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Synthesis of novel bifunctional polymer stabilizers—A combination of HALS and UV absorber

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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. Six combined polymerizable stabilizers, containing one or two allyl groups, as well as two unsaturated allyloxy-[1,3,5]triazinyl-2,2,6,6-tetramethylpiperidines and three unsaturated allyloxy-[1,3,5]triazinyl-2-hydroxyphenylbenzotriazoles as individual stabilizers were synthesized. Their copolymers and the corresponding terpolymers of the individual stabilizers with methyl methacrylate 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 molecular weight and the polydispersity of the copolymers. A significant stabilizing effect against photodegradation was determined. Polymerizable stabilizers, containing two different unsaturated groups in their molecule, showed considerably higher photostabilizing efficiency towards the compounds containing only one allyl group.

Keywords: Bifunctional polymerizable stabilizers; 2,2,6,6-Tetramethylpiperidines; 2-(2-Hydroxyphenyl)-benzotriazoles; Phase transfer catalysis; Copolymerization; Photostability

1. Introduction

Polymeric materials exposed to sunlight undergo degradation which shortens their service life, mainly by a sequence of photo-oxidation [1]. There are several ways to combat photo-oxidation in polymers. The addition of lightstabilizers is most convenient and effective. Among them, both 2-hydroxyphenylbenzotriazole and 2,2,6,6-tetramethylpiperidine derivatives are of a great interest due to their high photostabilizing efficiency. These two derivative groups, however, differ from each other in their action, no matter that both of them belong to the photodegradation stabilizers. 2,2,6,6-Tetramethylpiperidines inhibit the processes of autoxidation [2]. They form nitroxyl radicals either by reaction with peroxy radicals or occasionally by reaction with singlet oxygen. The nitroxyl radicals stop oxidative degradation by coupling of alkyl radicals [3]. In contrast to 2,2,6,6-tetramethylpiperidines, 2-hydroxyphenylbenzotriazoles prove to be UV-absorbers. They are transparent to visible light and are supposed to dissipate the absorbed energy in a harmless manner, i.e. to convert the absorbed photon energy into heat without being chemically affected [4]. If 2,2,6,6-tetramethylpiperidine and the 2-hydroxyphenylbenzotriazole fragments are combined through an *s*-triazine ring in one molecule this 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 the latter capability of covalent bonding to the polymer chain by copolymerization with different monomers. The covalent bonding to the polymer chain provides stability towards solvents and a migration stabilizing effect [5].

In previous papers the synthesis and application of polymerizable triazinylaminobenzotriazoles [6] and triazinyl-2,2,6,6-tetramethylpiperidines [7,8] as stabilizers for polymer materials and their influence on the rate of copolymerization and on the photostability of the styrene copolymers were described. Recently, a number of papers devoted to problem of synthesis of combined stabilizers containing fragments able to act according to different stabilizing mechanisms have been published. Thus,

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the hindered amine fragments have been combined with either 2-hydroxybenzophenone [9,10] or 2-hydroxyphenylbenzotriazole UV absorbers [11–13] as well as with 2-(*t*-Bu)phenol [14].

In this paper, the synthesis of novel polymerizable bifunctional 2,2,6,6-tetramethylpiperidine–2-hydroxyphenylbenzotriazole [1,3,5]triazine derivatives, containing one or two polymerizable groups, and their potential for photostabilization of poly(methyl methacrylate) (PMMA) have been studied.

2. Experimental

2.1. Materials

2,4-Dichloro-6-(2,2,6,6-tetramethyl-piperidin-1-yl)-[1,3,5] triazine (**2a**), 2-allyloxy-4-chloro-6-(2,2,6,6-tetramethyl-piperidin-1-yl)-[1,3,5]triazine (**3a**), 2-(5-amino-benzotriazol-2-yl)-4-Z-phenols (**4a-c**), 2-[5-(4-allyloxy-6-chloro-[1,3,5]triazin-2-ylamino)-benzotriazol-2-yl]-4-Z-phenol (**5a-c**) and 2-{5-[4-allyloxy-6-(2,2,6,6-tetramethyl-piperidin-1-yl)-[1,3,5]triazin-2-ylamino]-benzotriazol-2-yl}-4-Z-phenol (**6a-c**) were synthesized and purified as before [6,11,13,15]. 2,2,6,6-Tetramethylpiperidin-4-ol, 2,2,6,6-tetramethylpiperidine **1a**, allyl alcohol, allyl bromide, cyanuric chloride and triethylbenzylammonium chloride (TEBA) (Fluka products), p.a. grade, were used without purification. Commercial methyl methacrylate (MMA) was used after distillation under reduced pressure in a nitrogen (99.9%) atmosphere. Dibenzoyl peroxide (DBP, Fluka, 99.6%) recrystallized from chloroform was used as an initiator of the free-radical copolymerization. The solvents used were of p.a. or spectrophotometric grade.

2.2. Methods

The NMR spectra were recorded on a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for ^{1}H and ^{13}C, respectively, using a dual 5 mm probe head. The measurements were carried out in DMSO-d_6 solution at ambient temperature. The chemical shifts (given as δ in ppm) were referenced to tetramethylsilane (TMS) standard. Experiments with 30° pulses, 1 s relaxation delays, 16K time domain points, zero-filled to 64 K for protons and 32K for carbons were performed. The distortionless enhancement by polarization transfer (DEPT) spectra were recorded under the conditions used for the ^{13}C NMR spectra at $\tau = (2^{1}J_{CH})^{-1} = 3.45$ μs. The 2D ^{1}H/^{1}H correlated spectra (COSY) were performed with spectral width 2200 Hz, relaxation delay 2 s, number of increments 512, size 1 K × 1 K. The 2D ^{1}H/^{13}C heteronuclear multiple quantum coherence (HMQC) experiments were carried out with a spectral width of 2200 Hz for ^{1}H and 9000 Hz for ^{13}C, relaxation delay 1.5 s, FT size 1 K × 256 W. Electronic spectra were recorded at room temperature on a Varian Cary-50 UV–vis spectrophotometer at a concentration 10^{-4} mol dm^{-3} in chloroform. 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 Å, 1000 Å, linear Ultrastyragel columns; the solvent was THF at a flow rate of 1.0 cm^{3} 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 piperidine–2-hydroxyphenylbenzotriazole stabilizers (*6d-f*)

