

Synergistic Efficiency of Combined HALS–UV Absorber Polymerizable Stabilizers

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ABSTRACT: The influence of combined 2,2,6,6-tetramethylpiperidine – 2-hydroxyphenyl-benzotriazole [1,3,5]triazine polymerizable stabilizers on the photostability of their copolymers with methyl methacrylate as well as the interaction of the photoreactive HALS and UV absorber fragments in the combined molecules have been studied. Chemical bonding of the stabilizers in the polymer was confirmed spectrophotometrically. The participation of the combined stabilizers in the polymerization did not affect considerably the molecu-

lar weight and the molecular weight distribution of the copolymers. A significant stabilizing effect against photodegradation was determined. Strong synergistic interaction between different HALS and UV absorber fragment in the combined stabilizers was established. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2408–2415, 2006

Key words: HALS; 2-hydroxyphenylbenzotriazoles; copolymerization; stabilization; synergism

INTRODUCTION

At present, polymer materials such as plastics and rubbers are indispensable for our life. However, polymers are very easily degraded in atmospheric conditions: one of the causes is the autoxidation chain reaction occurring by action of heat, oxygen, and sunlight. Polymer materials, therefore, need additives such as antioxidants and UV absorbers for their stabilization. The addition of light stabilizers is most convenient and effective way to combat photoxidation in polymers. Among the stabilizers used, both 2-hydroxyphenylbenzotriazole and 2,2,6,6-tetramethylpiperidine (HALS) derivatives are of a great interest due to their high photostabilizing efficiency.¹ These two derivative groups, however, differ from each other in their action, no matter that both of them belong to the photodegradation stabilizers.

Hindered amine light stabilizers (HALS) have been used widely as antioxidants. They inhibit the processes of autoxidation generating nitroxyl radicals either by reaction with peroxy radicals or occasionally by reaction with singlet oxygen.^{2–4} The nitroxyl radicals stop oxidative degradation by coupling of alkyl radicals.^{5,6} 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.^{7,8}

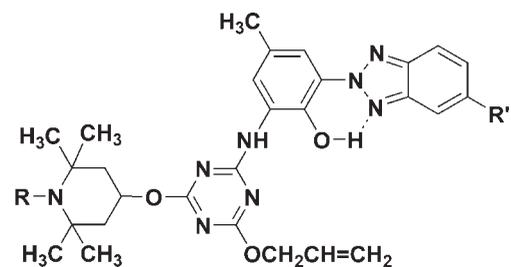
The introduction of a polymerizable group into the stabilizer molecule ensures capability of the latter for covalent bonding to the polymer chain. The advantage of using polymerizable stabilizers over conventional stabilizers is that the stabilizer becomes chemically bonded to the polymer. The stabilizer, therefore, cannot be extracted from the polymer. The solvent-fastness of a polymer stabilized with a polymerizable stabilizer is, as a consequence, much greater than a polymer stabilized with conventional stabilizers. Additionally, the chemical bonding of the stabilizer to a polymer prevents the stabilizer from migrating within the polymer.⁹ In previous papers the synthesis of polymerizable triazinylaminobenzotriazoles¹⁰ and triazinyl-2,2,6,6-tetramethylpiperidines^{11,12} as polymer stabilizers was reported. Their influence on the rate of styrene polymerization and on the styrene copolymers photostability was described.

A combination of 2,2,6,6-tetramethylpiperidine and 2-hydroxyphenylbenzotriazole fragments in one molecule through an *s*-triazine ring could result in a new stabilizer type of combined stabilizing effect. Recently, a number of papers devoted to the problem of the synthesis of combined stabilizers containing fragments able to act according to different stabilizing mechanisms have been published. Thus, the hindered amine fragments have been combined with either 2-hydroxybenzophenone^{13–17} or 2-hydroxyphenylbenzotriazole^{18–20} UV absorbers as well as with hindered phenols.^{21–23}

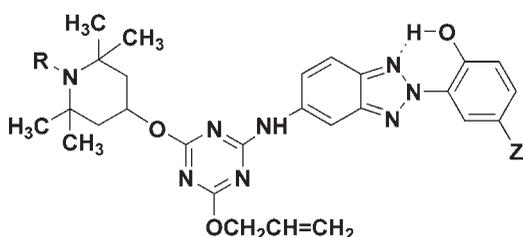
In this study, the influence of some combined 2,2,6,6-tetramethylpiperidine–2-hydroxyphenylbenzotriazole [1,3,5]triazine polymerizable stabilizers on

