



The application of halomethyl 1,3,5-triazine as a photoinitiator or co-initiator for acrylate monomer polymerization

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ABSTRACT

2,4-Bis-(trichloromethyl)-6-(4-methoxy)phenyl-1,3,5-triazine (XL-353) as a new radical reactive photoinitiator has been used for UV-crosslinking of acrylic pressure-sensitive adhesives containing double bonds. On the other hand, this compound in the presence of suitable sensitizers acts as a very effective co-initiator in two- and three-component photoinitiating systems under a visible light. It is shown, that the use of 1,3,5-triazine derivative (XL-353) in a three-component photoinitiating system leads to an increased efficiency of the polymerization reaction under visible light irradiation in comparison with two-component ones.

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1. Introduction

Radiation curing technologies provide a number of economic advantages over the usual thermal operation among them: rapid through cure, low energy requirements, room temperature treatment, non-polluting, solvent-free formulations and low costs. They use light beams to start photochemical and chemical reactions in organic materials to form a new polymeric material.

Photoinduced polymerization reactions of monomers and oligomers cover a particular area in the field of polymer science. Photochemical processes occurring in the suitable compounds are basically important to initiate the reaction. In most cases, the photoinitiation step of a polymerization reaction requires the presence of a molecule (photoinitiator PI), which absorbs the exciting light and undergoes the fragmentation to radical, cationic or anionic species onto monomer, through processes which occur in its excited states [1].

The intrinsic reactivity of a photoinitiator which plays an important role on curing speed determines its interest and is directly connected with (i) its molecular structure (which governs the intensity of the light absorbed, the absorption wavelength range, the energy or electron transfer reactions ability) and (ii) the efficiency of the photophysical and photochemical processes involved in the excited states (which determines the yield of cleavage reactions, electron transfer reactions, quenching by monomer or

oxygen other additives such as, e.g. hydrogen donors, light stabilizers, interactions with photosensitizer).

Applications of UV-crosslinking polymerization reactions are largely encountered in the industrial radiation curing area. Industrial applications of UV crosslinkable pressure-sensitive adhesive (PSA) materials have grown tremendously over the past decade. An entire industry has evolved based on the existence of compounds, which respond to UV radiation. The growing success of UV crosslinking technologies in a wide variety of industrial products and processes can be attributed to the productivity and environmental benefits that result from such technologies. UV technology is well established in the market and allows the production of a wide range of UV-crosslinkable pressure-sensitive adhesives with interesting features. Growing applications are expected, e.g. in thick pigmented coating, multi-layer coatings, antistatic coatings, good weatherability or scratch resistance coatings, coatings with good adhesion on metal, spray coatings, silicon coatings, water reducible coatings, coatings for exterior applications, optical fibre coatings, UV cured powders, pressure sensitive adhesives PSA, solvent free PSA, hot melt adhesives, laminating adhesives, optically clear adhesives, lenticular films, flexographic inks, UV inks and OPV's for food packaging, UV inkjet inks, UV gravure printing, metal decorating, wood protection products, automotive uses (plastic parts, metal) and automotive refinishing, stereolithography, 3D inkjet printing, 3D microfabrication with two-photon PIS, nanocomposites, photolatent base technology [1].

The balance between adhesive and cohesive strengths within the crosslinked coatings is critical for their performance [2–4]. It is necessary to find process settings that lead to balanced values of tack, peel and shear resistance for the aimed application [2,5,6].

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Extension of the spectral sensitivity of a photoinitiator can be achieved by addition of a photosensitizer PS which will absorb the light and then transfer the energy to PI. Accordingly to the applications which are developed, the advantages of such a shift in the wavelengths used are, for example: (i) the recovery of visible photons emitted by the Hg lamps which are lost when the light is absorbed only by a UV photoinitiator, (ii) a better matching of the emission spectrum of the light source and the absorption spectrum of the sample when laser light is used, (iii) the possibility to find spectral windows when pigmented formulations have to be polymerized, (iv) the opportunity to use the sunlight for the curing of outdoor coatings. Such multi-component photoinitiating systems PIS (containing PI, PS and optionally additives) are very often used to polymerize pigmented formulations under a visible light.

The photopolymerization is traditionally initiated by direct photolysis of a precursor to provide free radicals by bond photodecomposition. It needs the energy from the ultraviolet or blue region of a visible light. But the panchromatic sensitization of vinyl polymerization requires the presence of suitable dye as a light absorber [1].

Typical photoinitiating systems are classified in:

- One-component
- Two-component (working, e.g. through electron transfer/proton transfer, energy transfer, photoinduced bond cleavage via electron transfer reaction, electron transfer).
- Three-component (where the basic idea is to try to enhance the photosensitivity by a judicious combination of several components)
- Multi-component (more than three partners).

As it was previously mentioned, a photoinitiator is one of the important and necessary components in UV crosslinking of pressure-sensitive adhesives [7,8]. Bis-(trichloromethyl)-substituted 1,3,5-triazine derivatives are very often used as the crosslinking agents and photoinitiators of free radical polymerization [9].

Photoinduced polymerization of an acrylic monomer mixture containing 1,3,5-triazine derivative alone took place under irradiation with UV-visible light ($\lambda > 300$ nm) but not when a light at $\lambda > 450$ nm was used.

Among few examples of UV or near visible photoinitiators, the substituted bis(trichloromethyl)-s-triazine derivatives are widely mentioned in the patent literature, alone or in the presence of the sensitizers or/and co-initiators, such as titanocene, peroxide/amine or mercaptan [10–12].

Buhr et al. studied various 2-substituted 4,6-bis(trichloromethyl)-1,3,5-triazines in solution using direct excitation [13]. The application of 1,3,5-triazine derivatives enhances sensitivity to a thermally activated, acid-catalyzed cross-linking step which results in cross-linking quantum yields greater than 1. Thus, a key element in all resist systems is a compound that yields an acid as one product of photolysis, a so-called photoacid generator (PAG). A wide range of acids can be generated by a variety of PAGs, including carboxylic acids, sulfonic acids, hydrogen bromide and hydrogen chloride [14].

One of the ways of changing the response range of the PAG is photosensitization of the triazine using an appropriate sensitizer that absorbs in the spectral region of interest [14].

Visible photosensitizers (mostly referred as dyes) are attractive systems either for a direct initiation through visible light (conventional lamps or laser beams or even sun) or to increase the energy dose received by a substrate irradiated by a polychromatic light.

The finding of efficient PIS under visible lights allows to explore the possibility of sun curing [1].

For example, high speed photoinitiating systems sensitive to a visible light were developed on the basis of initiating systems, using cyanine or merocyanine dyes or 3,3'-carbonyl(coumarine) derivatives [15–17].

The present paper is focused on the application of 2,4-bis-(trichloromethyl)-6-(4-methoxy)phenyl-s-triazine as both photoinitiator and co-initiator in photopolymerization reactions and intends to provide: (i) an approach of the photochemical reactivity of these systems, (ii) an overview on the structure/properties relationships, (iii) an example of investigation of the processes involved, and (iv) typical applications in the field of the photocuring. The reactivity of UV radical photoinitiator and photosensitizers systems for high speed photopolymers is also described.

