

PHOTO STABILIZERS FOR POLYMERS - NEW TRENDS (Review)

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ABSTRACT

This paper is a review presenting some new trends for photostabilization of polymers by application of polymerizable stabilizers, so that chemically or "self-stabilized" polymers can be obtained. The derivatives of 2-(2-hydroxyphenyl)-2H-benzotriazole (HBT) and 2,2,6,6-tetramethylpiperidine (HALS) are among the most effective stabilizers used, so their polymerizable derivatives have been the objects of many investigations. The combination of different types and chemical structures of stabilizers, acting according to different mechanisms, is a very promising method to obtain a new type of stabilizer.

The influence of these compounds on the photostability of copolymers with some vinyl monomers was demonstrated. New approaches for "one-step" coloration and stabilization of polymers by a combination "in-one molecule" of a chromophore and a stabilizer were described. Two of the possibilities are presented - when the stabilizer and the chromophore are combined in-one molecule through an s-triazine ring and - when the stabilizer's fragment is connected directly to the chromophore.

Keywords: 2-hydroxibenzophenone, 2-(2-hydroxyphenyl)-2H-benzotriazole, 2,2,6,6-tetramethylpiperidine, 2-amino-terephthalic derivatives, 1,8-naphthalimide derivatives, "one-step" coloration and stabilization of polymers.

INTRODUCTION

The photostabilization of polymers is of great importance and interest. It involves retardation or elimination of photochemical processes and can be obtained in many ways [1]:

1. Screening of radiation - in this case the photostabilizing activity consists of preventing the penetration of UV radiation into the material, thus limiting the degradation to the surface layer;
2. Absorption of radiation - the stabilizer absorbs first by UV light and then luminescence (fluorescence and phosphorescence) light;
3. Intersystem crossing - the UV absorber is excited to a triplet state in which a photochemical rearrangement can occur;
4. Internal conversion - the light energy absorbed is

converted into a vibrational one;

5. Quenching process - in this process the photostabilizer (quencher) deactivates the excited states (singlet or triplet) of the polymer. This is well known as the "energy transfer mechanism".

Different additives are applied to the materials in order to prevent or decrease their photodegradation. A large number of different types of compounds are described in the literature as photostabilizers. Besides Carbon black, some inorganic pigments such as iron oxides, chromic oxide (Cr_2O_3), red lead oxide (Pb_3O_4), titanium dioxide and ferro cyanides, are widely used in the polymer industry. Many organic pigments, such as azo-, anthraquinone, perylene, dioxazines and phthalocyanines are also applied.

The most important and efficient stabilizers are the organic ones, containing 2,4-hydroxybenzophenones,

s-triazines, hydroxyphenylbenzothiazoles and especially 2,2,6,6-tetramethylpiperidine (HALS) derivatives [2].

APPLICATION OF STABILIZERS AND ECOLOGICAL PROBLEMS

The most applied methods for stabilization of the polymers are “on surface” and “in-mass”. Both of them have some important disadvantages.

Method of surface stabilization

According to this method the polymer is treated with a stabilizing agent to lacquer covering or thermal fixation. The disadvantage of this method is that only the surface layer of the polymer is protected and it is vulnerable to mechanical influence.

Method of stabilization “in mass”

This is the most common method. It consists of mixing the stabilizer into the melt or into the polymer solution where the molecules of the stabilizer diffuse into the polymer or dissolve in it. In order to apply this method the stabilizers and the polymers must satisfy certain requirements. The stabilizer must be in a finely dispersed form in order to be able to diffuse or to dissolve into the polymer mass. The compounds have to be treated in advance by fine grinding to a definite size and mixed with other additives, facilitating the processes of diffusion. The main disadvantage of this method is that the resulting polymer is a mixture of higher and lower molecular fractions. The lower molecular substance (the stabilizer) may evaporate during the molding and extrusion processes and migrate to the surface of the polymer during storage and/or application. This can change some of the properties of the polymer. Besides, some widely applied polymers as polyesters and polyamides, due to the high density of their polymeric structure, have problems with this method of stabilization.