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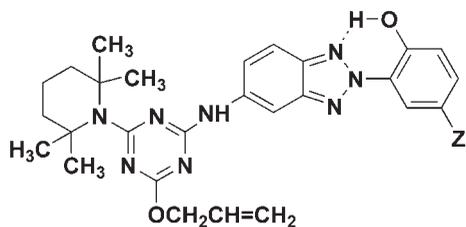
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R=H, R'=H (3a); R=H, R'=Me (3b);
R=Me, R'=H (3c); R=Me, R'=Me (3d)



R=H, Z=H (3e); R=H, Z=Cl (3f);
R=H, Z=NO₂ (3g); R=Me, Z=H (3h);
R=Me, Z=Cl (3i); R=Me, Z=NO₂ (3j)



Z=H (3k); Z=Cl (3l); Z=NO₂ (3m)

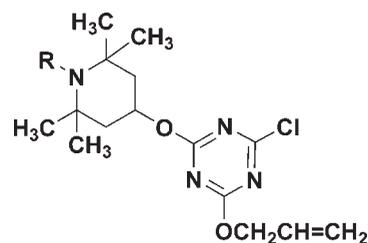
Figure 1 Combined 2,2,6,6-tetramethylpiperidine-2-hydroxyphenylbenzotriazole stabilizers 3a–m.

the photostability of their copolymers with methyl methacrylate (MMA) as well as the interaction of the photoreactive HALS and UV absorber fragments in the combined molecules have been studied.

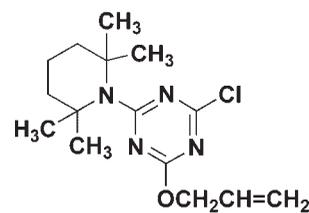
EXPERIMENTAL

Materials

Bifunctional combined stabilizers 3a–m (Fig. 1), monofunctional 2,2,6,6-tetramethyl-piperidin-[1,3,5]triazines 1a–c (Fig. 2) and 2-hydroxyphenylbenzotriazol-[1,3,5]triazines 2a–e (Fig. 3) as well as amino-2-hydroxyphenylbenzotriazoles 4a–e (Fig. 4) were synthesized and characterized before.^{11,13,18–20} Commercial methyl methacrylate



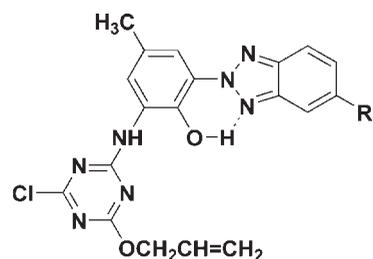
R=H (1a); R=Me (1b)



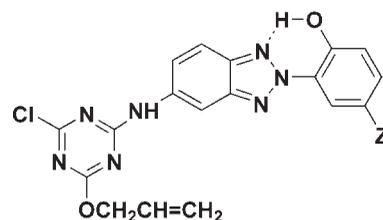
1c

Figure 2 Polymerizable allyloxy-[1,3,5]triazinylpiperidines 1a–c.

(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.

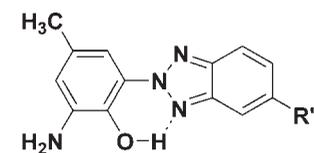


R' = H (2a); R' = CH₃ (2b)

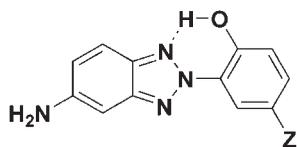


Z = H (2c); Z = Cl (2d); Z = NO₂ (2e)

Figure 3 Polymerizable allyloxy-[1,3,5]triazinyl-2-hydroxyphenylbenzotriazoles 2a–e.



R' = H (4a) ; R' = CH₃ (4b)



Z = H (4c) ; Z = Cl (4d) ; Z = NO₂ (4e)

Figure 4 2-Hydroxyphenylbenzotriazoles 4a–e.

Methods

Electronic spectra were recorded at room temperature on a Hewlett–Packard 8452A UV/Vis spectrophotometer with 2 nm resolution at a concentration 10^{-4} mol/L in chloroform. The polymer molecular weights were determined on a GPC Waters 244 apparatus equipped with a combination of 100 Å, 1000 Å, linear Ultrastyrigel columns; the solvent was THF at a flow rate of 1.0 mL/min at 45°C. Both differential refractive index and UV–visible absorption detectors were used. Polystyrene calibration was used for all molecular weight calculations.