2. Experimental

2.1. Materials

2.1.1. Basic acrylic pressure-sensitive adhesive (PSA)

All starting materials such as acrylate monomers, solvent and AIBN were technical grade and were used without further purification unless otherwise noted. Other photoreactive crosslinking agents were synthesized in the laboratory scale with about 98% of purity.

The following experiments were conducted using standard solvent-borne acrylic PSA synthesized from 61.7 wt.% of 2-ethylhexyl acrylate, 33 wt.% of methyl acrylate, 5 wt.% of acrylic acid and 0.3 wt.% 1,6-hexanedioldiacrylate in ethyl acetate as a solvent at the boiling point temperature about 77 °C. 2,2'-Azo-bis-diisobutyronitrile (AIBN) in the amount of 0.1 wt.% was used as the thermal initiator to start radical polymerization.

The polymerization process was conducted under the following conditions:

- | | |
|--|---------|
| • addition of monomers blended with AIBN into ethyl acetate before the polymerization (reactor charge) | 50 wt.% |
| • dosage time of residual monomers with residual AIBN | 1 h |
| • time of post-reaction | 5 h |

2.1.2. The kinetic of free radical polymerization

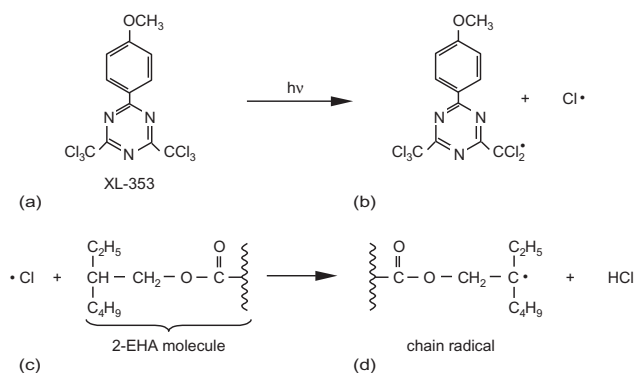
Following polymethine dyes were used as sensitizers: mono-cationic hemicyanine dyes: styrylquinolinium dye (dye I), styrylbenzothiazolium dye (dye II); two- and four-cationic monomethine dyes (dye III and dye IV) and mono-cationic thiocarbocyanine dye (dye V).

The following compounds were investigated as co-initiators: 2-mercaptobenzothiazole (Aldrich, purity 98%), 2-mercaptobenzoxazole (Aldrich, purity 95%), 2-mercaptobenzimidazole (Aldrich, purity 98%) and 2,4-bis-(trichloromethyl)-6-(4-methoxy)phenyl-1,3,5-triazine. They were used as received. 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and 1-methyl-2-pyrrolidinone (MP) were purchased from Aldrich and used as monomer and solvent, respectively.

2.2. The influence of 1,3,5-triazine on the main performance of solvent-borne acrylic pressure-sensitive adhesives

The tack, adhesion and shear strength (cohesion) were determined by standard A.F.E.R.A. (Association des Fabricants Européens de Rubans Auto-Adhésifs) procedures. Exact details can be found in AFERA 4015 (tack), AFERA 4001 (peel adhesion) and AFERA 4012 (shear strength). Administrative address: 60, rue Auber-94408 Vitry Sur Seine Cedex, France.

The coating weight (thickness of the layer) of dry pressure-sensitive adhesives after the removal of the organic solvent



Scheme 1. Mechanism of *s*-triazine photoreactive crosslinker photolysis.

influences essentially their tack, peel adhesion and shear strength. The base weight of the adhesive layer covering the polyester foil was 60 g/m².

The viscosity of the investigated solvent-borne acrylics pressure-sensitive adhesives was determined with a Rheomat RM 189 from Rheometric Scientific, with spindle No. 3 at 23 °C.

The evaluated photoreactive UV-crosslinked pressure-sensitive adhesives were cured with a ultraviolet light lamp U 350-M-IDL from IST Company with a UV-A wavelength between 315 and 380 nm.

Three samples were tested for each adhesive property.

2.3. Polymerization kinetics

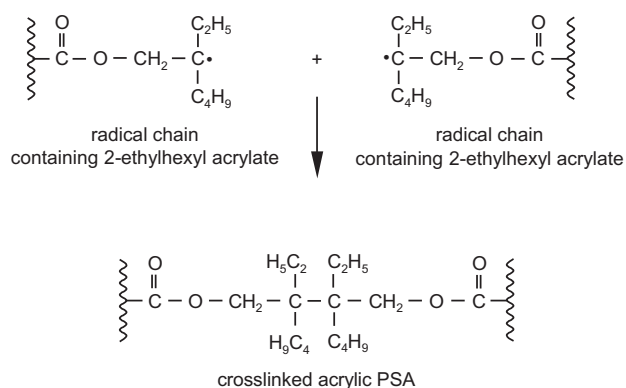
Photoinitiated polymerization rate (R_p) profiles were determined by a differential scanning calorimetry (DSC), under isothermal conditions at room temperature using a photo-DSC apparatus constructed on the basis of a TA Instruments DSC 2010 Differential Scanning Calorimeter. The 0.035 ± 0.002 g of sample was polymerized in open aluminium pans having the diameter of 6.6 mm. The irradiation of the polymerization mixture was carried out using the visible emission (488 and 514 nm) of an Air-cooled Ion Laser Systems model 177-G01 (Spectra-Physics, USA). The average power of irradiation was 20 mW/0.196 cm² at 514 nm. The light intensity was measured by a Coherent Model Fieldmaster power meter.

A polymerization solution was composed of 1 mL of 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). The polymethine dye concentration used in experiments was 1 × 10⁻³ M. The co-initiators concentrations were varied from 5 × 10⁻³ M to 5 × 10⁻² M. As a reference sample, a polymerizing mixture containing cyanine iodide (dye without a co-initiator) was used. The polymerizing mixture was not deaerated. In order to reduce the effect of diffusion-controlled termination, the effect of a network formation, the Norrish–Troomsdorf effect and radicals trapping effect, the initial rates of polymerization were taken into account for further consideration.

3. Results and discussion

3.1. 1,3,5-Triazine derivative as a photoinitiator (basic acrylic pressure-sensitive adhesive (PSA))

The efficiency of bis-trichloromethyl-*s*-triazines as photoinitiators in radically initiated photocrosslinking systems, as well as photoacid generators, may be explained and described by the mechanism outlined in Scheme 1.



Scheme 2. UV-crosslinking of acrylic pressure-sensitive adhesives by use of photoreactive *s*-triazines.

Electronically excited fragments (a) suffer homolytically transformation to the radical (b) and a chlorine radical, which abstracts hydrogen from a donor (c) resulting in the formation of hydrogen chloride and the radical (d). While hydrochloric acid serves as the catalyst in chemical amplification systems the chain radical (d) may be used to start a chain crosslinking reaction (Scheme 2).