APPROACHES FOR SOLVING THE PROBLEMS

In the present study we will present the main trends in the synthesis and application of stabilizing additives, focusing our attention on the modern directions in the area. There are two ways of overcoming the problems:

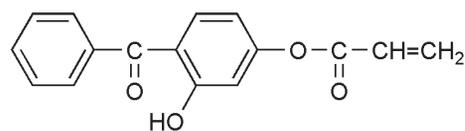
Chemical stabilization, when the stabilizer is connected by a covalent bond to the main or a side polymer

chain;

- Application of a polymeric photostabilizer, previously obtained.
- Photostabilizers for chemical stabilization
- To be applied in this manner the stabilizers have to possess suitable functional (polymerizable) group(s) in their molecule, to be able to copolymerize with the appropriate monomer, to be stable under the conditions of polymerization and the action of the initiators, and not to hinder the process of polymerization.

Derivatives of 2-hydroxybenzophenone

The polymerizing stabilizers of this type are some derivatives of 2-hydroxybenzophenones, containing acryl- (Formula 1), methacryl-, allyl- or vinyl- group [3-5].

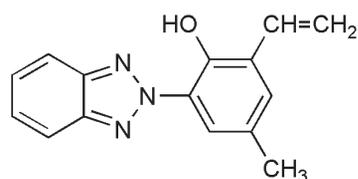


Formula 1

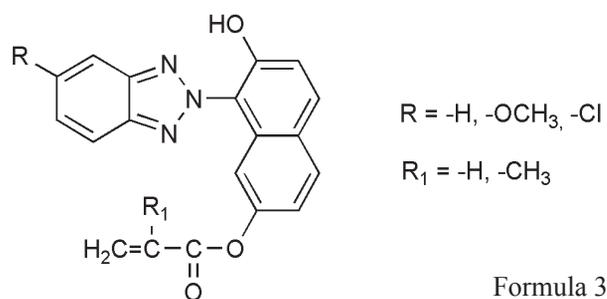
The UV stabilizers that are 2-OH-4-allyloxybenzophenones and oximes have been prepared as well [6] and their copolymers with styrene have been obtained. Later, 2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)benzophenone (BPMA) was synthesized to prepare poly(MMA-co-BPMA) by emulsion polymerization [7] and 2-hydroxy-4-(2-methacryloxyethoxy)benzophenone was obtained for copolymers with 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA) [8].

Derivatives of 2-(2-hydroxyphenyl)-2H-benzotriazole (HBT)

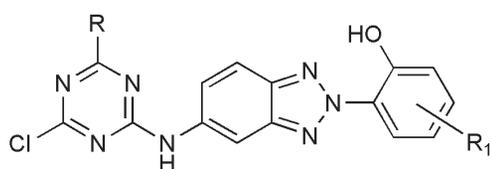
UV absorbers of 2-(2-hydroxyphenyl)-2H-benzotriazole have been extensively studied as well. Usually polymerizable derivatives were obtained when vinyl (Formula 2), allyl-, acryl- and methacryl (Formula 3) groups were introduced in the benzene or in the naphthalene ring [9,10]. Their copolymers with MMA were obtained and investigated.



Formula 2



In our earlier papers we also reported the synthesis of some functional (polymerizable) 2-hydroxyphenyl-benzotriazole stabilizers, 1,3,5-triazine derivatives [11-13]. They can be presented with the general Formula 4.

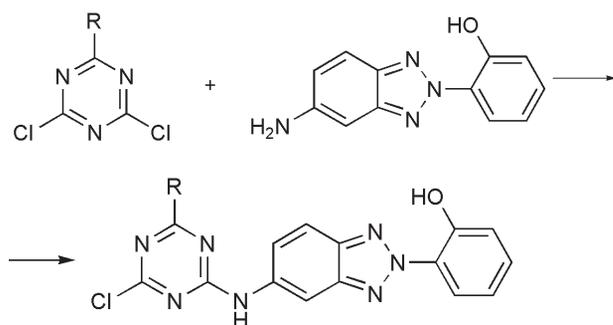


R = -OCH₂CH=CH₂, -NHCH₂CH=CH₂, -N(CH₂CH=CH₂)₂

R₁ = -Cl, -CH₃

Formula 4

The main advantage of these compounds is that the polymerizable group is isolated from the benzotriazole part of the molecule, thus preventing any influence of this group on the stabilizing action of the whole compound. Furthermore, the synthesis of such compounds is easily accomplished by acylation of the amino group in the benzotriazole ring with cyanuric chloride. The polymerizable group (allyloxy or allylamino) can be involved easily in the triazine fragment previously (Scheme 1 where R are residues of allyl alcohol, allyl- or diallylamine).