Synthesis of polymers

The free-radical copolymerization and terpolymerization of the monomeric stabilizers 1a–c, 2a–e, and 3a–m with MMA was carried out in ampoules previously purged with pure dry nitrogen.^{24–26} The processes of copolymerization and terpolymerization of MMA were conducted in a thermostat for 10 h at 70°C in the presence of 1.0 wt % of DBP and 1.0 wt % of the corresponding monomeric stabilizer (1a–c, 2a–e, or 3a–m) as well as a mixture of stabilizers 1a–c and 2a–e (each with the concentration of 0.5 wt %). The side-chain transparent, solid and colorless copolymers and terpolymers thus obtained were reprecipitated several times with methanol from chloroform to remove the noninteracted monomers. This process was controlled by TLC until the filtrates were free of monomers 1, 2, or 3. The precipitated copolymers poly(MMA-co-1, 2, or 3) and terpolymers poly(MMA-ter-1 + 2) were repeatedly washed with methanol and dried *in vacuo* to constant weight at 40°C. All measurements for the characterization and the investigation were carried out with precipitated copolymers and terpolymers.

Photodestruction of copolymers

The solid polymeric films were irradiated in a solar simulator (Suntest CPS+, HERAEUS), equipped with an air-cooled Xenon arc lamp (Hanau, 1.5 kW, 765 W/m²), protected with an adequate filter to simulate the solar spectrum between 290 and 800 nm. The photodegradation was followed by the changes of the polymer molecular weights before and after irradiation of their solid films using GPC (gel-permeation chromatography). The polymeric films of poly(MMA-co-stabilizer), poly(MMA-ter-stabilizers) and PMMA were sufficiently thin (50 μm) and absorbed in the range of validity of the Lambert-Beer law.

RESULTS AND DISCUSSION

The combined HALS–UV absorber stabilizers 3 investigated in the present study are represented in Figure 1. Their molecules consist of two stabilizer fragments differ from each other in their action as well as an allyl group capable of covalent bonding to the polymer.

To receive a more complete comparative picture for the influence of the combined stabilizers 3 on the photostability of their copolymers with methyl methacrylate, the corresponding polymerizable triazinylpiperidines 1 (Fig. 2) and triazinylbenzotriazoles 2 (Fig. 3), not containing benzotriazole and piperidine fragments respectively, were investigated under the same conditions.

Spectroscopic measurements of the stabilizers

2-Hydroxyphenylbenzotriazole fragments in combined stabilizers 3a–d are substituted in the *s*-triazine ring by the primary amino groups, situated in the phenyl moiety of the 2-hydroxyphenylbenzotriazoles 4a–b (Fig. 4). The substitution of the combined stabilizers 3e–m in the *s*-triazine ring is fulfilled by the primary amino groups, situated in the benzotriazole moiety of the 2-hydroxyphenylbenzotriazoles 4c–e (Fig. 4).

The position effect of the amino group on the absorption properties of the 2-(2-hydroxyphenyl)-benzotriazoles 4a–b and 4c–e can be seen in the UV–vis spectra of the model compounds 4a and 4c (Fig. 5). The absorption maximum of benzotriazole 4c is 34 nm bathochromically shifted with respect to those of benzotriazole 4a. This may be related to the position of the electron-donating amino group in the benzotriazole moiety, and in this connection, to the increased strength of the intramolecular hydrogen bond. In the benzotriazole 4a, the amino group is situated in the 2-hydroxyphenyl moiety, which leads to decreased strength of the intramolecular hydrogen bond.

In confirmation of discussed above, after acylation with 2,2,6,6-tetramethylpiperidin-[1,3,5]triazines 1 the electron-donating activity of the amino groups strongly decrease. The benzotriazole absorption of the