To a solution of 2-(5-amino-benzotriazol-2-yl)-4-Z-phenol **4a-c** (0.01 mol) in 60 ml of glacial acetic acid were added 1.5 g (0.01 mol) of sodium acetate and 3.67 g (0.01 mol) of 2-allyloxy-4-(4-allyloxy-2,2,6,6-tetramethyl-piperidin-1-yl)-6-chloro-[1,3,5]triazine (**3b**). The resulting mixture was stirred at 120 °C for 2 h. The crude product that precipitated on cooling was filtered off and then dried. Two-fold recrystallization from acetic acid afforded pure target combined stabilizers **6d-f** as pale yellow crystals.

*2.3.1.1. 2-{5-[4-Allyloxy-6-(4-allyloxy-2,2,6,6-tetramethyl-piperidin-1-yl)-[1,3,5]triazin-2-ylamino]-benzotriazol-2-yl}-phenol (**6d**).* ^{1}H NMR (DMSO-d_6, 250.13 MHz) δ (ppm): 10.78 (s, 1H, OH); 8.51 (dd, 1H, J = 8.4 Hz, J = 1.2 Hz, benzotriazole 7-H); 8.06 (d, 1H, J = 8.9 Hz, phenyl 6-H); 7.92 (d, 1H, J = 1.2 Hz, benzotriazole 4-H); 7.42 (m, 2H, benzotriazole 6-H and phenyl 4-H); 7.14 (d, 1H, J = 8.9 Hz, phenyl 3-H); 7.03 (td, 1H, J = 8.9 Hz, J = 1.1 Hz, phenyl 5-H); 6.14 (m, 1H, triazine allyl CH=); 5.98 (m, 1H, piperidine allyl CH=); 5.52 (dd, 1H, J_{trans} = 17.3 Hz, J = 1.4 Hz, triazine allyl HCH=); 5.38 (dd, 1H, J_{cis} = 10.4 Hz, J = 1.4 Hz, triazine allyl HCH=); 5.29 (d, 1H, J_{trans} = 17.0 Hz, piperidine allyl HCH=); 5.17 (d, 1H, J_{cis} = 10.3 Hz, piperidine allyl HCH=); 4.94 (dd, 2H, J = 4.9 Hz, J = 1.4 Hz, triazine allyl OCH_2); 4.84 (d, 2H, J = 4.0 Hz, piperidine allyl OCH_2); 4.31 (m, 1H, piperidine CH); 2.09 (dd, 2H, J = 11.5 Hz, J = 3.7 Hz, piperidine CH_2); 1.90 (br s, 1H, NH); 1.52 (td, 2H, J = 11.5 Hz, J = 3.7 Hz, piperidine CH_2); 1.21 (s, 6H, piperidine 2 × CH_3); 1.05 (s, 6H, piperidine 2 × CH_3).

^{13}C NMR (DMSO-d_6, 62.90 MHz) δ (ppm): 188.2 (triazine O–C=N), 180.1 (triazine NH–C=N), 175.4 (triazine N–C=N), 154.2 (phenyl 2-C), 143.6 (benzotriazole 5-C), 136.5 (triazine allyl CH=), 133.8 (piperidine allyl CH=), 132.4-116.3 (Ar–C), 114.1 (triazine allyl =CH_2), 113.5 (piperidine allyl =CH_2), 72.9 (triazine allyl OCH_2), 70.6 (piperidine allyl OCH_2), 60.3 (piperidine CH), 43.7 (piperidine 2 × CH_2), 42.1 (piperidine 2 × C), 28.2-27.0 (piperidine 4 × CH_3).

Elemental analysis: Calculated for $C_{30}H_{36}N_8O_3$ (556.66) C 64.73, H 6.52, N 20.13%; Found C 64.89, H 6.60, N 20.24%.

*2.3.1.2. 2-{5-[4-Allyloxy-6-(4-allyloxy-2,2,6,6-tetramethyl-piperidin-1-yl)-[1,3,5]triazin-2-ylamino]-benzotriazol-2-yl}-4-chloro-phenol (**6e**).* ^{1}H NMR (DMSO-d_6, 250.13 MHz) δ (ppm): 10.69 (s, 1H, OH); 8.60 (d, 1H, J = 8.1 Hz, benzotriazole 7-H); 8.48 (d, 1H, J = 1.4 Hz, phenyl 6-H); 8.22 (d, 1H, J = 9.0 Hz, phenyl 4-H); 8.08 (d, 1H, J = 2.5 Hz, benzotriazole 4-H); 7.49 (d, 1H, J = 8.1 Hz, benzotriazole 6-H); 7.26 (d, 1H,

J = 9.0 Hz, phenyl 3-H); 6.19 (m, 1H, triazine allyl CH=); 6.02 (m, 1H, piperidine allyl CH=); 5.49 (dd, 1H, J_{trans} = 17.4 Hz, J = 1.6 Hz, triazine allyl HCH=); 5.40 (dd, 1H, J_{cis} = 10.6 Hz, J = 1.6 Hz, triazine allyl HCH=); 5.22 (d, 1H, J_{trans} = 17.2 Hz, piperidine allyl HCH=); 5.15 (d, 1H, J_{cis} = 10.2 Hz, piperidine allyl HCH=); 4.90 (dd, 2H, J = 5.2 Hz, J = 1.4 Hz, triazine allyl OCH_2); 4.79 (d, 2H, J = 4.6 Hz, piperidine allyl OCH_2); 4.31 (m, 1H, piperidine CH); 2.15 (dd, 2H, J = 11.6 Hz, J = 4.0 Hz, piperidine CH_2); 1.84 (br s, 1H, NH); 1.49 (td, 2H, J = 11.6 Hz, J = 4.0 Hz, piperidine CH_2); 1.23 (s, 6H, piperidine 2 × CH_3); 1.08 (s, 6H, piperidine 2 × CH_3).

