Synthesis and application of new combined 2,2,6,6-tetramethylpiperidine–2-hydroxybenzophenone 1,3,5-triazine derivatives as photostabilizers for polymer materials

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Abstract

The synthesis of new stabilizer type compounds (a combination between 2,2,6,6-tetramethylpiperidine and 2-hydroxybenzophenone in one molecule) under phase transfer catalysis (PTC) conditions is reported. The most favorable reaction conditions (the type of two-phase system, solvent, catalyst) were selected. Two polymerizable combined stabilizers as well as two unsaturated triazinyl-2,2,6,6-tetramethyl-piperidines and an unsaturated triazinyl-2-hydroxybenzophenone as individual stabilizers were synthesized under these conditions. Their copolymers and the ter-copolymers of the individual stabilizers with methyl methacrylate (MMA) were obtained. The influence of these additives on the rate of copolymerization and 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, molecular weight and polydispersity of the copolymers. A significant stabilizing effect against photodegradation was determined. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Combined 2,2,6,6-tetramethylpiperidine–2-hydroxybenzophenone 1,3,5-triazine derivatives; Polymerizable photostabilizers; Phase transfer catalysis; Photostability; Photodegradation

1. Introduction

The requirements on the properties and environmental behavior of polymeric materials are increasing together with their production and application. It is well known that all commonly used plastics degrade under the influence of sunlight. That is why the problem of their stabilization is of eminent importance. As a possible way to solve such problem, both 2,2,6,6-tetramethylpiperidine and 2-hydroxybenzophenone derivatives have successfully been used. So far, they have found a wide application due to their efficiency as light stabilizers for polymeric materials [1]. 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 nitroxide radicals [3] either by reaction with peroxy radicals or occasionally by reaction with singlet oxygen. The nitroxide radicals stop oxidative degradation by coupling of alkyl radicals [4]. In contrast to 2,2,6,6-tetramethylpiperidines, 2-hydroxybenzophenones are 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 [5].

If 2,2,6,6-tetramethylpiperidine and 2-hydroxybenzophenone are combined in one molecule, this could result in a new combined stabilizing effect after incorporation into a polymer. Recently, the synthesis of some polymerizable triazinyl-2,2,6,6-tetramethylpiperidine [6] and triazinyl-aminobenzotriazole [7,8] derivatives was reported. Their covalent bonding to the polymer chain provided stability towards solvents and a migration stabilizing effect.

A lack of information on the synthesis of combined 2,2,6,6-tetramethylpiperidine–2-hydroxybenzophenone derivatives and our experience on the synthesis of different compounds [9,10], including stabilizers [6,11], under phase transfer catalysis conditions (PTC) encouraged a preliminary investigation on the synthesis of the above mentioned

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derivatives and their influence on the properties of methyl methacrylate (MMA) copolymers, the results of which are reported here.

2. Experimental part

2.1. Materials

1,2,2,6,6-Pentamethylpiperidine-4-ol **1b** [12] and 2-(2,2, 6,6-tetramethylpiperidine-4-oxy)-4-allyloxy-6-chloro-1,3,5-triazine **2a** [6] were synthesized and purified by methods previously described. 2,2,6,6-Tetramethylpiperidine-4-ol, 2,4-dihydroxybenzophenone, allyl alcohol, cyanuric chloride, tetrabutylammonium bromide (TBAB) and Aliquat 336 (Fluka products), p.a. grade, were used without purification. Commercial MMA (Agrochim, Bulgaria) was used after distillation under reduced pressure in a nitrogen (99.9%) atmosphere. Dibenzoyl peroxide (DBP, Fluka) recrystallized from chloroform was used as initiator of the free radical copolymerization. Used solvents were of p.a. grade or spectrophotometric grade.

2.2. Analysis

IR spectra were taken on Perkin-Elmer 1600 FT-IR spectrometer at $4\,cm^{-1}$ resolution (KBr pellets). ^{1}H-NMR spectra were recorded on JEOL JNM-PS spectrometer, operating at 100 MHz in CDCl$_3$ (chemical shifts are given as δ in ppm). UV–VIS spectra were recorded on a Hewlett Packard 8452A UV–VIS spectrophotometer with 2 nm resolution, at room temperature in ethanol. 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 ethyl acetate:cyclohexane = 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–VIS absorption detectors were used. Polystyrene calibration was used for all molecular weight calculations.