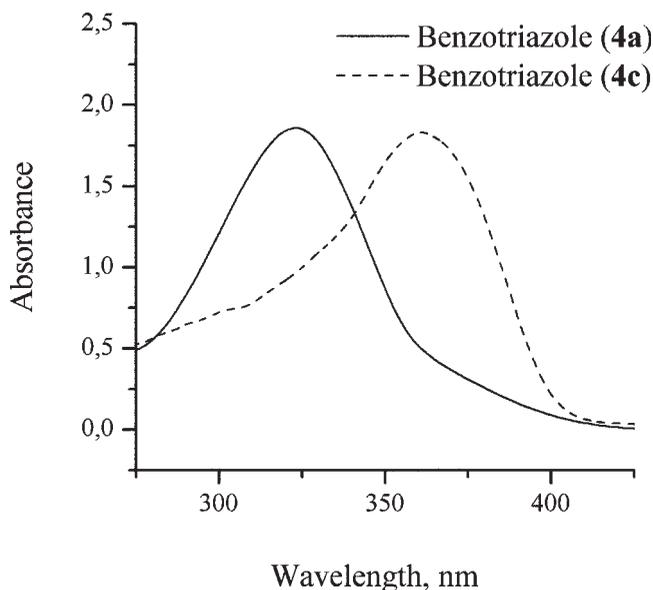


Figure 5 Absorption spectra of 2-hydroxyphenylbenzotriazoles **4a** and **4c**.

bifunctional stabilizer **3a** (derived from benzotriazole **4a**) is shifted hypsochromically, while those of stabilizer **3e** (derived from benzotriazole **4c**) – bathochromically (Fig. 6).

The influence of the C-5 phenyl substituent (**Z**) on the absorption properties of combined stabilizers **3e–m** (Fig. 1) can be seen in the UV–vis spectra of the model compounds **3e–g** represented in Figure 7. The absorption maximum of the benzotriazole fragment in compound **3e** ($\lambda_A = 342$ nm) is 8 and 16 nm hypsochromically shifted than those of combined stabilizers **3f** ($\lambda_A = 350$ nm) and **3g** ($\lambda_A = 358$ nm), respectively. This may be related to the decreased electron density on

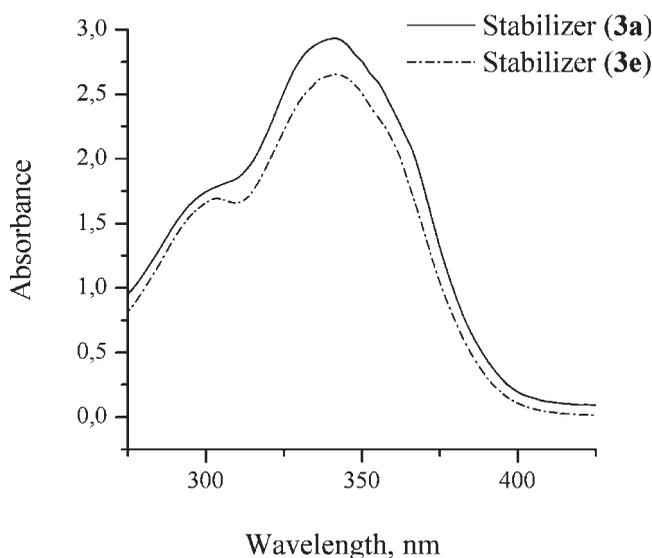


Figure 6 Absorption spectra of combined stabilizers **3a** and **3e**.

the phenyl oxygen for compounds **3f** and **3g**, containing an electron-deficient 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. This effect was enhanced with the increasing the electron-withdrawing ability of the substituent.

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 **1a–c**, **2a–e**, and **3a–m** was investigated under conditions described before.^{24–26} Transparent 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.²⁰

The UV–vis absorption spectra of the copolymers showed similar absorption maxima as those of the monomers **1**, **2**, and **3**. 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 I).

As it is seen (Table I), the content of a chemically bonded stabilizer **3a–m** is relatively smaller. It is probably because of the lower activity of the polymerizable group in these compounds or the stabilizer was bonded mainly in the lower molecular weight fractions

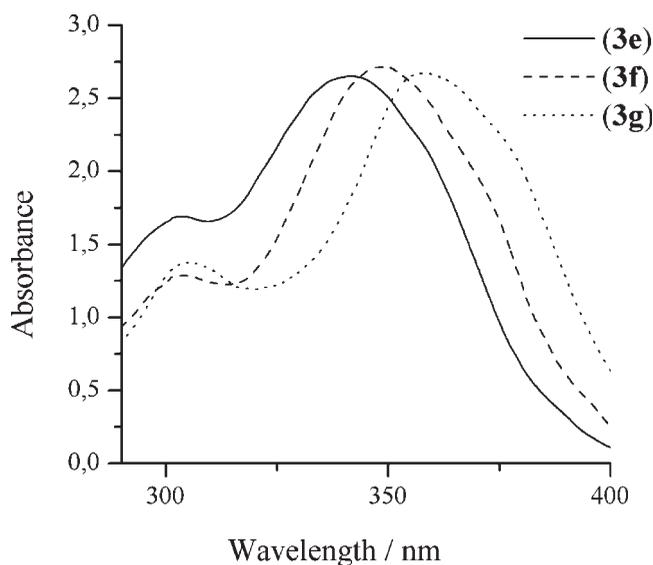


Figure 7 Absorption spectra of combined stabilizers **3e**, **3f**, and **3g**.