^{13}C NMR (DMSO-d_6, 62.90 MHz) δ (ppm): 187.3 (triazine O–C=N), 179.6 (triazine NH–C=N), 174.1 (triazine N–C=N), 158.1 (phenyl 2-C), 145.5 (benzotriazole 5-C), 137.1 (triazine allyl CH=), 134.2 (piperidine allyl CH=), 133.7-118.1 (Ar–C), 116.4 (triazine allyl =CH_2), 114.1 (piperidine allyl =CH_2), 73.0 (triazine allyl OCH_2), 69.7 (piperidine allyl OCH_2), 60.8 (piperidine CH), 44.2 (piperidine 2 × CH_2), 41.9 (piperidine 2 × C), 26.8-25.9 (piperidine 4 × CH_3).

Elemental analysis: Calculated for $C_{30}H_{35}ClN_8O_3$ (591.10) C 60.96, H 5.97, N 18.96%; Found C 60.81, H 6.04, N 19.05%.

*2.3.1.3. 2-{5-[4-Allyloxy-6-(4-allyloxy-2,2,6,6-tetramethyl-piperidin-1-yl)-[1,3,5]triazin-2-ylamino]-benzotriazol-2-yl}-4-nitro-phenol (**6f**).* ^{1}H NMR (DMSO-d_6, 250.13 MHz) δ (ppm): 10.72 (s, 1H, OH); 8.62 (d, 1H, J = 1.5 Hz, phenyl 6-H); 8.57 (d, 1H, J = 8.6 Hz, benzotriazole 7-H); 8.31 (d, 1H, J = 9.1 Hz, phenyl 4-H); 7.88 (d, 1H, J = 1.9 Hz, benzotriazole 4-H); 7.53 (d, 1H, J = 8.6 Hz, benzotriazole 6-H); 7.40 (d, 1H, J = 9.1 Hz, phenyl 3-H); 6.21 (m, 1H, triazine allyl CH=); 6.06 (m, 1H, piperidine allyl CH=); 5.50 (dd, 1H, J_{trans} = 17.1 Hz, J = 1.8 Hz, triazine allyl HCH=); 5.39 (dd, 1H, J_{cis} = 10.3 Hz, J = 1.8 Hz, triazine allyl HCH=); 5.23 (d, 1H, J_{trans} = 17.0 Hz, piperidine allyl HCH=); 5.18 (d, 1H, J_{cis} = 10.4 Hz, piperidine allyl HCH=); 4.92 (dd, 2H, J = 5.0 Hz, J = 1.2 Hz, triazine allyl OCH_2); 4.80 (d, 2H, J = 4.8 Hz, piperidine allyl OCH_2); 4.28 (m, 1H, piperidine CH); 2.21 (dd, 2H, J = 11.2 Hz, J = 4.2 Hz, piperidine CH_2); 2.05 (br s, 1H, NH); 1.52 (td, 2H, J = 11.2 Hz, J = 4.2 Hz, piperidine CH_2); 1.27 (s, 6H, piperidine 2 × CH_3); 1.11 (s, 6H, piperidine 2 × CH_3).

^{13}C NMR (DMSO-d_6, 62.90 MHz) δ (ppm): 188.5 (triazine O–C=N), 182.6 (triazine NH–C=N), 178.3 (triazine N–C=N), 167.2 (phenyl 2-C), 153.6 (phenyl 5-C), 146.1 (benzotriazole 5-C), 139.2 (triazine allyl CH=), 135.9 (piperidine allyl CH=), 135.4-119.5 (Ar–C), 115.9 (triazine allyl =CH_2), 114.3 (piperidine allyl =CH_2), 74.7 (triazine allyl OCH_2), 70.4 (piperidine allyl OCH_2), 59.5 (piperidine CH), 42.9 (piperidine 2 × CH_2), 41.2 (piperidine 2 × C), 27.9-26.3 (piperidine 4 × CH_3).

Elemental analysis: Calculated for $C_{30}H_{35}N_9O_5$ (601.66) C 59.89, H 5.86, N 20.95%; Found C 60.07, H 5.80, N 20.86%.

*2.3.2. Synthesis of allyloxytriazinylpiperidine (**3b**)*

A solution of 4-allyloxy-2,2,6,6-tetramethylpiperidine **1b** (7.9 g, 0.04 mol) and cyanuric chloride (3.7 g, 0.02 mol) in 20 ml of toluene was refluxed for 10 h then cooled to room temperature and the solid precipitate was filtered off. The crude product was isolated from the yellow filtrate after washing with water, drying over anhydrous sodium sulfate and evaporating in vacuum. Recrystallization from ethanol gave the pure 2-(4-allyloxy-2,2,6,6-tetramethylpiperidine-1-yl)-4,6-dichloro-1,3,5-triazine **2b** as white needles. A solution of an intermediate **2b** (5.18 g, 0.015 mol) in benzene (40 ml) was added dropwise under vigorous stirring at room temperature to a mixture of allyl alcohol (0.87 g, d = 0.854, 0.015 mol), sodium hydroxide as a 50% aqueous solution (10 ml), TEBA (0.17 g, 0.00075 mol, 5 mol.%) and benzene (20 ml) over a period of 15 min. After 25 min stirring under the same conditions, the organic layer was separated, washed with water and dried over anhydrous sodium sulfate. Then the target 2-allyloxy-4-(4-allyloxy-2,2,6,6-tetramethyl-piperidin-1-yl)-6-chloro-[1,3,5]triazine **3b** was isolated as colorless crystals after evaporation of the benzene in vacuum.