The influence of the tested *s*-triazine photoreactive crosslinking agent (ranging from about 0.2 to 3.0 wt.%) on solvent borne acrylic pressure-sensitive adhesive properties, such as tack, peel adhesion and shear strength, at 100 mJ/cm² UV dose after 3 min UV-crosslinking time is presented in Figs. 1–3.

It was unequivocally shown (Fig. 1) that the investigated photoreactive *s*-triazine crosslinker (XL-353) in amounts of 0.2–0.8 wt.% increases the tack of UV-crosslinked solvent-borne acrylic pressure-sensitive adhesives. The tack maximum remains at the same level until the amount of added XL-353 is lower than 1 wt.%.

The peel adhesion results presented in Fig. 2 show that the photoreactive *s*-triazine crosslinker increases the peel adhesion of UV-crosslinked acrylic PSAs.

The shear strength after UV-crosslinking is proportional to the concentration of the photoreactive *s*-triazine XL-353 (Fig. 3). During the UV-curing reaction, the elastomeric acrylic PSA chains react with each other to form chemical crosslinks. At a certain stage, after application of the photoreactive *s*-triazine crosslinker XL-353, a very strong chemical 3-dimensional network is created.

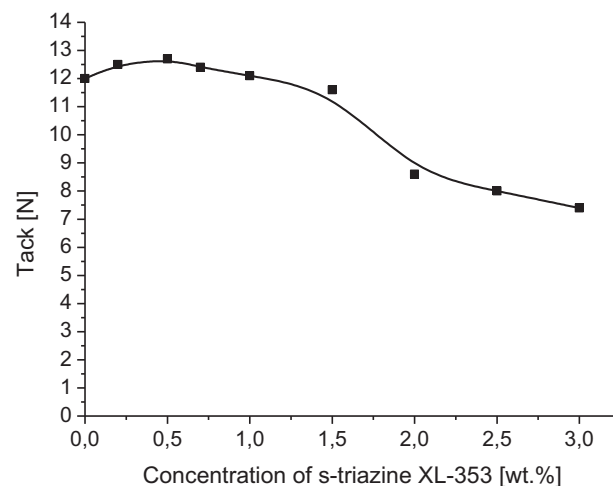


Fig. 1. Tack of UV-crosslinked acrylic PSA as a function of *s*-triazine photoinitiator XL-353 concentration.

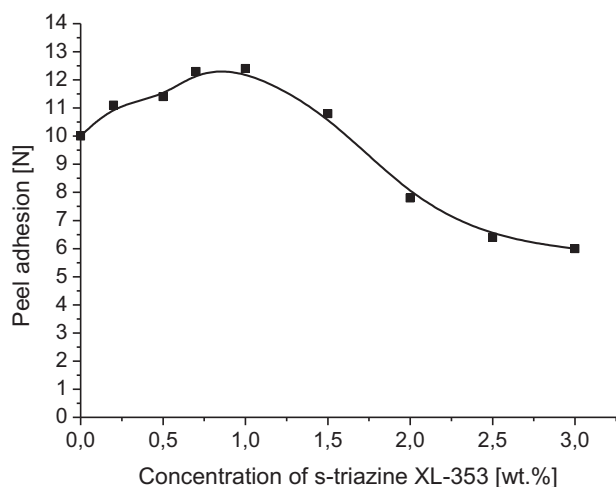


Fig. 2. Peel adhesion of a UV-crosslinked acrylic PSA as a function of the s-triazine photoinitiator XL-353 concentration.

For tested s-triazine XL-353, the measured temperature resistance (shear strength at 70 °C) was on the very low level.

For UV technology it is essential to define an operating window, where the acrylic PSA exhibits good tack, good adhesive properties, and sufficient mechanical resistance. The combination of these main different properties in an acrylic PSA layer containing a photoreactive s-triazine crosslinker can be achieved with XL-353, in an amount ranging between 0.8 and 1.0 wt.-%.

The extent of crosslinking is dependent upon the UV-crosslinking time and upon the energy imparted to the PSA layer, which in UV curing is a function of the UV lamp power. The further investigations with UV-crosslinkable acrylic PSAs containing the chosen photoreactive s-triazine crosslinker XL-353, in concentrations between 0.5 and 1.5 wt.-%, were conducted with UV-crosslinking times between 30 s and 3 min and by using a UV lamp dose between 50 and 250 mJ/cm². For illustration, the selected experimental results are presented in Figs. 4 and 5.

At relatively high concentrations (1.0 and 1.5 wt.-%) of XL-353, the UV-crosslinked acrylic PSAs become harder and the tack reduced. As a result of these findings, the highest tack value was achieved with 0.7 wt.-% photoreactive crosslinker XL-353 after a UV-exposure of 1 min. But the peel adhesion increased with irradiation time and was the highest for 0.7 wt.-% photoreactive s-triazine crosslinker XL-353 after 3 min crosslinking time.

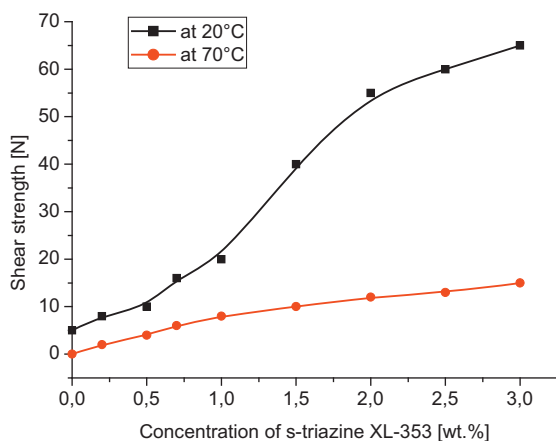


Fig. 3. Shear strength of a UV-crosslinked acrylic PSA as a function of the s-triazine photoinitiator XL-353 concentration.

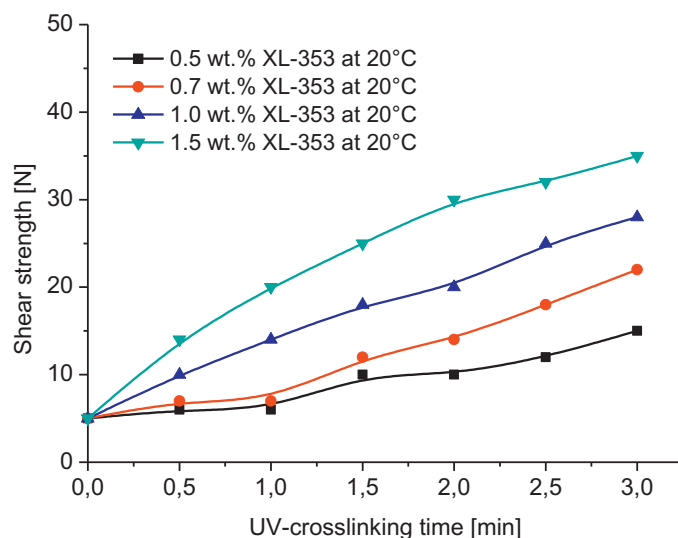


Fig. 4. Shear strength of a UV-crosslinked acrylic PSA as a function of UV-crosslinking time for various amounts of the photoreactive s-triazine XL-353.