2.3. Synthesis of stabilizers

2.3.1. Synthesis of 2-(1,2,2,6,6-pentamethylpiperidine-4-oxy)-4-allyloxy-6-chloro-1,3,5-triazine **2b**

Cyanuric chloride (1.85 g, 0.01 mol) dissolved in dichloromethane (15 ml) was added dropwise to a room temperature mixture of **1b** (3.4 g, 0.01 mol) solution (15 ml dichloromethane), 50% hydrous sodium hydroxide solution (10 ml) and TBAB (0.32 g, 0.001 mol) under vigorous stirring. To this two-phase system a solution of allyl alcohol

(0.58 g, 0.01 mol) in dichloromethane (10 ml) was added dropwise under the same conditions. The resulting mixture was stirred for 30 min at room temperature then diluted in 30 ml of water before separation of the organic layer. The latter was washed with water, dried over anhydrous sodium sulfate and evaporated under reduced pressure to give colorless needles of pure **2b** after recrystallization in *n*-hexane.

2.3.2. General procedure for the synthesis of combined piperidine –2-hydroxybenzophenone derivatives **4a–b.**

Piperidine **2a–b** (0.01 mol) dissolved in benzene (15 ml) was added dropwise to a room temperature mixture of 2,4-dihydroxybenzophenone (2.14 g, 0.01 mol) solution (15 ml benzene), sodium hydroxide (0.4 g, 0.01 mol) water solution (10 ml) and Aliquat 336 (0.001 mol) under vigorous stirring. The resulting mixture was stirred for 50 min at room temperature, then diluted in 20 ml of water before separation of the organic layer. The latter was washed with water, dried over anhydrous sodium sulfate and evaporated to give colorless crystals of pure **4a–b** after recrystallization in petroleum ether.

2.3.3. Synthesis of 2-(2-hydroxybenzophenon-4-oxy)-4-allyloxy-6-chloro-1,3,5-triazine **3**

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. The organic layer was separated and added dropwise to a room temperature mixture of 2,4-dihydroxybenzophenone (2.14 g, 0.01 mol) dichloromethane solution (15 ml), sodium hydroxide (0.4 g, 0.01 mol) water solution (10 ml) and Aliquat 336 (0.001 mol) under vigorous stirring. The resulting mixture was stirred for 50 min at room temperature, then diluted in 20 ml of water before separation of the organic layer. The latter was washed with water, dried over anhydrous sodium sulfate and evaporated to give colorless crystals of pure **3** after recrystallization in *n*-hexane.

2.4. Synthesis of polymers

The free radical copolymerization of the monomeric stabilizers **2–4** with MMA was carried out in ampoules previously purged with pure dry nitrogen. The process of copolymerization of MMA was conducted as before [13,14] at 70 °C for 10 h, in the presence of 1.0 wt.% of DBP and 1.0 wt.% of the stabilizers **2–4** and a mixture of stabilizers **2** and **3** (each with the concentration of 0.5 wt.%), under nitrogen atmosphere. The side-chain copolymers thus obtained were several times reprecipitated with ethanol from chloroform for PMMA-based copolymers. The precipitated copolymers were repeatedly washed with ethanol, recovered

by filtration and dried in vacuum to constant weight. Transparent copolymers were obtained. All measurements for the characterization and investigation were carried out with precipitated copolymers.

2.5. Photodegradation of the copolymers

The solid copolymeric 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 copolymeric films of poly (MMA-co-stabilizer) 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 ter-copolymers 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.
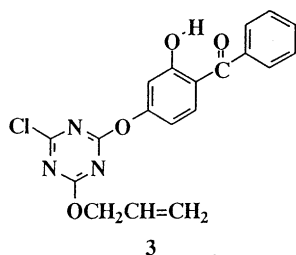
Following way (1), we synthesized polymerizable hindered piperidine type stabilizers **2a–b** (formula 1) which inhibit the processes of autoxidation [2], and polymerizable 2-hydroxybenzophenone stabilizer **3** (formula 2) proved to be UV-absorber [5].