^{1}H NMR (DMSO-d_6, 250.13 MHz) δ (ppm): 6.20 (m, 1H, triazine allyl CH=); 5.92 (m, 1H, piperidine allyl CH=); 5.57 (d, 1H, J_{trans} = 17.4 Hz, triazine allyl HCH=); 5.46 (d, 1H, J_{cis} = 10.5 Hz, triazine allyl HCH=); 5.28 (d, 1H, J_{trans} = 17.1 Hz, piperidine allyl HCH=); 5.19 (d, 1H, J_{cis} = 10.2 Hz, piperidine allyl HCH=); 4.92 (d, 2H, J = 4.2 Hz, triazine allyl OCH_2); 4.80 (d, 2H, J = 3.8 Hz, piperidine allyl OCH_2); 3.88 (m, 1H, piperidine CH); 1.96 (td, 2H, J = 11.8 Hz, J = 3.4 Hz, piperidine CH_2); 1.32 (dd, 2H, J = 11.8 Hz, J = 3.4 Hz, piperidine CH_2); 1.14 (s, 12H, piperidine 4 × CH_3).

Elemental analysis: Calculated for $C_{18}H_{27}ClN_4O_2$ (366.89) C 58.93, H 7.42, N 15.27%; Found C 58.71, H 7.37, N 15.35%.

*2.3.3. Synthesis of 4-allyloxy-2,2,6,6-tetramethylpiperidine (**1b**)*

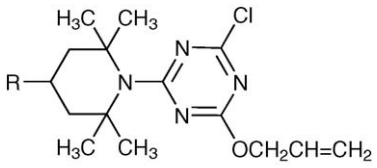
Allylbromide (6.05 g, d = 1.398, 0.05 mol) dissolved in dichloromethane (10 ml) was added dropwise to a mixture of 2,2,6,6-tetramethylpiperidin-4-ol (7.85 g, 0.05 mol) dichloromethane solution (100 ml), 50% hydrous sodium hydroxide solution (30 ml) and TEBA (1.13 g, 0.005 mol, 10 mol.%) under vigorous stirring. The resulting mixture was stirred for 4 h at room temperature and then diluted in 80 ml of water. Organic layer was separated, washed with water, dried over anhydrous sodium sulfate and evaporated in vacuum to give pure 4-allyloxy-2,2,6,6-tetramethylpiperidine **1b** as pale yellow oil in almost quantitative yield.

^{1}H NMR (DMSO-d_6, 250.13 MHz) δ (ppm): 5.88 (m, 1H, allyl CH=); 5.26 (d, 1H, J_{trans} = 17.2 Hz, allyl HCH=); 5.15 (d, 1H, J_{cis} = 10.4 Hz, allyl HCH=); 4.84 (d, 2H, J = 4.1 Hz, allyl OCH_2); 4.16 (m, 1H, piperidine CH); 2.32 (td, 2H, J = 12.0 Hz, J = 3.9 Hz, piperidine CH_2); 1.78 (br s, 1H, piperidine NH); 1.64 (dd, 2H, J = 12.0 Hz, J = 3.9 Hz, piperidine CH_2); 1.26 (s, 6H, piperidine 2 × CH_3); 1.02 (s, 6H, piperidine 2 × CH_3).

Elemental analysis: Calculated for $C_{12}H_{23}NO$ (197.32) C 73.04, H 11.75, N 7.10%; Found C 72.78, H 11.82, N 7.06%.

2.4. Synthesis of polymers

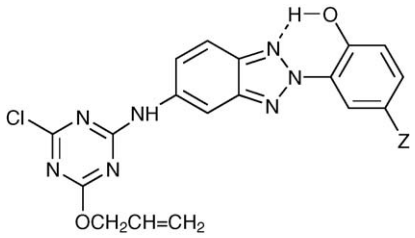
The free-radical copolymerization and terpolymerization of the monomeric stabilizers **3a-b**, **5a-c** and **6a-f** with MMA was carried out in ampoules previously purged with pure dry nitrogen [16]. The processes of copolymerization and terpolymerization



3a-b

R = H (**3a**) , R = CH_2=$CHCH_2O$ (**3b**)

Scheme 1. Polymerizable allyloxy-[1,3,5]triazinylpiperidines **3a-b**.



5a-c

Z = H (**5a**) , Z = Cl (**5b**) , Z = NO_2 (**5c**)

Scheme 2. Polymerizable allyloxy-[1,3,5]triazinyl-2-hydroxyphenylbenzotriazoles **5a–c**.

of MMA were conducted in a thermostat for 10 h at 70 °C in the presence of 1.0 wt.% of DBP and 0.5 wt.% of the corresponding monomeric stabilizer (**3a-b**, **5a-c** or **6a-f**) as well as a mixture of stabilizers **3a-b** and **5a-c** (each with the concentration of 0.25 wt.%). The side-chain transparent, solid and colorless copolymers and terpolymers thus obtained were reprecipitated several times with methanol from chloroform in order to remove the non-interacted monomers. This process was controlled by TLC until the filtrates were free of monomers **3**, **5** or **6**. The precipitated copolymers poly(MMA-co-**3**, **5** or **6**) and terpolymers poly(MMA-ter-**3** + **5**) were repeatedly washed with methanol and dried in vacuum to constant weight at 40 °C. All measurements for the characterization and the investigation were carried out with precipitated copolymers and terpolymers.

2.5. Photodestruction of the polymers

The solid polymeric films were irradiated in a solar simulator (Suntest CPS+, HERAEUS), equipped with a 1.5 kW xenon arc lamp, protected with an adequate filter to simulate the solar spectrum between 290 and 800 nm. The experiments were performed in air at 45 °C. The photodegradation was followed by the changes of the polymer molecular weights 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 which two different types of stabilizers are combined into one molecule.