TABLE I
Yields, Polymerization Rate R_p , and Chemically Bonded Amount of Stabilizers
1, 2, and 3 for MMA Copolymers and Terpolymers

Polymer	Yield (%)	R_p (mmol/L × s)	Stabilizer feed (wt %)	Chemically bonded stabilizer ^a	
				%	mol (10 ³)
poly(MMA-co-1a)	76	1.98	1.0	86	2.63
poly(MMA-co-1b)	77	2.01	1.0	87	2.56
poly(MMA-co-1c)	81	2.11	1.0	89	2.63
poly(MMA-co-2a)	72	1.90	1.0	79	1.93
poly(MMA-co-2b)	74	1.92	1.0	81	1.91
poly(MMA-co-2c)	73	1.91	1.0	83	2.10
poly(MMA-co-2d)	71	1.85	1.0	81	1.88
poly(MMA-co-2e)	71	1.85	1.0	80	1.82
poly(MMA-co-3a)	65	1.71	1.0	67	1.26
poly(MMA-co-3b)	66	1.73	1.0	69	1.27
poly(MMA-co-3c)	67	1.74	1.0	71	1.30
poly(MMA-co-3d)	68	1.77	1.0	73	1.31
poly(MMA-co-3e)	65	1.70	1.0	74	1.43
poly(MMA-co-3f)	64	1.67	1.0	71	1.29
poly(MMA-co-3g)	64	1.67	1.0	72	1.28
poly(MMA-co-3h)	68	1.78	1.0	76	1.43
poly(MMA-co-3i)	66	1.72	1.0	73	1.29
poly(MMA-co-3j)	66	1.72	1.0	74	1.29
poly(MMA-co-3k)	70	1.83	1.0	70	1.43
poly(MMA-co-3l)	69	1.80	1.0	72	1.29
poly(MMA-co-3m)	68	1.80	1.0	74	1.28
poly(MMA-ter-1a + 2a)	54	1.45	0.5 + 0.5	72 + 65	1.10 + 0.79 = 1.89
poly(MMA-ter-1a + 2b)	55	1.47	0.5 + 0.5	73 + 69	1.12 + 0.81 = 1.93
poly(MMA-ter-1b + 2a)	56	1.48	0.5 + 0.5	75 + 66	1.10 + 0.81 = 1.91
poly(MMA-ter-1b + 2b)	58	1.50	0.5 + 0.5	77 + 71	1.13 + 0.84 = 1.97
poly(MMA-ter-1a + 2c)	52	1.36	0.5 + 0.5	61 + 54	0.93 + 0.68 = 1.61
poly(MMA-ter-1a + 2d)	50	1.31	0.5 + 0.5	59 + 52	0.92 + 0.60 = 1.52
poly(MMA-ter-1a + 2e)	50	1.30	0.5 + 0.5	58 + 51	0.89 + 0.58 = 1.47
poly(MMA-ter-1b + 2c)	56	1.46	0.5 + 0.5	66 + 58	0.97 + 0.73 = 1.70
poly(MMA-ter-1b + 2d)	54	1.41	0.5 + 0.5	65 + 56	0.94 + 0.65 = 1.59
poly(MMA-ter-1b + 2e)	54	1.41	0.5 + 0.5	63 + 55	0.93 + 0.63 = 1.56
poly(MMA-ter-1c + 2c)	58	1.51	0.5 + 0.5	69 + 61	1.11 + 0.77 = 1.88
poly(MMA-ter-1c + 2d)	56	1.46	0.5 + 0.5	70 + 62	1.13 + 0.72 = 1.83
poly(MMA-ter-1c + 2e)	57	1.49	0.5 + 0.5	67 + 65	1.08 + 0.74 = 1.82
PMMA	83	2.17			

^a Chemically bonded stabilizer per 100 g polymer.

removed during the precipitation. The reason for such behavior may be the large steric volume of the combined stabilizer molecule. In contrast to compounds **3a–m**, the content of a chemically bonded monomer **1a–c** 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.