As it is shown in Fig. 4 the use of the photoreactive s-triazine crosslinker XL-353 in increased amounts yielded satisfactory shear strength values, measured at 20 °C and 70 °C, after the relatively long UV-crosslinking time of 3 min (Fig. 4). The noticed shear strength at 20 °C was of a similar level to the obtained by the use of typical hydrogen atom abstracting photoinitiators. From Fig. 4 it is seen, that the shear strength of 1.5 wt.-% of XL-353 at 1 min is 20 N and that at 3 min is 34 N. The increase of UV-crosslinking time from 1 min to 3 min allows an increase of the shear strength at room temperature using s-triazine XL-353 by about 1.7 times.

With the increase of the UV dose to 250 mJ/cm², the tack of s-triazine free layer and acrylic adhesive containing 1.0 and 1.5 wt.-% of XL-353 decreases. The tack maximum was found for 0.5 wt.-% XL-353 at about 100 mJ/cm² UV dose.

The highest peel adhesion value was indicated for 0.5 wt.-% XL-353 at 150 mJ/cm² UV radiation. After application of this UV power, the investigated peel adhesion of UV-crosslinked pressure-sensitive acrylic adhesives decreases.

The shear strength results at 20 °C show that the cohesion of UV-crosslinked acrylic PSAs (Fig. 5) is proportional to the amount of the photoreactive crosslinker XL-353 used and to the UV dose. The achieved cohesion values at 20 °C were similar, or slightly better

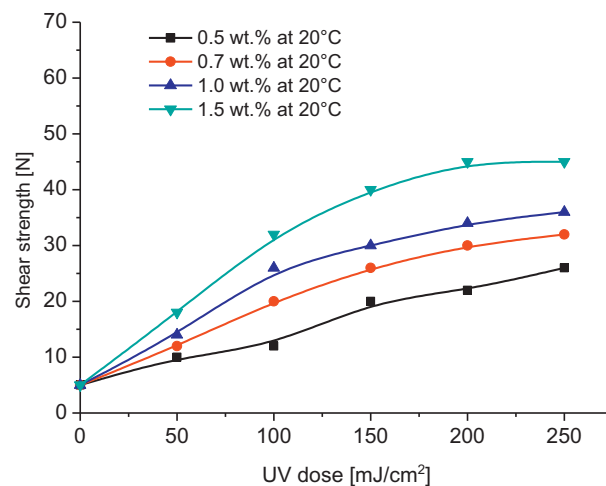
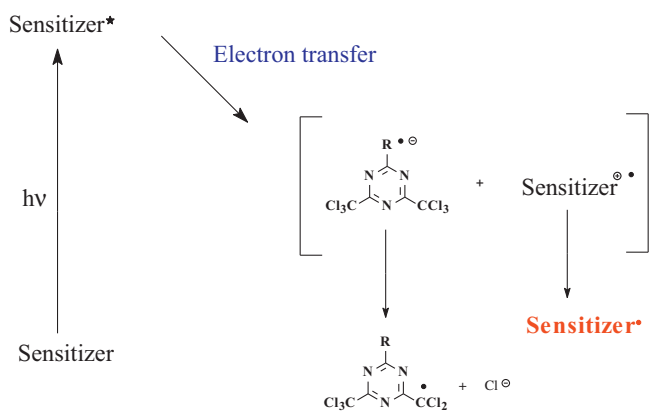


Fig. 5. Shear strength of a UV-crosslinked acrylic PSA as a function of UV dose for various amounts of the photoreactive s-triazine XL-353.



Scheme 3. The photochemical processes occurring in the two-component photoinitiating system: sensitizer/1,3,5-triazine derivative.

to those obtained in the case of multifunctional H-abstractors. The cohesion at 70 °C was on an unacceptably low level.

3.2. 1,3,5-Triazine derivative as a co-initiator in a visible light photoinitiating system (kinetic of polymerization)

In the presence of a suitable sensitizer 1,3,5-triazine derivatives can be used as the co-initiators in the very efficient photoinitiating systems. Usually, in such systems after irradiation with a visible light the electron transfer from an excited state of sensitizer to ground state of 1,3,5-triazine occurs. The triazinyl radical (initiating polymerization) and chloride anion are formed as a result of C–Cl bond cleavage in triazinyl radical anion (Scheme 3).

The resulting 1,3,5-triazine-based radical is active for initiation, but the dye radical is a terminating radical.

1,3,5-Triazine derivative is very often added to the two-component photoinitiating systems as a second co-initiator. The third component is thought to oxidize this inactive dye-based radical, regenerating the original dye and producing an active second radical.

The detailed photochemical behavior of 1,3,5-triazine in the three-component photoinitiating systems composed of Rose bengal/tertiary amine/1,3,5-triazine derivative and Eozine/tertiary amine/1,3,5-triazine derivative was previously described by Grotzinger et al. [10]. In such photoinitiating systems the electron transfer from an amine to an excited state of sensitizer is primary photochemical process. The secondary process is the electron transfer from dye-based radical to the ground state of 1,3,5-triazine derivative [10]. Other photoinitiating systems were composed of merocyanine dye/1,3,5-triazine derivative and were studied by Kawamura and Matsumoto [18].

The three-component photoinitiating systems under investigation consist of unsymmetrical cyanine dyes (hemicyanines) (dye I and dye II), two- and four-cationic monomethine dyes (dye III and dye IV) and mono-cationic symmetrical carbocyanine dye (dye V) as absorbing chromophore paired with *n*-butyltriphenylborate anion (B2) (electron donor) and 1,3,5-triazine derivative as a second co-initiator (XL-353) or polymethine dye, heteroaromatic mercaptan and 1,3,5-triazine derivative (Chart 1).

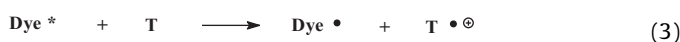
The influence of the 1,3,5-triazine derivative on the photoinitiating ability of well known visible light photoinitiating system composed of cyanine dye and alkyltriphenylborate salt as an ion pair is shown in Figs. 6 and 7.

The addition of XL-353 as a second co-initiator to the dye/borate salt system produces a synergic effect in the polymerization reactions (Figs. 6 and 7). The rates of polymerization initiated by the three-component photoinitiating systems polymethine dye/borate

salt/XL-353 are about 10–500 times higher than those observed for two-component photoinitiating system: dye/borate salts.

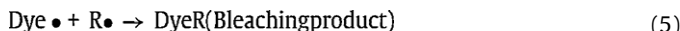
The efficiency of the three-component photoinitiating system: polymethine dye/borate salt/XL-353 is not a simple sum of the efficiencies of two-component photoinitiating system: dye/borate salt and dye/1,3,5-triazine systems acting separately. Therefore, it seems that the improvement in photoinitiation for the system: polymethine dye/borate salt/1,3,5-triazine in comparison to the two-component photoinitiating system is a result of the secondary reactions between 1,3,5-triazine derivative and the species deriving from the first step of interaction, e.g. the electron transfer process between an excited singlet state of sensitizer and borate salt.