Formula 1
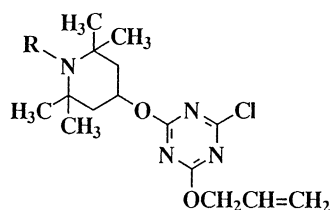
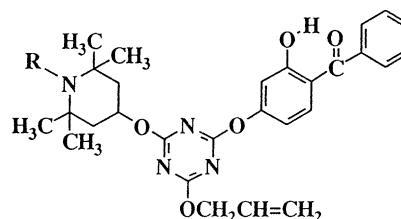

2a-b (2a: R = H; 2b: R = CH₃)

Formula 2

3

In order to follow the way (2), we synthesized monomers in which the hindered piperidine and 2-hydroxybenzophenone fragments are combined through the triazine ring in one molecule, containing a polymerizable allyloxy group (formula 3).

Formula 3

4a-b (4a: R = H; 4b: R = CH₃)

3.1. Synthesis of stabilizers

The combined stabilizers **4a–b** were synthesized in just three steps following Scheme 1.

First, 2,2,6,6-tetramethylpiperidine-4-ol **1a** was readily converted into 1,2,2,6,6-pentamethylpiperidine-4-ol **1b** by methylation with formalin in formic acid as previously described [12].

The monomer **2a** was synthesized as previously described [6]. The monomer **2b** was synthesized by nucleophilic substitutions of two chlorine atoms of the cyanuric chloride with **1b** and allyl alcohol under PTC conditions. The reactions were performed in 50% hydrous sodium hydroxide solution/water-immiscible organic solvent two-phase system at room temperature in the presence of a quaternary ammonium salt.

Finally, a reaction of 1,3,5-triazines **2a–b** with 2,4-dihydroxybenzophenone under similar PTC conditions led to the target stabilizers **4a–b**.

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.

It was experimentally established that the best results of the synthesis of the monomer **2b** were obtained with the use of a concentrated water phase (50% aqueous sodium hydroxide).

However, this two-phase system type was not suitable for the interaction between triazine derivatives and 2,4-dihydroxybenzophenone, because of the possibility of substitution of the hydroxy group in the second position of the benzophenone ring. This required the reactions for obtaining monomer **3** and combined stabilizers **4a–b** to be conducted in a two-phase system with a diluted water phase using equimolar quantity of sodium hydroxide to the 2,4-dihydroxybenzophenone.

This was the reason for changing the way of monomer **3** synthesis (Scheme 2).

First, the allyloxy-1,3,5-triazine was synthesized under PTC conditions with the use of a concentrated water phase [15] and then treated with 2,4-dihydroxybenzophenone using a diluted water phase.

Because of the good solubility of cyanuric chloride, piperidine **1b** and 2,4-dihydroxybenzophenone in dichloro-
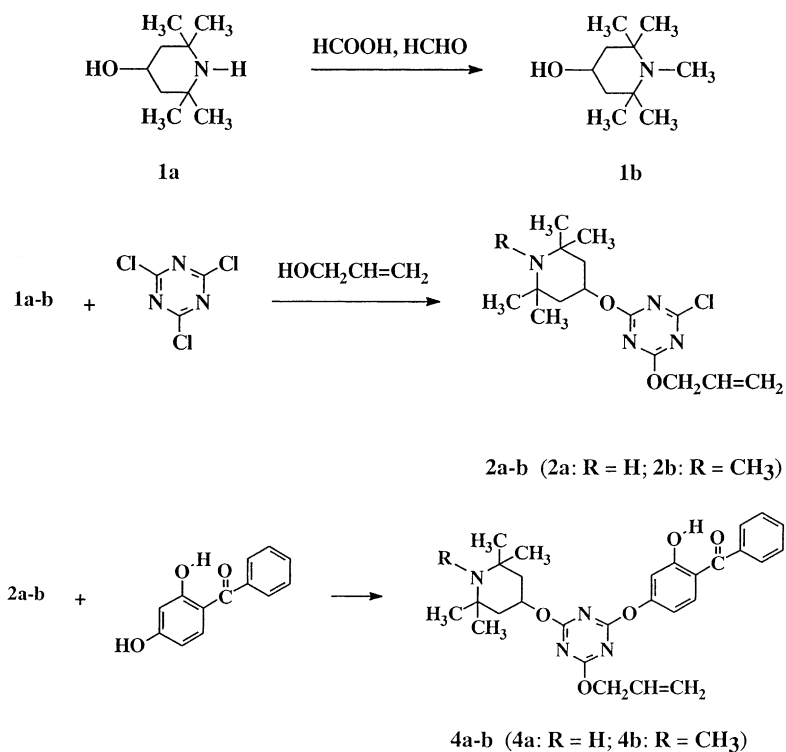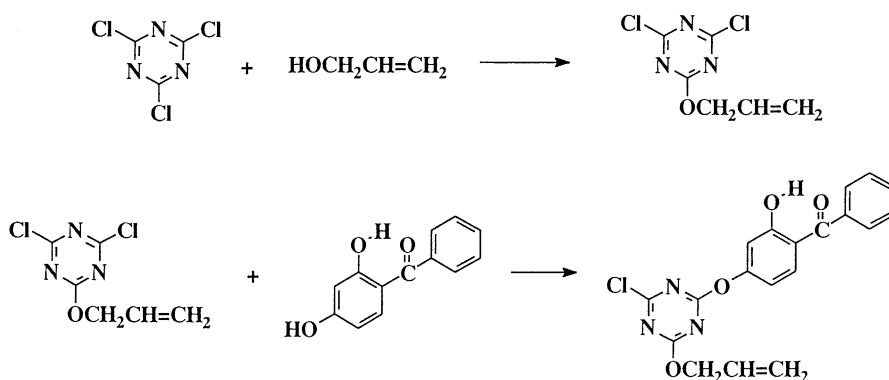
Scheme 1.