The polymerization rates R_p (Table I) were determined from the time-yield curves. It can be seen that stabilizers **1a–c**, **2a–e**, and **3a–m** did not affect the polymerization rate significantly, especially compounds **1a–c** and **2a–e**.

In the case of terpolymerization, the polymer yields and the chemically bonded amount of the stabilizer in the polymer chain were smaller, and the retardation effect on the polymerization process was stronger.

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 II. 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 $M_{wo} = (1.83 - 2.36) \times 10^5$ and $M_{no} = (0.73 - 1.15) \times 10^5$ respectively, and those of PMMA are $M_{wo} = 2.37 \times 10^5$ and $M_{no} = 1.29 \times 10^5$.

The polydispersity (M_{wo}/M_{no}) 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 **1a–c**, **2a–e**, and **3a–m**.

Photostability of poly(MMA-co-1,2,3), poly(MMA-ter-1 + 2) and PMMA

The influence of the monomer stabilizers **1**, **2**, and **3** upon the photodegradation of PMMA was studied by GPC with prior irradiation of their copolymers with

TABLE II
Molecular Characteristics of PMMA, MMA Copolymers, and Terpolymers

Polymer	Before irradiation			After irradiation			A	A _{add.}
	M _{no} (10 ⁻⁵)	M _{wo} (10 ⁻⁵)	M _{wo} /M _{no}	M _n (10 ⁻⁵)	M _w (10 ⁻⁵)	M _w /M _n		
poly(MMA-co-1a)	1.11	2.20	2.0	0.99	2.09	2.1	0.12	-
poly(MMA-co-1b)	1.09	2.16	2.0	0.96	2.03	2.1	0.13	-
poly(MMA-co-1c)	1.15	2.21	1.9	0.90	1.83	2.0	0.28	-
poly(MMA-co-2a)	1.07	2.16	2.0	0.91	2.02	2.2	0.17	-
poly(MMA-co-2b)	1.03	2.10	2.0	0.89	1.95	2.2	0.16	-
poly(MMA-co-2c)	1.06	2.11	2.0	0.86	1.82	2.1	0.23	-
poly(MMA-co-2d)	1.01	2.06	2.0	0.84	1.79	2.1	0.20	-
poly(MMA-co-2e)	0.99	2.01	2.0	0.83	1.76	2.1	0.19	-
poly(MMA-co-3a)	0.99	2.09	2.1	0.95	2.08	2.2	0.04	0.126
poly(MMA-co-3b)	0.96	2.04	2.1	0.93	2.05	2.2	0.03	0.121
poly(MMA-co-3c)	0.98	2.07	2.1	0.92	2.03	2.2	0.06	0.126
poly(MMA-co-3d)	0.95	2.01	2.1	0.90	1.99	2.2	0.05	0.121
poly(MMA-co-3e)	0.91	1.93	2.1	0.88	1.90	2.2	0.04	0.146
poly(MMA-co-3f)	0.87	1.86	2.1	0.84	1.85	2.2	0.03	0.149
poly(MMA-co-3g)	0.86	1.84	2.1	0.85	1.84	2.2	0.01	0.140
poly(MMA-co-3h)	0.92	1.90	2.1	0.87	1.88	2.2	0.06	0.153
poly(MMA-co-3i)	0.90	1.86	2.1	0.86	1.86	2.2	0.05	0.156
poly(MMA-co-3j)	0.88	1.85	2.1	0.85	1.84	2.2	0.03	0.145
poly(MMA-co-3k)	0.93	1.98	2.1	0.86	1.86	2.2	0.08	0.204
poly(MMA-co-3l)	0.88	1.87	2.1	0.83	1.85	2.2	0.06	0.193
poly(MMA-co-3m)	0.85	1.83	2.1	0.81	1.82	2.2	0.05	0.184
poly(MMA-ter-1a + 2a)	0.88	2.33	2.6	0.81	2.29	2.8	0.09	0.084
poly(MMA-ter-1a + 2b)	0.85	2.28	2.7	0.79	2.31	2.9	0.08	0.079
poly(MMA-ter-1b + 2a)	0.87	2.36	2.7	0.78	2.28	2.9	0.11	0.086
poly(MMA-ter-1b + 2b)	0.84	2.26	2.7	0.76	2.21	2.9	0.10	0.080
poly(MMA-ter-1a + 2c)	0.78	2.03	2.6	0.70	2.02	2.9	0.11	0.135
poly(MMA-ter-1a + 2d)	0.74	2.01	2.7	0.67	1.99	3.0	0.10	0.128
poly(MMA-ter-1a + 2e)	0.73	1.96	2.7	0.68	2.03	3.0	0.07	0.125
poly(MMA-ter-1b + 2c)	0.80	2.07	2.6	0.71	2.05	2.9	0.13	0.135
poly(MMA-ter-1b + 2d)	0.77	2.05	2.7	0.69	2.04	3.0	0.12	0.127
poly(MMA-ter-1b + 2e)	0.74	1.99	2.7	0.68	2.01	3.0	0.09	0.124
poly(MMA-ter-1c + 2c)	0.79	2.03	2.6	0.69	1.96	2.8	0.15	0.155
poly(MMA-ter-1c + 2d)	0.76	2.02	2.7	0.67	1.94	2.9	0.13	0.134
poly(MMA-ter-1c + 2e)	0.74	1.98	2.7	0.66	1.89	2.9	0.12	0.131
PMMA	1.29	2.37	1.9	0.65	1.93	3.0	0.98	-