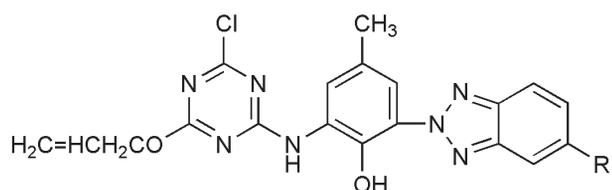


Scheme 1

The ability of 2-(2-hydroxyphenyl)-2H-benzotriazole compounds (HBT) to copolymerize with different monomers was studied. Their copolymers with styrene and MMA were obtained and the covalent bonding of the HBT fragment spectrophotometrically and by TLC was approved. It was found that over 50 – 90 % of the HBT in the initial monomer mixture (depending on their chemical structure) reacted to participate in the polymer chain, which was enough to provide a good photostability of the copolymers compared to those of the homo polymers [12 - 14]. These results related to reprecipitated polymers and, that during this reprecipitation, not only the unreacted monomers, but also some of the lower molecular fractions, containing bound HBT, were removed. This percent content can be considered to be satisfactory.

The concentration of 0.1 mass % of the HBT in the initial monomer mixture was suitable to achieve the good stabilizing effect (the chain breaks at number [12] A = 0.06 - 0.08 for polystyrene and 0.03 - 0.1 for co-polyMMA). Maximum stability was observed for 1 mass % initial concentration of the stabilizer. Spectrophotometrically was determined, that between 55 – 65 % of the HBT in the initial monomer mixture reacted and bonded covalently to the polymer. Investigations of the kinetics of copolymerization of the compounds with styrene and MMA were carried [14,15]. These investigations showed that the participation of the monomer HBT in the copolymerization of styrene slightly retarded the process without significant effect on the molecular mass and the thermostability of the copolymers [15], while the same HBT did not affect or slightly accelerated the rate of copolymerization of MMA [14, 16].

Bojinov [17] published the synthesis of the polymerizable HBT derivatives shown in Formula 5, where R are -H or -CH₃

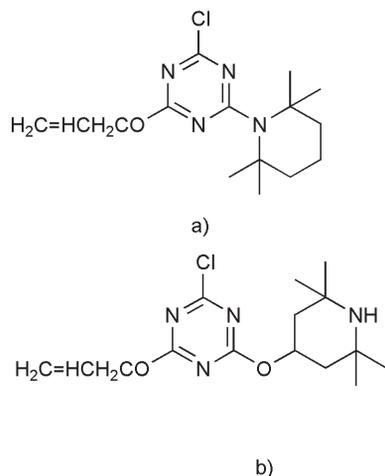


Formula 5

It was determined that these compounds copolymerized with MMA and had a good stabilizing effect (the chain breaks number A is between 0.17 - 0.23).

Derivatives of 2,2,6,6-tetramethylpiperidine (HALS)

These derivatives are of great interest due to their high photostabilizing efficiency [1]. Our experience on the synthesis of polymerizable HBT stabilizers provoked our interest to synthesize similar derivatives, but of 2,2,6,6-tetramethylpiperidine (TMP). Together with V. Bojinov two new polymerizable triazinyl-2,2,6,6-tetramethylpiperidine (TTMP) compounds were synthesized [18, 19] (Formula 6a and 6b).



Formula 6

Their copolymers with styrene were obtained and it was determined that the concentration of 0.1 mass % in the initial monomer mixture did not affect the rate of the process, the molecular mass and the polydispersity of the copolymer, at the same time providing a significant photostabilizing effect.

Later, Bojinov published the synthesis of polymerizable stabilizers that are a combination of a HBT and 2-hydroxibenzophenone or TMP fragment in one molecule [17, 18, 20 - 22]. It is important to note the excellent approach, based on our earlier formulated idea [12], using an s-triazine ring as an isolating link, to combine in one molecule two different in their mechanism of action photostabilizers together with a polymerizing group, is successfully demonstrated in these studies. The copolymers of these compounds with acrylonitrile (AN) and MMA were obtained and their influence on the photostability of the copolymers was studied. A significant stabilizing effect of the combined structures, in comparison with the action of the single (HBT or TMP) monomers bonding in a ter-polymer was found.

All these investigations demonstrated the possibility for stabilization of polymers by covalent bonding of

suitable stabilizer(s) to the polymer molecule, i.e. the synthesis of self-stabilized polymers.

