277	70 + 62	1.13 + 0.72 = 1.85
2 + **4c**	0.5 + 0.5	0.161 + 0.114 = 0.275	67 + 65	1.08 + 0.74 = 1.82

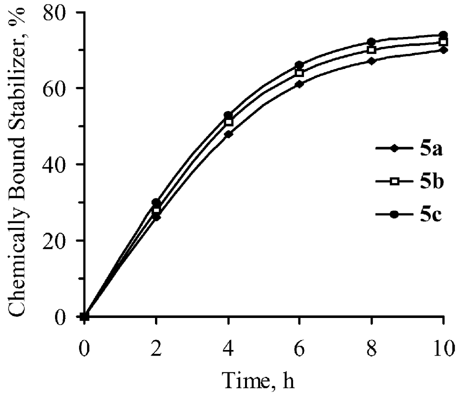


Fig. 1. Dependence of the chemically bonded adducts **5a**–**c** on the time of polymerization.

The kinetics of the bonding of the new adducts **5a**–**c** to the polymer chain is represented in Fig. 1.

3.3. *Photostability of the poly(methyl methacrylate)s*

The influence of the monomeric stabilizers (**2**, **4a**–**c** and **5a**–**c**) upon the photodestruction of PMMA was studied by GPC with prior irradiation of their copolymers and ter-copolymers with MMA in SUNTEST CPS equipment for 10 h. The products' molecular weights M_w and M_n were determined before and after the irradiation and compared to the data for PMMA.

The number of chain breaks per molecule A was calculated by the following equation [18]:

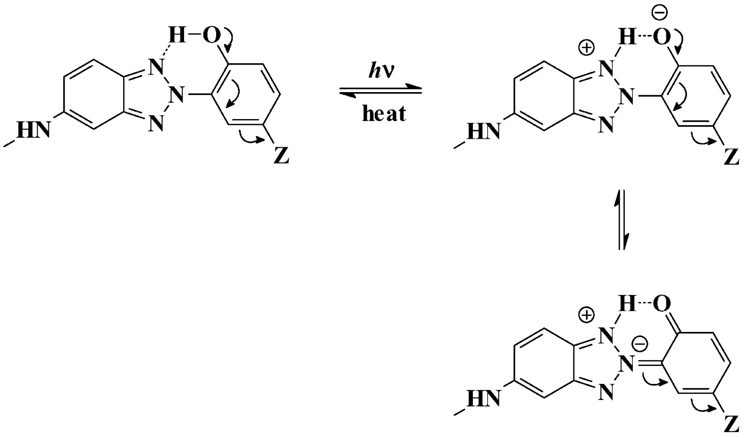
$$A = \frac{(M_n)o}{M_n} - 1$$

where $(M_n)o$ and M_n are the number-average molecular weights before and after irradiation, respectively. The results are listed in Table 3. It is evident that poly(MMA-co-stabilizer) does not significantly changes its polydispersity and molecular weight distribution while the values M_w and M_n for PMMA decrease strongly. The data also show that all stabilizers (**2**, **4** and **5**) considerably improves the polymer stability. The combined stabilizers **5a**–**c** show the best photostabilizing effect among the tested compounds in spite of their lower mole content in the polymer (Table 4), which can be explained by a "synergism" of the two stabilizer fragments different in their action.

The terpolymers exhibit properties similar to those of poly(MMA-co-stabilizer **5a**–**c**)s (A values), but the polymer photostability under the same conditions is relatively lower (Table 3) not withstanding the higher mole stabilizers content in the polymer chain (Table 4). The reason for this could be the unequal distribution of the different stabilizers in the polymer, which leads to decrease in the synergism. These results are in agreement with those, published in our earlier papers [9,10].

It was of interest to study the stabilizer structure–photostabilizing efficiency relationship. On the basis of data obtained (Table 3), it could be assumed that the presence of an electron-deficient substituent at the C-5′ position in the benzotriazole part favors the photostabilizing effect of the whole molecule and this effect is enhanced from chloro (compound **5b**) towards nitro group (compound **5c**). It could be explained by the increased ability of the hydroxyl group to form intermolecular hydrogen bond and stabilizing the formed quinoid benzotriazole structure (Scheme 4). On the other hand, the effect of the *N*-substitution of the piperidine moiety is just the opposite probably because of the reduced ability of the piperidine nitrogen to form *N*-oxil radicals [2]. The data showed (Table 3) that the photostabilizing efficiency of both the piperidine monomer **2** and the stabilizers **5a**–**c** is relatively lower in comparison with other *N*-free analogues [10].

In order to make a precise evaluation on the structure–activity relationship, investigations on a wider range of structures are necessary, which will be the subject of future study.



Scheme 4. Tautomerism of 2-hydroxyphenylbenzotriazole.

4. Conclusions

As a result of our investigations, it can be concluded that the synthesized new adducts—a combination of two stabilizers, different in their action, are capable of copolymerizing with MMA and shows a good stabilizing effect to PMMA. It was established that the presence of both 2,2,6,6-tetramethylpiperidine and 2-hydroxyphenylbenzotriazole fragments together in the polymer significantly improved its photostability. Moreover, the presence of an electron-deficient substituent at the C-5′ position in the benzotriazole part enhances the photostabilizing efficiency of the whole combined molecule. However, the photostabilizing effect of the combined stabilizers is better than that of the mechanical mixture of the same stabilizers as individual monomers most probably because of the equimolecular ratio of the two different stabilizer fragments in the polymer chain.

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