methane, the latter was used as the organic phase in the synthesis of monomers **2b** and **3**. Among the quaternary ammonium salts tested as PTC, the best synthesis results were obtained with the use of TBAB when the water phase was concentrated and with the use of Aliquat 336 when the water phase was diluted. Since the Aliquat 336 works better in benzene [16] and the solubility of the monomers **2a–b** was good enough in the same solvent, the latter was used as an organic phase in the synthesis of combined stabilizers **4a–b**.

The results obtained under favorable PTC conditions are summarized in Table 1.

Table 1
PTC conditions and yields in the synthesis of monomeric stabilizers **2b**, **3** and **4a–b**

Product	Catalyst	Solvent	Time (min)	Yield (%)
2b	TBAB	Dichloromethane	30	85
3	Aliquat 336	Dichloromethane	50	88
4a	Aliquat 336	Benzene	50	92
4b	Aliquat 336	Benzene	50	95

Scheme 2.

Table 2
Characteristic data obtained for monomers **2a–b** and **3** and combined stabilizers **4a–b**

Product	Melting point (°C)	R_f	Analysis (%)	λ_{max} (nm)	FT-IR (cm^{-1})	(^{1}H-NMR (δ, ppm)
2a	124–126	0.44	$C_{15}H_{23}ClN_4O_2$ cald. C, 55.13, H, 7.04, N, 17.15; found C, 55.22, H, 7.09, N, 17.23	266	ν_{NH} 3330, $\nu_{C=C}$ 1645, $\nu_{C=N}$ 1580, ν_{C-O} 1250, ν_{C-Cl} 750	6.46 (br.s, 1H, NH); 5.96 (m, 1H, CH=); 5.26–5.32 (m, 1H, CH); 5.20–5.08 (m, 2H, =CH$_2$); 4.81 (d, 2H, OCH$_2$); 1.94 (m, 4H, 2 × CH$_2$); 1.14 (d, 12H, 2 × C(CH$_3$)$_2$)
2b	84–86	0.52	$C_{16}H_{25}ClN_4O_2$, cald. C, 56.39, H, 7.34, N, 16.45; found C, 56.48, H, 7.40, N, 16.25	268	$\nu_{C=C}$ 1650, $\nu_{C=N}$ 1585, ν_{C-O} 1255, ν_{C-Cl} 760	5.94 (m, 1H, CH=); 5.24–5.30 (m, 1H, CH); 5.18–5.06 (m, 2H, =CH$_2$); 4.78 (d, 2H, OCH$_2$); 2.32 (s, 3H, NCH$_3$); 1.90 (m, 4H, 2 × CH$_2$); 1.08 (d, 12H, 2 × C(CH$_3$)$_2$)
3	92–94	0.53	$C_{19}H_{14}ClN_3O_4$, cald. C, 59.45, H, 3.65, N, 10.95; found C, 59.61, H, 3.71, N, 11.01	310	ν_{OH} 3410, $\nu_{C=O}$ 1670, $\nu_{C=C}$ 1645, ν_{C-Cl} 755	8.02–7.66 (m, 5H, Ar); 7.62–7.30 (m, 3H, Ar); 5.98 (m, 1H, CH=); 5.28–5.18 (m, 2H, =CH$_2$); 4.80 (d, 2H, OCH$_2$); 4.62 (s, 1H, OH)
4a	104–106	0.42	$C_{28}H_{32}N_4O_5$, cald. C, 66.67, H, 6.35, N, 11.11; found C, 66.81, H, 6.41, N, 11.16	320	ν_{NH} 3440, $\nu_{C=O}$ 1670, $\nu_{C=C}$ 1640, $\nu_{C=N}$ 1580, ν_{C-O} 1260	8.04–7.68 (m, 5H, Ar); 7.64–7.32 (m, 3H, Ar); 6.68 (br.s, 1H, NH); 6.02 (m, 1H, CH=); 5.42–5.36 (m, 1H, CH); 5.32–5.24 (m, 2H, =CH$_2$); 4.82 (d, 2H, OCH$_2$); 4.68 (s, 1H, OH), 1.84 (m, 4H, 2 × CH$_2$); 1.10 (d, 12H, 2 × C(CH$_3$)$_2$)