To address point (1), two polymerizable hindered piperidine-type stabilizers **3a-b** (Scheme 1), which inhibit the processes of autoxidation [17] have been synthesized. The compound **3a** was synthesized as before [7].

Among the other types of stabilizers, on the basis of our earlier investigations, three polymerizable 2-hydroxyphenylbenzotriazole stabilizers **5a-c** (Scheme 2) known to be UV-absorbers [4,18] have been synthesized. These compounds were obtained as described before [13].

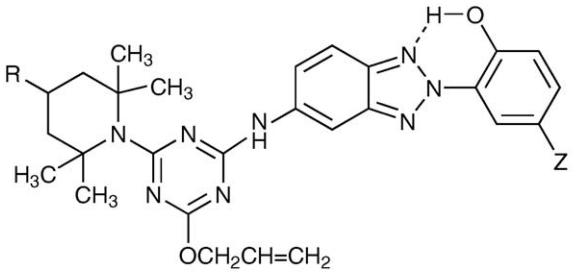
In order to address point (2) monomers **6a-f** in which the hindered piperidine and 2-hydroxyphenylbenzotriazole fragments are combined through an *s*-triazine ring into one molecule, containing one or two polymerizable allyloxy groups, have been synthesized (Scheme 3).

To receive a more complete comparative picture allyloxy-[1,3,5]triazinyl-2-hydroxyphenylbenzotriazoles **6a-c** (containing one polymerizable allyl group), synthesized as described before [11], were involved in the present study.

3.1. Synthesis of stabilizers

The combined stabilizers **6a-f** were synthesized by replacement of the *s*-triazine chlorine atom in the polymerizable triazinyl-piperidines **3a-b** with the primary amino group of the 2-hydroxyphenylbenzotriazoles **4a-c** as presented in Scheme 4. The reaction of allyloxy-[1,3,5]triazinylpiperidines **3a-b** with 2-(2′-hydroxyphenyl)-5-aminobenzotriazoles **4a-c** for obtaining the target stabilizers **6a-f** was conducted in boiling glacial acetic acid medium in the presence of anhydrous sodium acetate.

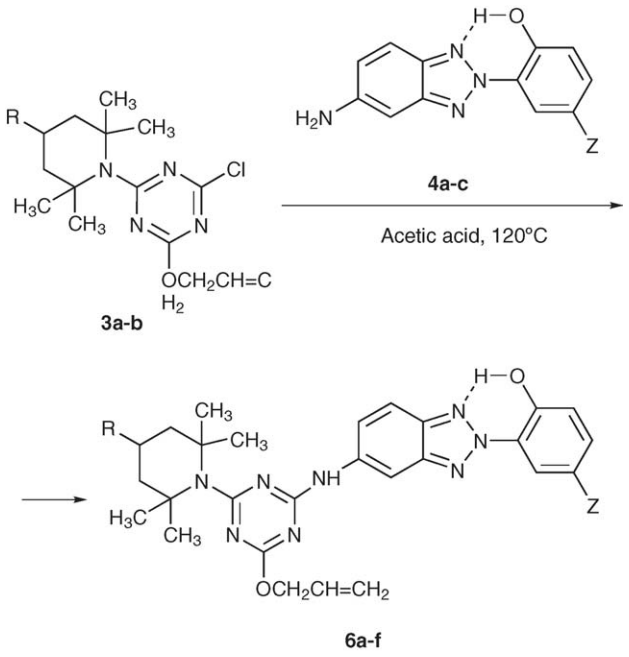
The monomers **3a-b** were synthesized by consecutive nucleophilic substitutions of two chlorine atoms of the cyanuric chloride, first with hindered amines **1a-b** by a method described



6a-f

R = Z = H (**6a**)
R = H , Z = Cl (**6b**)
R = H , Z = NO_2 (**6c**)
R = CH_2=$CHCH_2O$, Z = H (**6d**)
R = CH_2=$CHCH_2O$, Z = Cl (**6e**)
R = CH_2=$CHCH_2O$, Z = NO_2 (**6f**)

Scheme 3. Combined 2,2,6,6-tetramethylpiperidine–2-hydroxyphenylbenzotriazole stabilizers **6a–f**.

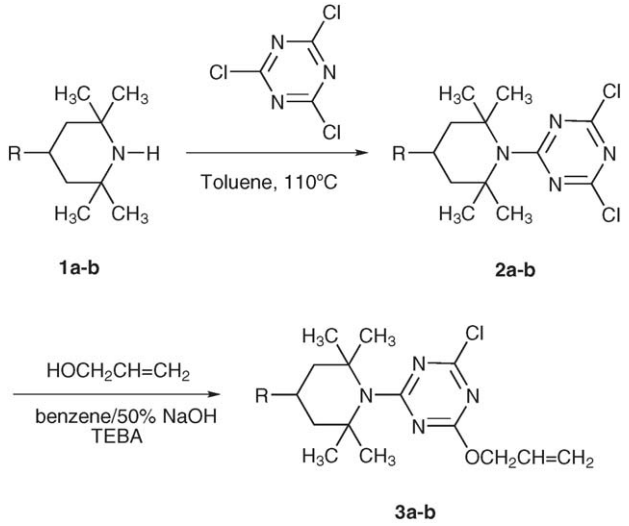


Scheme 4. Synthesis of combined 2,2,6,6-tetramethylpiperidine–2-hydroxyphenylbenzotriazole stabilizers **6a-f**.