Another very interesting approach in this direction is the possibility for “one-step” coloration and stabilization of polymers.

Photo stabilizers for “one-step” stabilization and coloration

The possibility of “one-step” coloration and stabilization of polymers is especially attractive. Realization of this idea, besides the other advantages, would improve the ecological behavior of the polymers, especially of these that are applied for preparation of food packages or children toys. The possibility of a combination of these two components in one molecule which was much more attractive, was realized in the last years. There are two approaches to achieve this:

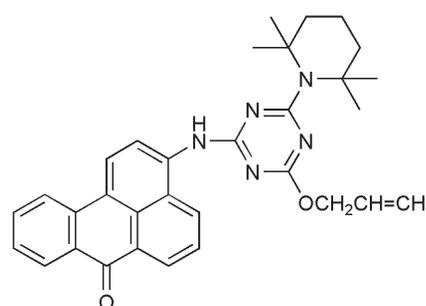
- When the stabilizer and the chromophore are combined in one molecule through an s-triazine ring;
- When the stabilizer’s fragment is connected directly to the chromophore.

Each of them has some advantages and disadvantages. Bojinov, Konstantinova and others experimented both of the above mentioned possibilities, starting with the first one.

Compounds where a stabilizer and a chromophore are combined in one molecule through a s-triazine ring.

The triazine ring is a well-known fragment, which is isolating the electron system of the chromophore from other substituents (the stabilizer and the polymerizing group), thus enabling these two parts to act independently.

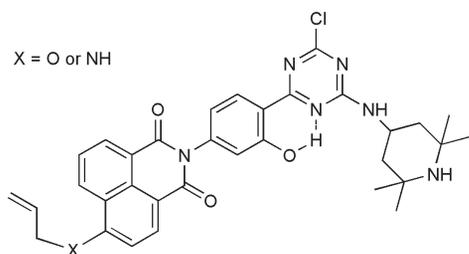
Based on the synthesis of the polymerizable triazinyl TMP stabilizers published before [19], we have studied the synthesis of a compound that combines in one molecule, through an s-triazine fragment, a benzanthrone chromophore, a TMP stabilizer and a polymerizable allyloxy group (Formula 7) [23].



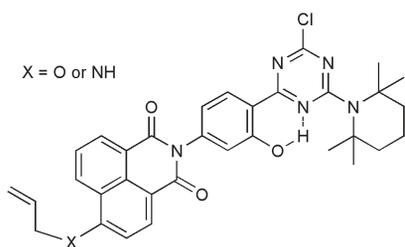
Formula 7

The copolymer of styrene with this combined molecule was obtained. Studies on the influence of the compound on the kinetics of the copolymerization as well as on the properties of the copolymer have been investigated. It was found that the participation of the combined molecule did not affect the rate of the process, when compared to that for the polymerization of pure styrene, the copolymerization with a single dye, or with a stabilizer. The stabilizing effect of this compound on the photodegradation of the Poly-St was excellent. For example, the chain breaks number A after 10 h irradiation of the copolymer in a Suntest test (UV light with $\lambda_{\max} = 290 \text{ nm}$) was 0.002, when the same number for the ter-copolymers, obtained with the mixture of three monomers - St, single monomer dye and monomer stabilizer was 0.011.

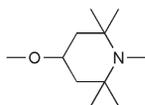
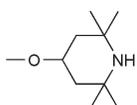
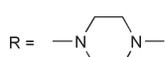
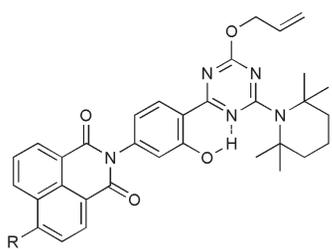
Bojinov and co-workers published the synthesis of a combined in one molecule, through an s-triazine absorber, a 1,8-naphthalimide or 9-phenylxanthene chromophore, a TMP stabilizer and a polymerizable allyloxy group (Formulas 8 - 12) [24 - 28].