For three-component systems theoretically following primary reactions are possible (Eqs. (1)–(3)):



where Dye* is an excited singlet state of polymethine dye, B2 is *n*-butyltriphenylborate salt, T is 1,3,5-triazine derivative (XL-353). The calculated values of free energy changes for the electron transfer processes (ΔG_{el}) presented above are in the range from –0.592 eV to 0.33 eV (from 57.12 kJ mol^{–1} to 31.84 kJ mol^{–1}). The calculated free energies of the electron transfer reactions between the excited states of the dye and 1,3,5-triazine show that an electron transfer from an excited singlet state of the dye to the triazine is more feasible, leading to oxidation of the dye and reduction of triazine. As it was mentioned above, this reaction leads to the C–Cl bond cleavage and formation of free radicals and chloride ions [10].

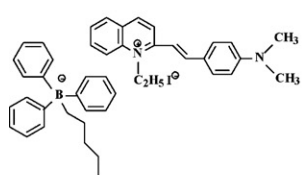
There are at least two possible explanations of observed acceleration of the free radical polymerization. The first reasonable hypothesis suggests that the synergic effect of the three-component photoinitiating system behavior could be explained by an electron transfer interaction of reduced dye (dye radical) with the triazine. Cyanine dye radical can act as a weak terminator of the growing macromolecular chains. On the other hand, it reacts efficiently with an alkyl radicals. This reaction leads to the decrease of a concentration of initiating radicals. The linear relationship between the rate of polymerization and the square root of the light intensity absorbed confirms this postulate, suggesting that photoinitiated polymerization of the system proceeds by a conventional mechanism in which bimolecular termination occurs by the reaction between two macroradicals. This allows to conclude that the cyanine radicals do not act as terminator of polymer chain (Eqs. (4) and (5)) [17].



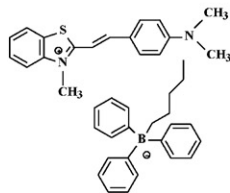
Such interaction can sharply decrease an efficiency of initiation process, and this in turn, causes a decrease in observed rate of polymerization. The possible explanation of observed synergic effect for three-component system may consider possible redox reaction between cyanine dye radical and 1,3,5-triazine derivative. The second explanation considers the back electron transfer reaction between the dye radical and 1,3,5-triazine radical anion. Such back electron transfer reaction can completely stop the formation of radicals from 1,3,5-triazine radical anion. This type of behavior was observed for certain cyanine dye-borate anion photoredox pairs [19,20].

The interactions between the cyanine dye radical and 1,3,5-triazine can strongly reduce a terminating effect caused by dye radical, and additionally leads to the formation the new initiating

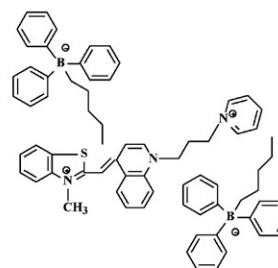
Two-component photoinitiating system



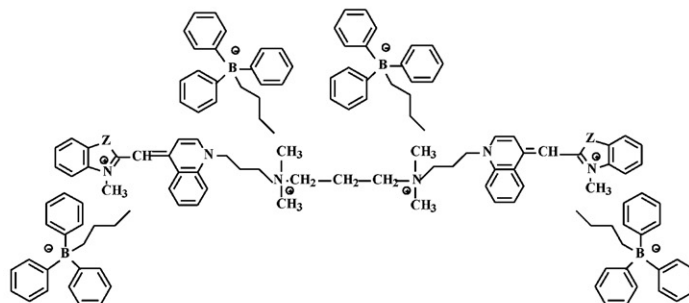
(Dye I)



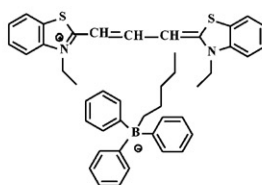
(Dye II)



(Dye III)



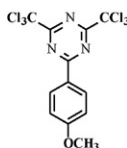
(Dye IV)



(Dye V)

Second co-initiators

1,3,5-triazine derivative

2,4-Bis-(trichloromethyl)-6-(4-methoxy)phenyl-1,3,5-triazine
(XL-353)

Heteroaromatic thiols

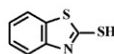
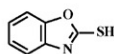
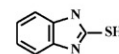
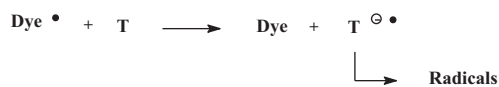
2-Mercaptobenzothiazole
(MS)2-Mercaptobenzoxazole
(MO)2-Mercaptobenzimidazole
(MI)

Chart 1. Two- and three-component photoinitiating system.

radicals (Eq. (6)) [10].



(6)

The following mechanism of free radical formation after irradiation of three-component photoinitiating system with visible light is proposed (Scheme 4) (reducible series mechanism) [19].

The photoexcited dye molecule encounters *n*-butyltriphenylborate anion and accepts an electron from borate

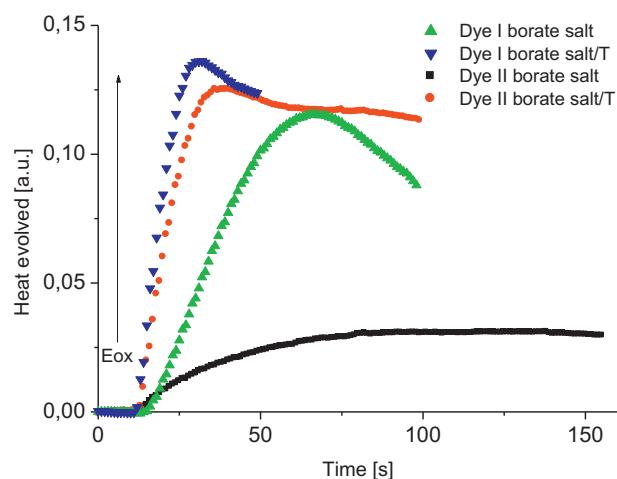


Fig. 6. Family of kinetic curves recorded during the measurements of the flow of the heat during the photoinitiated polymerization of TMPTA/MP (9:1) mixture initiated by hemicyanine dyes in the presence of different co-initiators marked in Figure. The dye and co-initiators concentrations were 1×10^{-3} M and 4.5×10^{-2} M for T, respectively.

anion, forming boranyl radical and cyanine radical. In the next step, the electron transfer from cyanine radical to XL-353 occurs. This reaction regenerates the original dye and produces 1,3,5-triazine radical anion, which rapidly fragments into a halogene anion and triazinyl radical. The enhanced rate of reaction observed in the presence of the 1,3,5-triazine is explained in part by the fact that the 1,3,5-triazinyl radical, unlike cyanine dye radical is active for