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 chain breaks per a polymer molecule *A* was calculated by eq. (1), where *M*_{no} and *M*_n are the number-average molecular weights before and after irradiation respectively.²⁷

$$A = \frac{M_{no}}{M_n} - 1. \quad (1)$$

The data obtained for the chain breaks per a polymer molecule *A* demonstrate the very good stabilizing effect of the compounds under study. All stabilizers (1, 2, and 3) improve considerably the polymer photostability (Table II).

Monofunctional 2-hydroxyphenylbenzotriazoles 2a–e showed very good photostabilizing efficiency. It could be related to a rapid excited state intramolecular proton transfer (ESIPT) between the phenolic hydroxyl group and the benzotriazole nitrogen when compounds 2a–e

are excited into the benzotriazole absorption band.^{8,28} As can be seen the photostabilizing efficiency of the benzotriazoles 2c–e increase with the enhancement of the electron-accepting ability of the 5-phenyl substituent (2e > 2d > 2c). This could be explained with the increased stability of the protonated form in the same order at the ESIPT process (Fig. 8).

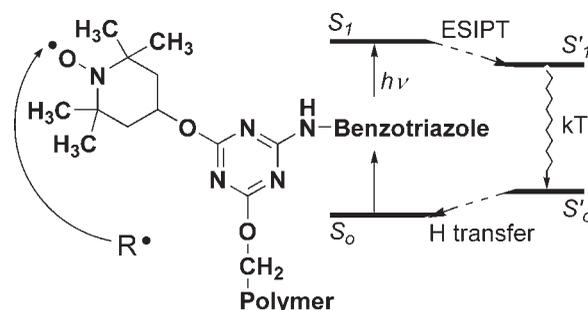


Figure 8 Radical scavenger and ESIPT processes in the combined stabilizers.

The photostabilizing effect of the piperidine monomers **1a–c** is better with respect to the monomeric 2-hydroxyphenylbenzotriazoles **2a–e**, probably because of their higher mole content in the polymer chain (Table I). On the other hand, the methylation (**1b**) and especially the acylation (**1c**) in the *N*-position of the piperidine moiety reduce ability of the piperidine nitrogen to form *N*-oxyl radicals, which results in lower photostabilizing activity of the [1,3,5]triazinylpiperidines **1b–c**.

The combined stabilizers **3a–m** showed the best photostabilizing effect among the tested compounds in spite of their lower content in the polymer chain. The photostabilizing efficiency of the bifunctional stabilizers follows the discussed above tendencies toward increasing the stabilizer activity with enhancement of the electron-accepting ability of the 5-phenyl substituent (**3g**, **3j**, **3m**) and to decreased photostabilizing ability after acylation of the piperidine nitrogen (**3k**). The latter could also be related to the formation of nitroxyl radicals by cleavage of the chemical bond between the piperidine nitrogen and the *s*-triazine ring (Fig. 9). Thus, the poly(MMA-*co*-**3k–m**) will lose the low molec-

ular piperidine fragment, while the piperidine moiety in stabilizers **3a–j** remains held to the polymer chain.

The terpolymers exhibit properties similar to those of poly(MMA-*co*-stabilizer **3a–m**)s (*A* values), but the polymer photostability under the same conditions was relatively lower. The reason for such behavior of the terpolymers could be the unequal distribution of the different stabilizer fragments in the polymer chain, resulting in decreased photostabilizing efficiency.