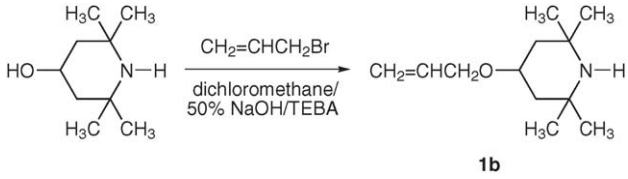
before [7] and then with allyl alcohol under phase transfer catalysis (PTC) conditions (Scheme 5).

The second step was performed in 50% aqueous sodium hydroxide solution/benzene two-phase system at room temperature in the presence of triethylbenzylammonium chloride (TEBA). The selection of favorable PTC conditions was very important for effective synthesis. Both the correct choice of the two-phase system and the solubility of the initial and final products in the water-immiscible organic solvents governed this selection.

The starting 2,2,6,6-tetramethylpiperidin-4-allyloxy **1b** was synthesized also under PTC conditions by alkylation of the hydroxyl group of the commercially available 2,2,6,6-



Scheme 5. Synthesis of allyloxy-[1,3,5]triazinylpiperidines **3a-b**.



Scheme 6. Synthesis of 4-allyloxy-2,2,6,6-tetramethylpiperidine **1b**.

Table 1
Yields and characteristic data obtained for the novel 4-allyloxy-2,2,6,6-tetramethylpiperidine **1b**, intermediate **2b**, monomer **3b** and combined stabilizers **6d-f**

Compound	Yield (%)	MP (°C)	R_f	λ_A (nm)	log ε (dm^3 mol^{-1} cm^{-1})
1b	99	–	0.61	278[a]	4.498
2b	79	133–137	0.57	274[a]	4.430
3b	97	66–68	0.53	278[a]	4.518
6d	73	201–203	0.19	340[b]	4.161
6e	69	172–174	0.21	346[b]	4.170
6f	70	183–185	0.24	352[b]	4.149

[a] Absorption maxima for HALS fragments.
[b] Absorption maxima for UV absorber fragments.

tetramethylpiperidin-4-ol with allylbromide (Scheme 6). The reaction was conducted in a dichloromethane/50% aq. sodium hydroxide two-phase system at room temperature in the presence of TEBA.

The synthesis was monitored by TLC on silica gel and the new compounds **1b**, **3b** and **6d-f** were characterized by their melting points, TLC R_f values and UV–vis spectra (Table 1) and identified by elemental analyses, ^{1}H- and ^{13}C NMR spectra.

The influence of the C-5 phenyl substituent on the absorption properties of the 2-(2-hydroxyphenyl)-benzotriazoles **4a-c** can be seen in their UV–vis spectra presented in Fig. 1. The absorption maximum of the benzotriazole **4a** (λ_A = 364 nm) is 6 and 14 nm hypsochromically shifted than those of benzotriazoles **4b** (λ_A = 370 nm) and 4c (λ_A = 378 nm), respectively. This may be related to the decreased electron density on the phenyl oxygen for compounds **4b** and **4c**, containing an electron-deficient

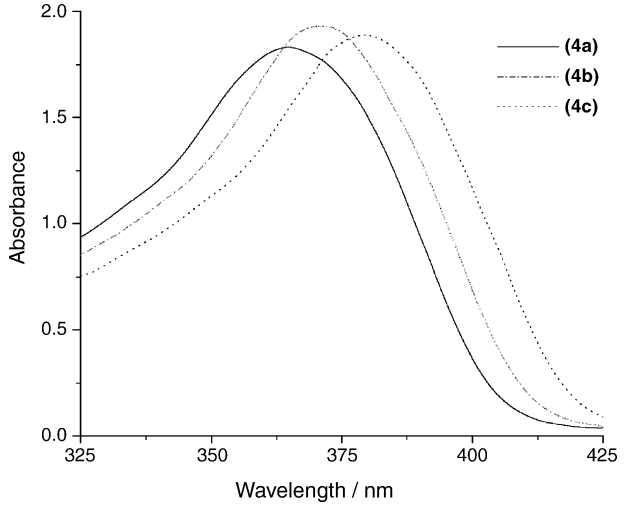


Fig. 1. Absorption spectra of 2-hydroxyphenylbenzotriazoles **4a-c**.

Table 2
Spectrophotometric data for copolymers and terpolymers of MMA with stabilizers **3a-b**, **5a-c** and **6a-f**

Polymer	λ_A (nm)	Stabilizer feed		Chemically bonded stabilizer[a]	
		wt.%	mol 10^3	wt.%	mol 10^3
poly(MMA-co-**3a**)	280	0.5	1.61	0.81	1.30
poly(MMA-co-**3b**)	280	0.5	1.36	0.87	1.19
poly(MMA-co-**5a**)	344	0.5	1.39	0.75	0.95
poly(MMA-co-**5b**)	348	0.5	1.16	0.74	0.86
poly(MMA-co-**5c**)	352	0.5	1.13	0.76	0.86
poly(MMA-co-**6a**)	342	0.5	1.00	0.71	0.71
poly(MMA-co-**6b**)	348	0.5	0.93	0.70	0.65
poly(MMA-co-**6c**)	354	0.5	0.92	0.69	0.63
poly(MMA-co-**6d**)	340	0.5	0.90	0.81	0.73
poly(MMA-co-**6e**)	346	0.5	0.85	0.79	0.67
poly(MMA-co-**6f**)	350	0.5	0.81	0.80	0.66
poly(MMA-ter-**3a + 5a**)	282, 340	0.25 + 0.25	0.80 + 0.63	0.61 + 0.55	0.49 + 0.55 = 0.84
poly(MMA-ter-**3a + 5b**)	280, 346	0.25 + 0.25	0.80 + 0.58	0.62 + 0.53	0.50 + 0.31 = 0.81
poly(MMA-ter-**3a + 5c**)	280, 350	0.25 + 0.25	0.80 + 0.57	0.60 + 0.56	0.48 + 0.32 = 0.80
poly(MMA-ter-**3b + 5a**)	278, 340	0.25 + 0.25	0.68 + 0.63	0.69 + 0.54	0.47 + 0.34 = 0.81
poly(MMA-ter-**3b + 5b**)	282, 344	0.25 + 0.25	0.68 + 0.58	0.68 + 0.50	0.46 + 0.29 = 0.75
poly(MMA-ter-**3b + 5c**)	280, 348	0.25 + 0.25	0.68 + 0.57	0.70 + 0.52	0.48 + 0.29 = 0.77
PMMA					

[a] Chemically bonded stabilizer per 100 g of the polymer.

substituent, which favors the intramolecular hydrogen bond formation by stabilization of the protonated benzotriazole form. It can be assumed that the electron-accepting group at the phenyl C-5 position shifts the benzotriazole absorption maximum at the long wavelength and the effect is enhanced with the increasing the electron-withdrawing ability of the substituent.