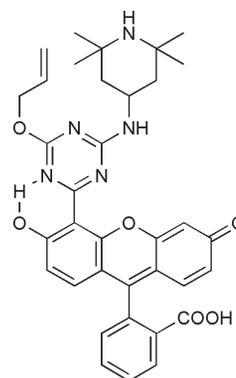
Formula 8



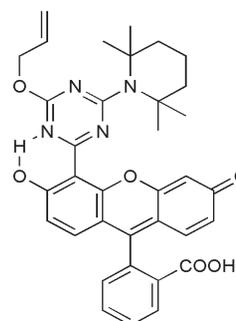
Formula 9



Formula 10



Formula 11

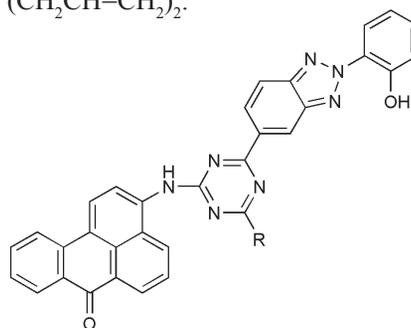


Formula 12

The ability of the combined dyes to copolymerize with acrylonitrile was demonstrated as stable to solvents of polyacrylonitriles with an intense colour, and fluorescence was obtained.

It was found that the incorporation of the dyes into the polymer chain significantly improved their photostability. A stabilizing effect was achieved at 0.1 mass % initial concentration of the compounds, which made them suitable for “one-step” colouration and stabilisation of polyacrylonitrile.

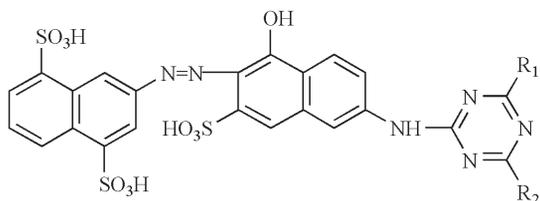
Later on, we decided to use the same benzanthrone chromophore as a color fragment to synthesize some combined structures, where the stabilizer was a HBT [13]. The compounds synthesized can be presented with formula 13, where R are different polymerizing groups like $-\text{OCH}_2\text{CH}=\text{CH}_2$, $-\text{NHCH}_2\text{CH}=\text{CH}_2$ or $-\text{N}(\text{CH}_2\text{CH}=\text{CH}_2)_2$.



Formula 13

Copolymerization of MMA with these novel monomer combined structures was investigated [16]. Chemical bonding of the compounds in the polymers obtained was confirmed (spectrophotometrically) to be over 50 %, providing a color and a fluorescence stable to solvents. It was found that the compounds under study did not affect considerably the rate of copolymerization. All compounds at 0.1 mass % initial concentration showed a positive stabilizing effect ($A \gg 0.02 - 0.03$) on the photodegradation of PMMA, and there was no significant difference, whether the monomers were applied as a combined molecule or as an individual structure.

Azodyes are among the dyes with a mediocre photostability. That is why it was interesting to study the possibility to synthesize some combined derivatives, using an azodye as a chromophore system [29 - 31]. These can be presented with Formula 14, (the meanings of R_1 and R_2 are presented in Table 1).



Formula 14

Table 1. Meanings of R_1 and R_2 in Formula 14.

Dye No	R_1	R_2
14.1		-Cl
14.2		-NHCH ₂ CH=CH ₂
14.3		-OCH ₂ CH=CH ₂
14.4	-NHCH ₂ CH=CH ₂	-Cl
14.5	-OCH ₂ CH=CH ₂	-Cl

Compounds **14.4** and **14.5** were synthesized in order to compare their properties to those of the derivatives, containing a stabilizer fragment in the molecule. Copolymers of compounds **14.2 - 14.5** with acryl amide (ACA) and acrylonitrile (AN) with an intense colour stable to solvents, were obtained. It was established that over 90 % of the dye in the initial monomer mixture reacted in copolymerization and there was a covalent bound in the polymer. The influence of the dyes on the photostability of copolymers was studied measuring their molecular mass M_n before, and after 8 h of irradiation. The data obtained for copolymers with ACA are presented in Fig. 1.