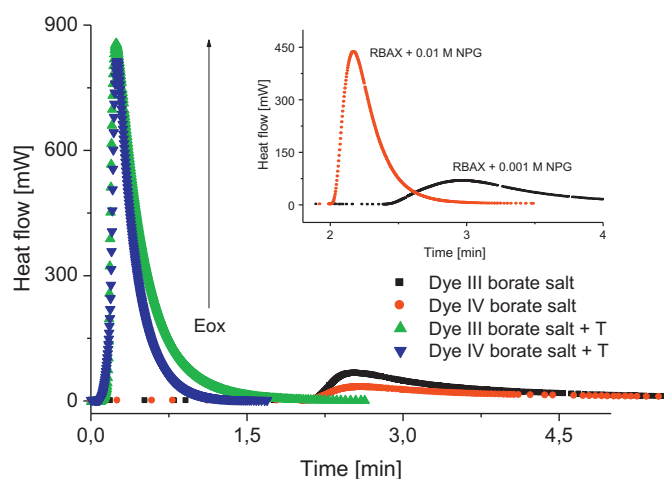
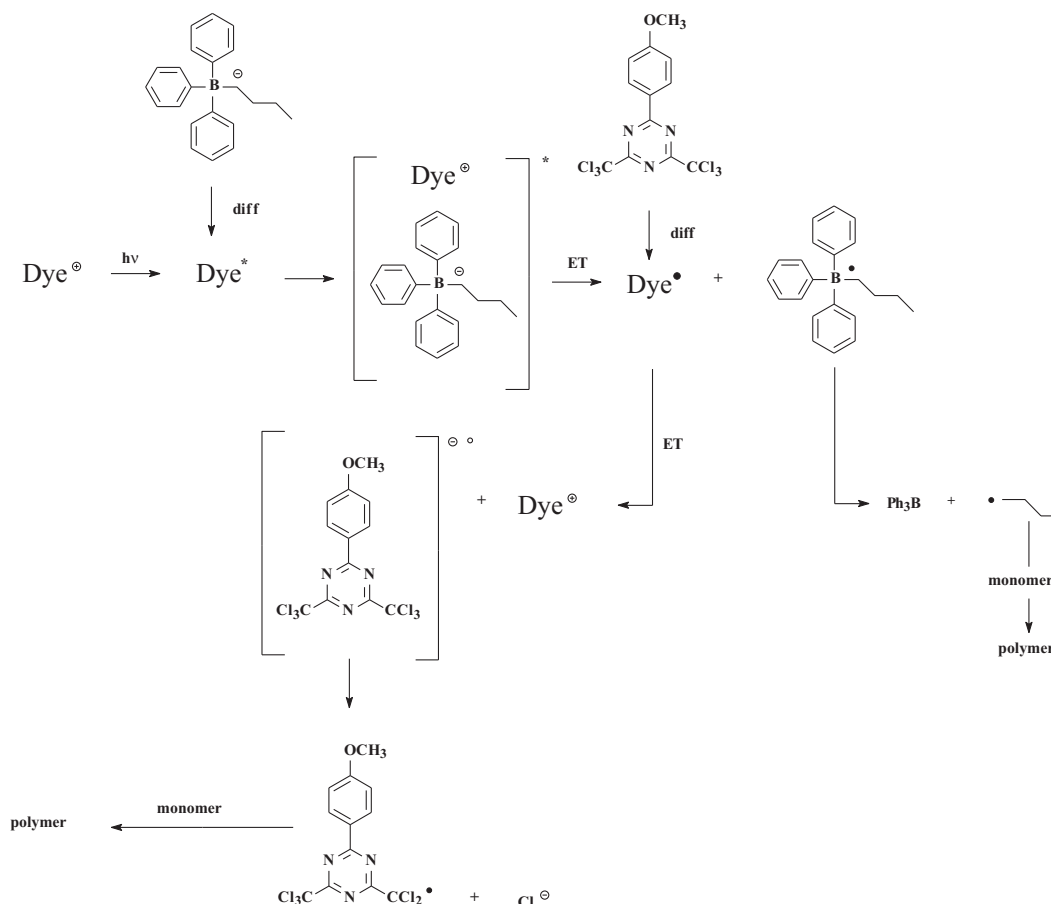


Fig. 7. Kinetic curves recorded during the measurements of the flow of the heat during the photoinitiated polymerization initiated by two- and four-cationic monomethine borates and for comparison by two- and four-cationic monomethine borates in the presence of XL-353 as a second co-initiator (5.0×10^{-2} M). Borate salt concentration was 1.0×10^{-3} M. Inset: Comparison of photoinitiation ability of RBAX-NPG (N-phenylglycine concentration was 1.0×10^{-2} M and 1.0×10^{-3} M) photoinitiating system, RBAX–Rose Bengal derivative (triplet state photoinitiator).

initiation. In addition, since the ground state of cyanine dye is regenerated in this reaction, the initiation rate will be enhanced further [17].

Next three-component photoinitiating system studied was composed of cyanine dye: N,N'-diethylthiocarbocyanine iodide



Scheme 4. The primary and secondary reactions for three-component photoinitiating system: polymethine dye/borate salt/XL-353.

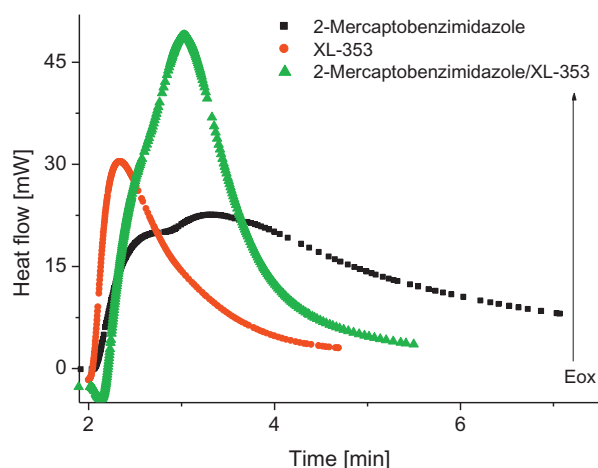


Fig. 8. The family of kinetic curves recorded during the measurements of the flow of heat emitted during the photoinitiated polymerization of the TMPTA/MP (9:1) mixture initiated by *N,N'*-diethylthiocarbocyanine dye (dye V) in the presence of different co-initiators (marked in figure). The cyanine dye and co-initiators concentrations were 1×10^{-3} M and 5×10^{-2} M, respectively. $I_a = 20$ mW/0.196 cm².

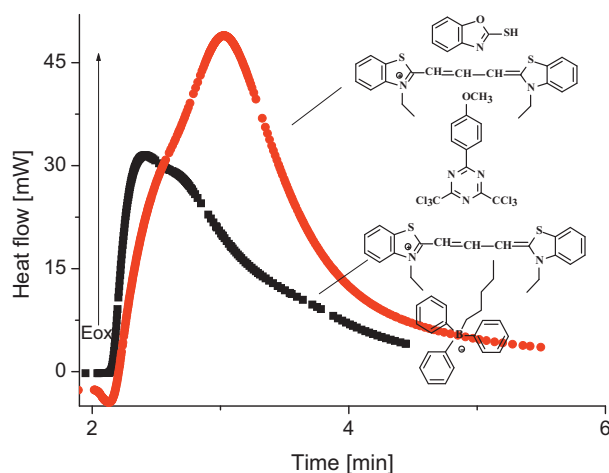


Fig. 9. The family of kinetic curves recorded during the measurements of the flow of heat emitted during the photoinitiated polymerization of the TMPTA/MP (9:1) mixture initiated by *n*-butyltriphenylborate *N,N'*-diethylthiocarbocyanine and *N,N'*-diethylthiocarbocyanine iodide (dye V) in the presence of 1,3,5-triazine derivative and thiol as the co-initiators, respectively. The cyanine dye and co-initiators concentrations were 1×10^{-3} M and 5×10^{-2} M, respectively. $I_a = 20$ mW/0.196 cm².