4b	80–82	0.50	$C_{29}H_{34}N_4O_5$, cald. C, 67.18, H, 6.56, N, 10.81; found C, 67.26, H, 6.60, N, 10.79	322	ν_{NH} 3440, $\nu_{C=O}$ 1670, $\nu_{C=C}$ 1640, $\nu_{C=N}$ 1580, ν_{C-O} 1260	8.00–7.64 (m, 5H, Ar); 7.61–7.30 (m, 3H, Ar); 6.00 (m, 1H, CH=); 5.38–5.32 (m, 1H, CH); 5.28–5.20 (m, 2H, =CH$_2$); 4.78 (d, 2H, OCH$_2$); 4.32 (s, 1H, OH), 1.78 (m, 4H, 2 × CH$_2$); 1.04 (d, 12H, 2 × C(CH$_3$)$_2$)

Table 3
Copolymerization rate R_p of MMA with stabilizers **2a–b**, **3** and **4a–b**

Polymer	R_p (mmol l^{-1} s^{-1})
Poly(MMA-co-stabilizer **2a**)	2.65
Poly(MMA-co-stabilizer **2b**)	2.67
Poly(MMA-co-stabilizer **3**)	2.59
Poly(MMA-co-stabilizer **4a**)	2.43
Poly(MMA-co-stabilizer **4b**)	2.45
Poly(MMA-co-stabilizers **2a + 3**)	2.13
Poly(MMA-co-stabilizers **2b + 3**)	2.14
Poly(MMA)	2.74

The synthesis was monitored by TLC on silica gel and the target products **2a–b**, **3** and **4a–b** were characterized and identified by their melting points, TLC R_f values, elemental analyses, UV–VIS, FT-IR and ^{1}H-NMR spectra (Table 2).

3.2. Polymer investigations

The free radical polymerization and ter-copolymerization of MMA in the presence of the stabilizers **2a–b**, **3** and **4a–b** were investigated. The data about the rate constants R_p, determined from the time-yield curves are presented in Table 3. It can be seen that stabilizers **2–4** slightly retard the polymerization process, especially stabilizers **2a–b** and **3**. In the case of ter-copolymerization, the retardation effect was stronger.

The presence of a covalent bond between the monomeric stabilizer units and polymer chain has been proved by GPC

and by TLC techniques. In the GPC chromatograms, only one peak was observed for copolymers containing stabilizers, its retention time being different from that of the PMMA.

The stabilizer effect upon the molecular weight of the copolymers was of great interest. The molecular characteristics of the copolymers determined by GPC are listed in Table 4. They confirm the formation of high molecular weight polymers. The molecular weights of the copolymers are $M_w = (2.03–2.56)10^5$ and $M_n = (0.95–1.13)10^5$ and those of PMMA are $M_w = 2.12 \times 10^5$ and $M_n = 1.18 \times 10^5$. The polydispersity is in the range of 1.9–2.7 for PMMA-based copolymers and 1.8 for PMMA, respectively. The polydispersity for the ter-copolymers is higher, compared to the copolymers with stabilizers **2–4**.