The excellent photostabilizing efficiency of the combined HALS–UV absorber stabilizers could be due to a “synergism” of the two, different in their action, stabilizer fragments. If the effect of the combination of two additives is larger than the sum of their separate effects when they are used alone, it is designated as synergism. Conversely, if the effect of the combination is smaller than the sum of the separate effects, it is called antagonism. Such definition of synergism suggests straightforward calculation of the additive effect for a combination of two stabilizers (*A* and *B*) and therefore of the determination of synergism or antagonism.

The additive effect of the combined stabilizers **3a–m** on the photostability of their copolymers with MMA and the additive effect of the combination of individual stabilizers on the photostability of the terpolymers were calculated by eq. (2) where the chain breaks per a polymer molecule (A_{AB})_{additive} is the additive effect of the combination of two stabilizers with relative amounts r_A and r_B , linked by eq. (3).³

$$(A_{AB})_{\text{additive}} = r_A A_A + r_B A_B, \quad (2)$$

$$r_A + r_B = 1. \quad (3)$$

The additive effect of the combined stabilizers was calculated at their concentration in the copolymers and the additive effect of the triple monomer mixture (terpolymerization)—at the concentration of the individual stabilizers in the terpolymers (Table I). The results obtained are listed in Table II. As can be seen, all of the bifunctional stabilizers show synergistic interaction between their HALS and UV absorber fragments (Fig. 8), which reflects up to 14 times decreasing of the *A* value with respect to the A_{additive} one.

The calculated additive effect of the individual monomer HALS and UV absorbers on their terpolymers with MMA was very close to the experimentally obtained *A* values. It was observed either slight synergism or slight antagonism, most probably because of the unequal distribution of the different in their action stabilizer fragments in the terpolymer chain.

CONCLUSIONS

As a result of this investigation, it can be assumed that the bifunctional HALS – UV absorber compounds—

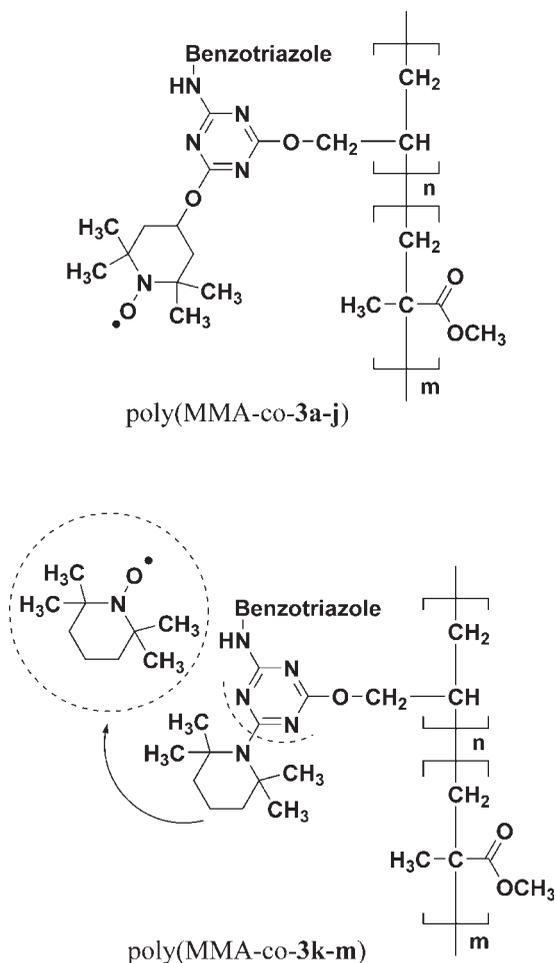


Figure 9 Nitroxyl radical formation in poly(MMA-*co*-**3a–j**) and poly(MMA-*co*-**3k–m**).

combination between two stabilizers, different in their action—are capable of copolymerizing with MMA and show high stabilizing effect on PMMA. Structure–activity relationship in the combined molecules was observed. It was established that the presence of both 2,2,6,6-tetramethylpiperidine and 2-hydroxyphenylbenzotriazole fragments together in the polymer significantly improve its photostability. Furthermore, strong expressed synergistic interaction between different HALS and UV absorber fragment in the combined stabilizers was demonstrated. Also, the photostabilizing effect of the combined stabilizers is better with respect to the mechanical mixture of the same stabilizers as individual monomers, most probably because of the equimolecular distribution of the two different stabilizer fragments in the polymer chain.

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