(dye V)/2,4-bis-(trichloromethyl)-6-(4-methoxy)phenyl-1,3,5-triazine/heteroaromatic thiol. The kinetic results are presented in Fig. 8.

The rate of polymerization initiated by the three-component photoinitiating system composed of cyanine dye/2-mercaptobenzothiazole/1,3,5-triazine derivative is higher than those observed for two-component system possessing cyanine dye and *n*-butyltriphenylborate salt (Fig. 9).

The formation of free radicals in photoinitiating systems: dye/thiol, dye/1,3,5-triazine derivative and dye/thiol/1,3,5-triazine may occur also via photoinduced electron transfer process (PET). For such photoinitiating systems theoretically following primary reactions are possible:

- In the case of cyanine dye/thiol, the formation of radicals may occur via photoinduced electron transfer (PET) followed by proton transfer (Eq. (7))

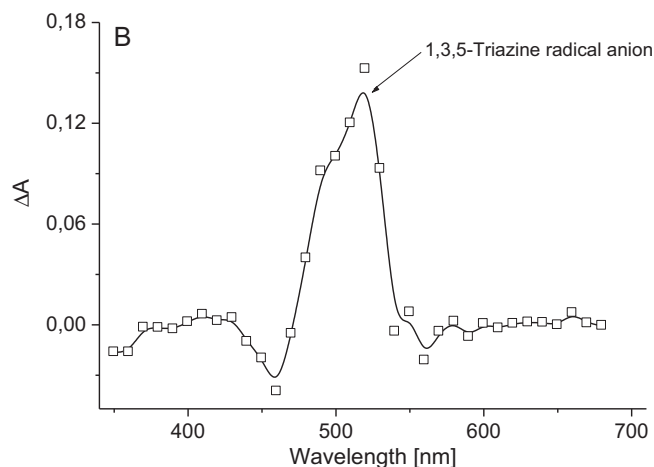
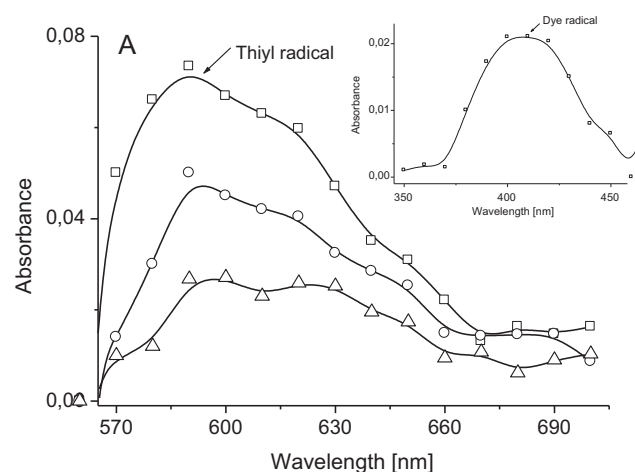
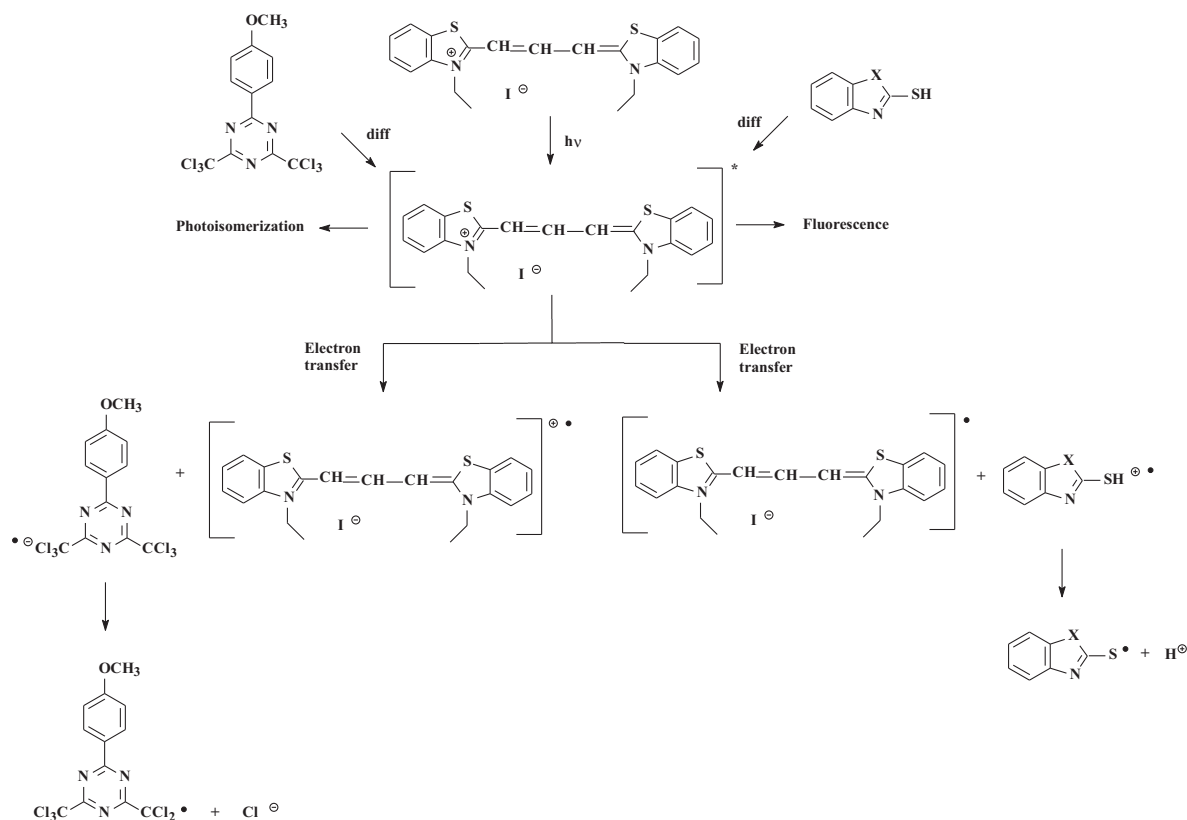


Fig. 10. (A) Transient absorption spectra of cyanine dye in the presence of 2-mercaptobenzothiazole (MS) recorded: 1 μs (squares), 4 μs (circles) and 10 μs (triangles) after laser pulse. Inset: transient absorption spectra of cyanine dye in the presence of 2-mercaptobenzothiazole (MS) recorded 100 ns after laser pulse (circles) (concentration of 2-mercaptobenzothiazole 1×10^{-2} M) in acetonitrile solution. Dye concentration was 2×10^{-4} M. (B) The transient absorption spectra of thiocarbocyanine dye (dye V) in the presence of 2,4-bis-(trichloromethyl)-6-(4-methoxy)phenyl-1,3,5-triazine (T) recorded 50 ns after laser pulse. Concentration of 2,4-bis-(trichloromethyl)-6-(4-methoxy)phenyl-1,3,5-triazine was equal 2×10^{-2} M in acetonitrile solution. Dye concentration was 5×10^{-4} M.