The electron-donating primary amino group situated in the benzotriazole moiety (**4a-c**) as well as the electron-accepting substituent at the phenyl C-5 position favors the intramolecular hydrogen bond formation. That is why, after acylation with [1,3,5]triazinylpiperidines **3a-b**, the electron-donating ability of the amino group decreases strongly and the benzotriazole absorption of the final compounds **6a-f** are shifted hypsochromically (Table 1) [11,13].

3.2. Polymer investigations

The applicability of the new combined compounds for stabilization of polymers was examined on the basis of their ability to copolymerize with MMA. The free-radical polymerization of MMA in the presence of the stabilizers **3a-b**, **5a-c** and **6a-f** was investigated under conditions described before [16]. Transparent fluorescent copolymers and terpolymers have been obtained. The presence of a covalent bond between the monomeric stabilizer units and the polymer chain has been proved by TLC and GPC techniques [13].

The UV–vis absorption spectra of the copolymers showed similar absorption maxima as those of the monomers 3, 5 and 6 (Table 2). This is an indication that no changes occurred in their chromophoric systems, neither during the polymerization, nor as a result of their incorporation to the polymer chain. That is why the method of the standard curve was used for spectrophotometric determination the content of a chemically bound monomer in the polymer (Table 2).

As it is seen (Table 2) the content of a chemically bonded stabilizer **6a-f** is relatively small probably because of the lower activity of the polymerizable group in these compounds or it is bonded mainly in the 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 **6a-f**, the content of chemically bonded monomer **3a-b** is higher 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. On the other hand, the content of the chemically bonded stabilizer in the polymer chain and the polymer yield for compounds **3b** and **6d-f**, containing a second polymerizable group is higher than those for compounds **3a** and **6a-c**, containing only one allyl group. It could be due to the better opportunity of chemical bonding to the polymer chain for compounds containing more than one unsaturated allyl group.

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 $M_{wo} = (1.85–2.52) \times 10^5$ and $M_{no} = (0.73–1.22) \times 10^5$, respectively, and those of PMMA are $M_{wo} = 2.49 \times 10^5$ and $M_{no} = 1.28 \times 10^5$. Some increasing of the copolymers' weight-average molecular weights M_{wo} was observed at the participation of the stabilizers **3b** and **6d-f**, containing two polymerizable allyloxy groups. This can be related to the action of the latter as network agents and as a result of such behavior—to obtaining of the cross-linked polymers.

The polydispersity (M_{wo}/M_{no}) is in the range of 1.9–2.8 for PMMA based copolymers and terpolymers and 1.9 for