The chemically-bonded stabilizers were proved also by TLC. The unprecipitated copolymers (containing also some amount of unreacted stabilizers), precipitated copolymers, monomeric stabilizers and mixtures of homopolymer and the stabilizers were studied. After the chromatography development, it was established that the stabilizers in the mechanical mixtures with homopolymer moved at the same speed as the monomeric stabilizers and had the same values of retention factor R_f, while the stabilizers (Table 2) in the copolymers, 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 [13,17–19].

Absorption UV–VIS spectra of the precipitated polymers were compared with those of the corresponding

Table 4
Molecular characteristics of MMA copolymers and PMMA (see text)

Stabilizer	Before irradiation			After irradiation			A
	$(M_n)_0 \times 10^5$	$(M_w)_0 \times 10^5$	$(M_w)_0/(M_n)_0$	$M_n \times 10^5$	$M_w \times 10^5$	M_w/M_n	
Poly(MMA-co-stabilizer **2a**)	1.13	2.15	1.9	0.97	2.04	2.1	0.16
Poly(MMA-co-stabilizer **2b**)	1.07	2.03	1.9	0.91	1.91	2.1	0.18
Poly(MMA-co-stabilizer **3**)	1.12	2.13	1.9	0.97	1.94	2.0	0.15
Poly(MMA-co-stabilizer **4a**)	1.05	2.10	2.0	0.98	2.06	2.1	0.07
Poly(MMA-co-stabilizer **4b**)	1.03	2.06	2.0	0.95	2.01	2.1	0.08
Poly(MMA-co-stabilizers **2a + 3**)	0.98	2.55	2.6	0.88	2.46	2.8	0.11
Poly(MMA-co-stabilizers **2b + 3**)	0.95	2.56	2.7	0.85	2.46	2.9	0.12
Poly(MMA)	1.18	2.12	1.8	0.64	1.92	3.0	0.84

Table 5
Spectrophotometric data for copolymers and ter-copolymers of MMA with stabilizers **2–4**

Stabilizer	Stabilizer feed		Chemically-bonded stabilizer	
	In wt.%	In mol%	In %	In mole $\times 10^{-3}$
2a	1	0.306	82	2.51
2b	1	0.294	84	2.47
3	1	0.261	79	2.06
4a	1	0.198	65	1.29
4b	1	0.193	68	1.31
2a + 3	0.5 + 0.5	0.153 + 0.130 = 0.283	73 + 61	1.12 + 0.79 = 1.91
2b + 3	0.5 + 0.5	0.147 + 0.130 = 0.277	76 + 62	1.12 + 0.81 = 1.93

pure monomeric stabilizers **2a–b**, **3** and **4a–b**. 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. The amount of chemically-bonded stabilizers **2–4** into the polymer chain was determined spectrophotometrically (Table 5).

As it is seen from the Table 5, the content of chemically-bonded stabilizers **4a–b** is relatively low 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.

3.3. Photostability of the poly(MMA)s

The influence of the monomeric stabilizers **2–4** upon the photodestruction of PMMA was studied by GPC with prior irradiation of their 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 with the data for PMMA.

The number of chain breaks per molecule A was calculated by the following equation [20]:

$$A = \frac{(M_n)_0}{(M_n)} - 1$$

where $(M_n)_0$ and (M_n) are the number-average molecular weights before and after irradiation, respectively. The results are listed in Table 4. It is evident that poly(MMA-co-stabilizer) does not change significantly its polydispersity and molecular weight distribution while the values M_w and M_n for PMMA decrease strongly. The data also show that stabilizers **2–4** improve considerably the polymer stability, especially in the case of combined stabilizers **4** in spite of their lower content in the polymer chain. The ter-copolymers exhibit properties similar to those of poly(MMA-co-stabilizer **4**)s (A values).

4. Conclusions

On the basis of the present study, it can be concluded that the synthesized new compounds, a combination between two stabilizers different in their action, show good stabilizing effect to PMMA. It was established that the presence of both 2,2,6,6-tetramethylpiperidine and 2-hydroxybenzophenone fragments together in the polymer significantly improved its photostability. However, the combined stabilizers retard the rate of copolymerization less than that of the ter-copolymerization of MMA with the same stabilizers as individual monomers, and their photostabilizing effect is better most probably because of the equimolecular ratio of the two different stabilizer fragments in the polymer chain.

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