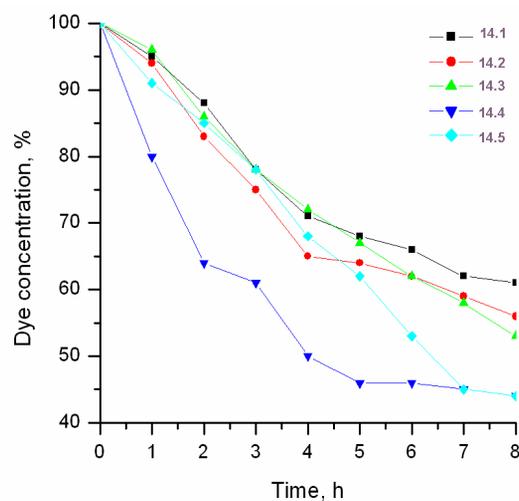
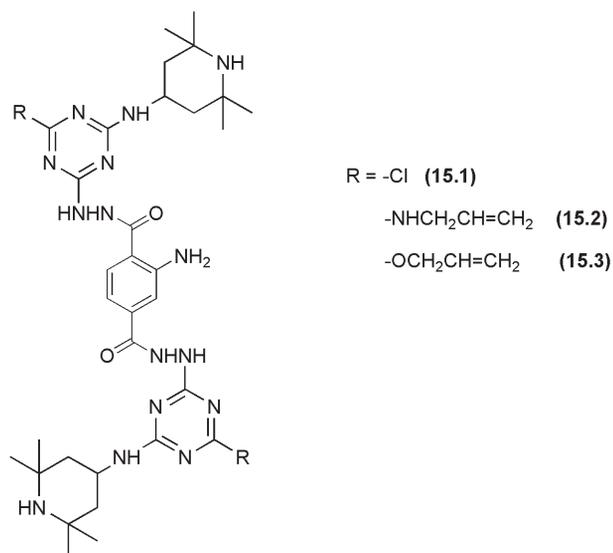


Fig. 1. Dependence of the concentration of the dye (%) in polymer PACA on the time of irradiation (h).

It can be seen from this figure that the combined structures, containing an azo dye, a TMP fragment and a polymerizable group have the best stabilizing effect on the photodegradation of the polymer, and should be recommended.

The derivatives of 2-aminoterephthalic acid (ATA) are of interest because of their intense blue-violet fluorescence and good thermostability [32] with fluorescent whitening agents (FWA), widely applied to all kinds of textile and polymer materials [33]. With this in mind, it was interesting to study the synthesis of some functional derivatives of ATA, which contained a polymerizable group and a stabilizer fragment in their molecule with Formula 15 [34].



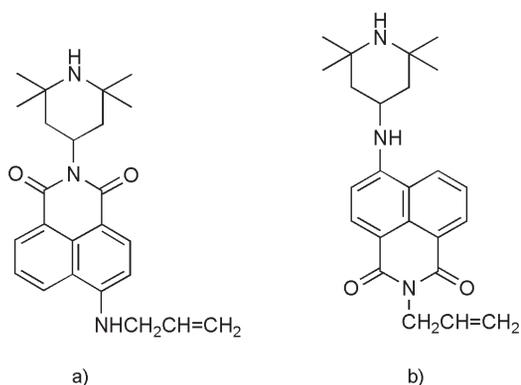
Formula 15

In order to compare the photostabilizing properties of compounds 15.1 - 15.3, the same derivatives without TMP were synthesized. Copolymerization of MMA with 15.2 and 15.3 and whitening of methyl methacrylate "in mass" with 15.1 was accomplished. The copolymers obtained have an intense stable to solvents fluorescence. It was determined that 78 – 82 % of the compound in the initial monomer mixture reacted in copolymerization and was covalent bound in the polymer. The influence of the FWAs on the photostability of copolymers was studied measuring their molecular mass M_n before, and after 8 h of irradiation. The photostability of the compounds, thus included in the polymer, increased with 22 % in comparison to those without TMP [35].

Combined structures where the stabilizer's fragment is directly connected to the chromophore

A direct connection of the stabilizer to the chromophore in most of the cases will be easily achieved, but this direct connection could affect properties of the chromophore like color and/or luminescence. Nevertheless, recently this idea has been the object of many studies.

Derivatives of 1,8-naphthalimide are well known as dyes for mass coloration of polymers, markers and so on, due to their bright color and an intense fluorescence. Bearing this in mind, in earlier papers [36] Bojinov and Konstantinova studied the possibility for obtaining 1,8-naphthalimide derivatives, containing a TMP stabilizer in their molecule. These compounds can be presented with Formula 16a and 16b.