- In the case of cyanine dye/1,3,5-triazine derivative, the formation of free radicals may occur via photoinduced electron transfer process (Eqs. (2) and (3)).

The values of the free energy change ΔG_{e1} for the electron transfer process were estimated by using the Rehm–Weller equation for the following cases:

- for the electron transfer from the thiol on an excited singlet state of the dye, using the oxidation potential of thiol, the reduction potential of sensitizer (-1.30 eV) and the energy of the excited state (2.10 eV). This process leads to the formation of thiyl radical as a result of the hydrogen abstraction.
- for the electron transfer process from an excited singlet state of the dye on the ground state of 1,3,5-triazine derivative, using the reduction potential of 1,3,5-triazine derivative (-0.84 eV) and the oxidation potential of *N,N'*-diethylthiocarbocyanine dye (1.00 eV).



Scheme 5. The primary and secondary reactions for the three-component photoinitiating system composed of polymethine dye/1,3,5-triazine derivative/heteroaromatic thiol after a visible light irradiation.

For two-component photoinitiating system composed of cyanine dye and thiol, the efficiency of thiyl radical formation and, hence initiation of polymerization depends on the observed efficiency of electron transfer from a thiol on an excited singlet state of sensitizer. For such photoredox pair the values of ΔG_{el} are in the range from -0.13 eV to 0.08 eV (e.g. -27.02 eV do 7.72 kJ mol $^{-1}$). The calculated free energy change for the electron transfer process from an excited singlet state of the dye on the ground-state 1,3,5-triazine derivative has negative value. The value of ΔG_{el} for the reverse process is very high (0.45 eV, 43.42 kJ mol $^{-1}$).

For the sensitizer employed in our studies, since the oxidation of the dye may occur, the two-component photoinitiating system composed of dye/1,3,5-triazine derivative can also be an effective photoinitiating system. The kinetic results obtained for this photoinitiating pair seems confirming this prediction. The value of ΔG_{el} is equal -0.28 eV (-27.02 kJ mol $^{-1}$). But in the three-component photoinitiating system an effective interaction between all components can take place. In such photoinitiating system both electron transfer processes can occur:

- from the ground state of a thiol to an excited singlet state of the thiocarbocyanine dye and
- from an excited singlet state of the dye to the ground-state of 1,3,5-triazine derivative.

The second reaction is followed by a C-Cl bond cleavage process which leads to the formation of radicals and chloride anions [10]. In this case the initiating radicals are formed (Fig. 9).

The mechanism of free radical formation was proposed basing on the laser flash photolysis (Fig. 10).

In the three-component photoinitiating system an excited singlet state of thiocarbocyanine dye was reduced by heteroaromatic

thiol or oxidized by 1,3,5-triazine derivative. These reactions produce:

- cyanine dye radical and thiyl radical and
- cyanine dye radical cation and 1,3,5-triazine radical anion, which rapidly undergoes C-Cl fragmentation giving a halogene anion and triazynyl radical.

On the basis of the nanosecond laser flash photolysis and thermodynamical analysis, the mechanism for the primary and secondary reactions for sensitized generation of free radicals was proposed. After irradiation of the three-component photoinitiating system composed of thiocarbocyanine dye/heteroaromatic thiol/2,4-bis-(trichloromethyl)-6-(4-methoxy)phenyl-1,3,5-triazine an excited singlet state of chromophore is formed. The deactivation of an excited state occurs by fluorescence, photoisomerization or electron transfer process. In the presence of heteroaromatic thiol the cyanine dye undergoes one-electron reduction. The cyanine dye radical and thiyl radical cation are formed. The thiyl radical cation undergoes the hydrogen abstraction, giving the thiyl radical that can start the polymerization reaction [21]. However, in the presence of 2,4-bis-(trichloromethyl)-6-(4-methoxy)phenyl-1,3,5-triazine the electron transfer from the ground state of thiol on an excited singlet state of cyanine dye competes with the electron transfer from an excited singlet state of sensitizer on the ground state of triazine derivative. This process leads to the formation of cyanine dye radical cation and 1,3,5-triazine-derived radical anion. The last undergoes fast fragmentation forming the chlorine anion and triazynylmethyl radical (Scheme 5) (oxidation-reduction series mechanism, e.g. parallel series mechanism).

4. Conclusion

It is shown that 2,4-bis-(trichloromethyl)-6-(4-methoxy)phenyl-1,3,5-triazine can be used both as an effective photoinitiator of free radical polymerization under UV irradiation and as a very effective co-initiator in visible light two- and three-component photoinitiating systems. The mechanism of formation of free radicals depends on the composition of the photoinitiating system and may be a result of: (i) photolysis of halomethyl 1,3,5-triazine, (ii) the electron transfer process from a sensitizer-based radical to the ground state of triazine (reducible mechanism) or (iii) the electron transfer from the excited state of sensitizer to the ground state of triazine (parallel-series mechanism).

2,4-Bis-(trichloromethyl)-6-(4-methoxy)phenyl-1,3,5-triazine is very effective for use in the photocrosslinking of pressure-sensitive adhesives and ameliorating the adhesive properties (tack and peel adhesion) liberate hydrogen chloride as the product (following hydrogen abstraction by chlorine radicals which are responsible for initiating the crosslinking). The examined photoreactive s-triazine crosslinking agent shows a very high shear strength level, the best balance of properties of tack, peel adhesion and shear strength.

2,4-Bis-(trichloromethyl)-6-(4-methoxy)phenyl-1,3,5-triazine may be used also in the visible light photoinitiating systems. The addition of halomethyl 1,3,5-triazine to two-component dye photoinitiating systems results in a very efficient acceleration of the rate of free radical polymerization of acrylate monomers. The synergistic effect observed in this three-component system composed of cyanine dye/borate salt/XL-353 during the polymerization is based on the secondary reactions between the triazine and the reduced dye (Dye*) arising from the interaction of the excited states of the dye and borate salt. This interaction results in a decreased inhibition effect of cyanine dye-based radical and in some cases can give rise to new initiating radicals.

In the case, when the photosensitizer (dye) has reduction potential and oxidation potential, the photo-excited dye may act as both an electron donor and an electron acceptor resulting in a parallel-series mechanism. In this kinetic pathway, the electron transfer between an excited dye molecule and the electron donor competes with the corresponding electron transfer between an excited dye and an electron acceptor as the primary photochemical reaction, for example in the case of a three-component photoinitiating system composed of polymethine dye/heteroaromatic thiol/XL-353.

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