Table 3
Molecular characteristics of PMMA, MMA copolymers and terpolymers

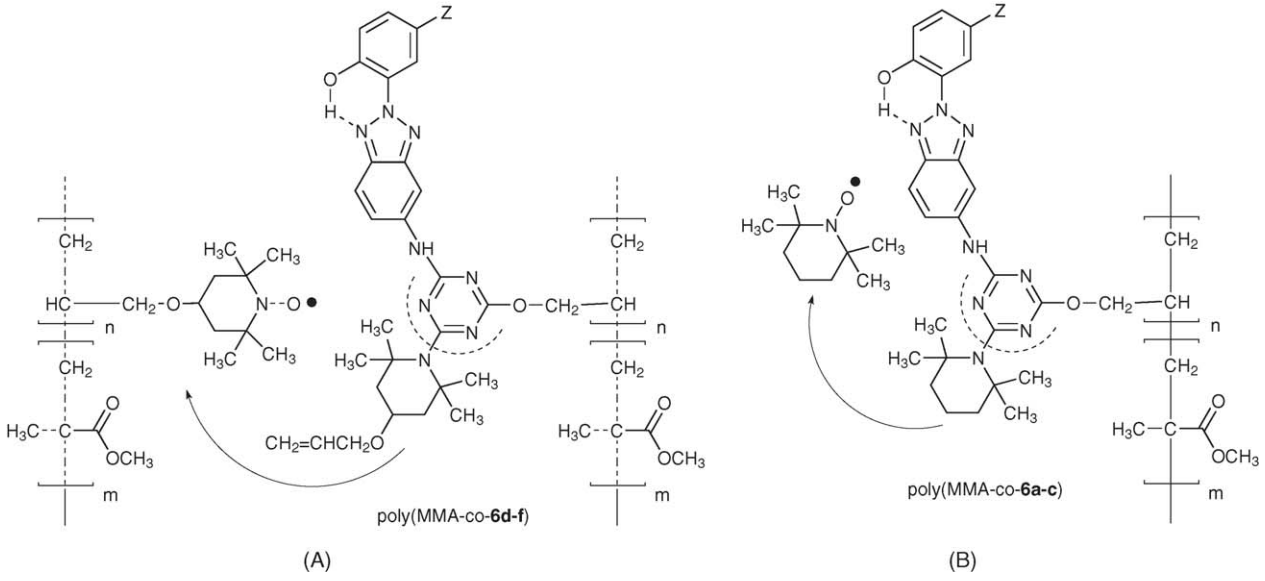
Polymer	Before irradiation			After irradiation			$A = \frac{M_{no}}{M_n} - 1$
	$M_{wo}\ 10^{-5}$	$M_{no}\ 10^{-5}$	M_{wo}/M_{no}	$M_w\ 10^{-5}$	$M_n\ 10^{-5}$	M_w/M_n	
poly(MMA-co-**3a**)	2.24	1.18	1.9	1.82	0.89	2.0	0.326
poly(MMA-co-**3b**)	2.52	1.22	2.1	2.13	0.98	2.2	0.245
poly(MMA-co-**5a**)	2.06	1.05	2.0	1.81	0.86	2.1	0.221
poly(MMA-co-**5b**)	2.01	1.01	2.0	1.77	0.83	2.1	0.217
poly(MMA-co-**5c**)	1.99	0.98	2.0	1.74	0.82	2.1	0.195
poly(MMA-co-**6a**)	1.93	0.91	2.1	1.82	0.83	2.2	0.096
poly(MMA-co-**6b**)	1.87	0.89	2.1	1.80	0.82	2.2	0.085
poly(MMA-co-**6c**)	1.85	0.87	2.1	1.79	0.81	2.2	0.074
poly(MMA-co-**6d**)	2.18	0.97	2.2	2.13	0.92	2.3	0.054
poly(MMA-co-**6e**)	2.15	0.96	2.2	2.11	0.92	2.3	0.043
poly(MMA-co-**6f**)	2.11	0.94	2.2	2.10	0.91	2.3	0.033
poly(MMA-ter-**3a + 5a**)	2.08	0.78	2.7	1.84	0.66	2.8	0.182
poly(MMA-ter-**3a + 5b**)	2.03	0.75	2.7	1.79	0.64	2.8	0.172
poly(MMA-ter-**3a + 5c**)	2.00	0.73	2.7	1.76	0.63	2.8	0.159
poly(MMA-ter-**3b + 5a**)	2.38	0.86	2.8	2.17	0.75	2.9	0.147
poly(MMA-ter-**3b + 5b**)	2.32	0.84	2.8	2.15	0.74	2.9	0.135
poly(MMA-ter-**3b + 5c**)	2.24	0.81	2.8	2.08	0.72	2.9	0.125
PMMA	2.49	1.28	1.9	1.92	0.63	3.0	1.032

PMMA. The polydispersity for the terpolymers is higher (2.6-2.7), compared to the copolymers with stabilizers **3a-b**, **5a-c** and **6a-f**.

3.3. *Photostability of poly(MMA-co-**3**,**5**,**6**), poly(MMA-ter-**3** + **5**) and PMMA*

The influence of the monomer stabilizers **3**, **5** and **6** upon the photodegradation of PMMA was studied by GPC with prior irradiation of their copolymers with MMA in a SUNTEST CPS equipment for 12 h. The polymer weight-average and number-average molecular weights were determined before and after of irradiation and compared to the data for PMMA.

The data obtained for the chain breaks per a polymer molecule A ($A = M_{no}/M_n - 1$), where M_{no} and M_n are the number-average molecular weights before and after irradiation, respectively [19] (Table 3), demonstrate the very good stabilizing effect of the new compounds. All stabilizers (**3**, **5** and **6**) improve considerably the polymer photostability. The data also show that the photostabilizing efficiency of the 2-hydroxyphenylbenzotriazoles **5a-c** is better than that of the [1,3,5]triazinylpiperidines **3a-b** in spite of their lower mole content in the copolymer chain (Table 2). It could be related to a rapid exited state intramolecular proton transfer (ESIPT) between the phenolic hydroxyl group and the benzotriazole nitrogen when compounds **5a-c** are exited into the benzotriazole absorption band [4,20]. As can be seen the



Scheme 7. Nitroxyl radical formation in poly(MMD-co-**6d-f**) and poly(MMA-co-**6a-c**).

photostabilizing efficiency of the benzotriazoles **5a-c** increase with the enhancement of the electron-accepting ability of the 5-phenyl substituent (**5c** > **5b** > **5a**), which can be explained with the increased stability of the protonated form in the same order at the ESIPT process.

On the other hand the acylation in the *N*-position of the piperidine moiety, consisting in the reduced ability of the piperidine nitrogen to form *N*-oxyl radicals, leads to lower photostabilizing activity of the [1,3,5]triazinylpiperidines **3a-b**.

The combined stabilizers **6a-f** show the best photostabilizing effect among the tested compounds in spite of their lower content in the polymer, which can be explained with a "synergism" of the two, different in their action, stabilizer fragments.

The photostabilizing efficiency of the piperidine **3b** and the bifunctional stabilizers **6d-f** is substantially higher in comparison with those of the corresponding stabilizers **3a** and **6a-c**, which could be related to the formation of nitroxyl radicals by cleavage of the chemical bond between the piperidine nitrogen and the triazine ring. Thus, the piperidine moiety in compounds **3b** and **6d-f** will remain hold to the polymer chain by the second (piperidine) allyl group (Scheme 7A), while such fixing the rest of the molecule for compounds **3a** and **6a-c** is missing, which leads to lose of the low molecular piperidine fragment (Scheme 7B).

The terpolymers exhibit properties similar to those of poly(MMA-co-stabilizer **6a-f**)s (*A* values), but the polymer photostability under the same conditions is relatively lower. The reason for this could be the unequal distribution of the different stabilizer fragments in the polymer, which leads to decrease in the synergism.

4. Conclusions

As a result of this investigation, it can be assumed that the new compounds – a combination between two stabilizers, different in their action – are capable of copolymerizing with MMA and show high 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. 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. Polymerizable stabilizers, containing two different unsaturated groups in their molecule, showed considerably higher photostabilizing efficiency towards compounds containing only one allyl group.

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