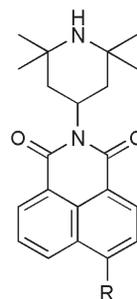


Formula 16

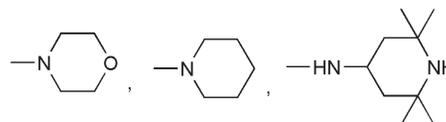
The ability of these two compounds to copolymerize with AN and MMA was demonstrated and the properties

of the copolymers were investigated [37]. Firstly, the photostability of the compounds themselves was studied and compared to those of some similar structures, not containing a TMP moiety in their molecule. It was observed that the photostability of the compounds with Formula 16a and 16b was between 83 – 86 %, which was 18 – 20 % higher than that for the other derivatives. The influence of the compounds on the stability of the copolymers with AN was studied. The data obtained showed that the chain-breaks number A for the copolymers after 10 h of irradiation were 0.13 (16a) and 0.05 (16b), when for the pure PMMA it was 1.66. Even applied "in-mass" these combined structures at the same concentration provided an intense color and fluorescence, and the same stabilizing effect (0.04).

Besides the synthesis of polymerizable structures, a combination between a dye and a stabilizer, it was of interest to obtain and study similar derivatives, not polymerizable, suitable for traditional application to the polymers and textile. Eight derivatives with Formula 17, containing a TMP fragment were synthesized [38]. The meanings of R in the molecule are different traditionally used amines.



R = $-\text{NHC}_2\text{H}_5$, $-\text{N}(\text{C}_2\text{H}_5)_2$, $-\text{NHCH}_3$, $-\text{N}(\text{CH}_3)_2$, $-\text{Br}$



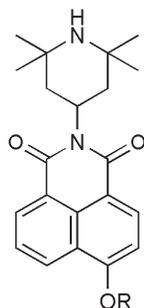
Formula 17

Photostability of the compounds in solution, in polymer (PMMA) and on polyamide fabrics was studied. Their stability was very good (over 90 % of the compounds remained after 2h of irradiation). Two of the compounds showed good stabilizing effect on the photodegradation of PMMA

and could be recommended for “one-step” coloration and stabilization of PMMA [38].

Furthermore, some fluorescent derivatives of 1,8-naphthalimide, containing a tetramethylpiperidine (TMP) stabilizer fragment, were synthesized [39, 40].

They have Formula 18, where the meanings of R are $-\text{CH}_3$, $-\text{CH}_2\text{CH}=\text{CH}_2$ or $-\text{CH}_2\text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$.



Formula 18

They absorbed in the near UV region and had a blue fluorescence, so they can be applied as FWA. Two compounds copolymerized with methylmethacrylate (MMA) and copolymers with an intense bluish fluorescence, stable to solvents, were obtained [39]. The participation of the monomer compounds did not affect significantly the process of copolymerization and the molecular masses of the copolymers obtained. The quantity of chemically bonded monomer in the copolymers was determined to be over 60 %. The spectral properties of the compounds, their photostability in solution and in co-polymer, their influence on the photostability of the copolymers were determined. The compounds showed a good positive stabilizing effect on the photodegradation of PMMA.

The synthesis of some triazine-stilbene fluorescent whitening agents, containing a phenolic antioxidant in the triazine molecule, has been reported as well [41].

Bojinov and co-workers presented the synthesis of polymerizable 1,8-naphthalimide, benzanthrone and 9-phenylxantene derivatives, containing a HBT or a TMP moiety [42 - 47] or both TMP and HBT stabilizer's fragments in their molecule [48 - 53]. They showed very good photostability in solution and in polymer. Their influence on the photodegradation of the corresponding polymers was studied and a good stabilizing effect was found.

CONCLUSIONS

Based on this review the following conclusions can be made:

Stabilization of polymers is an important problem and there are lots of investigations, having both practical and/or theoretical (fundamental) contribution.

Modern trends for solving the problem are related to the synthesis of functional (polymerizable) stabilizers, providing resistance to wet treatment, solvents and migration stabilization, by their incorporation in the polymer chain.

An important new trend is the synthesis of compounds that are a combination in-one molecule of two different by their mechanism of action stabilizers, with a polymerizable group.

The investigations connected to the synthesis of the structures, where a chromophore, a stabilizer and a polymerizable group are combined in one molecule, presenting the possibility for “one-step” coloration and stabilization of polymers are of special interest.

All these trends have very important ecological contribution, presenting a possibility to obtain the polymers with ecologically more compatible behavior.

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