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Photopolymerization of trimethylolpropane triacrylate induced by diselenide derivatives

Abstract — Six diselenides have been evaluated as novel photoinitiators for free radical polymerization induced with an argon-ion laser irradiation. Our studies show that the rate of photopolymerization depends on the structure and concentration of the photoinitiators. The relation between the rate of polymerization and the light intensity shows a linear dependence.

Key words: photoinitiators, diselenides, trimethylolpropane triacrylate, photopolymerization.

FOTOPOLIMERYZACJA TRIAKRYLANU TRIMETYLOLOPROPANU INICJOWANA DISELENKAMI

Streszczenie — Jako nowe fotoinicjatory polimeryzacji rodnikowej działające w zakresie światła UV zastosowano sześć organicznych diselenków. Scharakteryzowano ich podstawowe właściwości spektroskopowe. W badaniach fotopolimeryzacji triakrylanu trimetylolopropanu (TMPTA) inicjowanej diselenkami określono zależności szybkości tego procesu od budowy i stężenia inicjatora. Wykazano występowanie liniowej zależności szybkości badanej polimeryzacji od natężenia promieniowania emitowanego przez laser argonowo-jonowy.

Słowa kluczowe: fotoinicjatory, diselenki, triakrylan trimetylolopropanu, fotopolimeryzacja.

Although the element selenium was discovered in 1918 by Berzelius [1], only after the discovery of the selenoxide elimination in the early 1970s, the organoselenium chemistry has gained more attention. Organoselenium compounds are now commonly employed as very useful and powerful reagents in organic synthesis and asymmetric catalysis. They make possible the chemo-, regio- or stereoselective introduction of new functional groups into the complex organic substrates, to be carried out under very mild experimental conditions. They can be used in nucleophilic, electrophilic and in radical reactions [2–13].

In polymer chemistry diselenides were used as co-initiators in cationic polymerization of *N*-vinylcarbazole, photoinitiated by aromatic nitriles [14]. An initiation mechanism involved the formation of selenium radical cation as actual initiating species. Upon photoirradiation, these radical cations were formed by single electron transfer between the excited singlet state sensitizer and the ground state of diphenyldiselenide [14]. Free radical polymerization of styrene in the presence of diphenyl diselenide, initiated by 2,2'-azobisisobutyronitrile at 60 °C, was also investigated. In this case diphenyl diselenide worked as a chain transfer agent. Polymerization with bis(*p*-*tert*-butylphenyl) diselenide

gave a polystyrene containing 1-cyano-1-methylethyl group at the α -end and an arylseleno group at the ω -end, respectively [15, 16]. Kroll and Bolton developed for the large-scale the synthesis of bis(2-hydroxyethyl)selenide and bis(2-aminoethyl)selenide as well. These bifunctional selenides were converted into a series of polyesters, polyureas, and polyurethanes. Methods of synthesis and properties of these condensation polymers were described [17].

Photopolymerization is a field undergoing significant growth because it is an efficient, energy-saving, economical and environmentally friendly method of the formation of high molecular weight polymer material [18, 19]. Photopolymerization is applied generally to a variety of processes, which result in the conversion of smaller molecules into larger in a photochemical primary step or in a photoactivated process [20, 21]. Specific areas of interest include the development of ultrafast polymerization [22, 23], thin pigmented inks [24, 25] or thiol-ene initiations [26, 27].

The photoinitiator system generates the free radicals that initiate radical chain polymerization of the unsaturated monomer or monomers. It may be a single compound, typically called a photoinitiator rather than a photoinitiator system, that absorbs light and undergoes unimolecular reaction to form radicals. It may also consist of several different compounds (system) that undergo a complex series of reactions to produce the initiating radicals [28, 29]. Chain growth polymerizations *via* a propagating free radical or ion are exothermic reactions, *i.e.* heat is released as double bonds are converted into single bonds [30].

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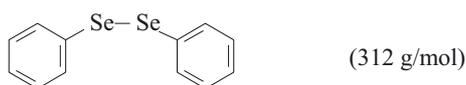
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There is still a need to search the new effective photo-initiating systems that will fulfill specific properties. This paper is a part of these studies. We describe here an attempt to develop new photoinitiators based on organoselenium compounds for acrylate polymerization.

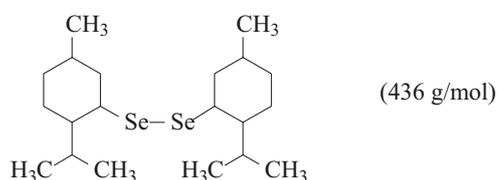
EXPERIMENTAL

Materials

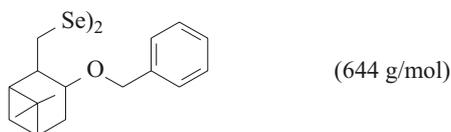
— All diselenides used in this study were obtained in the Faculty of Chemistry, Copernicus University (Toruń,



Se1
diphenyl diselenide



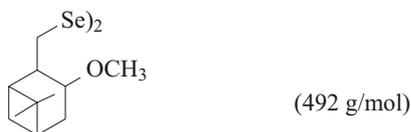
Se2
bis(2-isopropyl-5-methylcyclohexyl)diselenide



Se3
bis[(3-benzyloxy-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)-methyl]diselenide



Se4
bis[2-(methoxymethyl)-6,6-dimethylbicyclo[3.1.1]heptan-3-yl]diselenide



Se5
bis[(3-methoxy-6,6-dimethylbicyclo[3.1.1]heptan-2-yl)-methyl]diselenide



Se6
bis[2-[3-(hydroxy)-6,6-dimethylbicyclo[3.1.1]heptan-2-yl]-ethyl]diselenide

Poland) and were used without further purification. These compounds were synthesized according to the procedures described in the literature [31–33].

The molecular structures and denotations of diselenides under the study are as follows.

The absorption spectra of photoinitiations were recorded in *n*-hexane using a Shimadzu UV-vis Multispec-1501 spectrophotometer.

— Monomer, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), and all solvents were purchased from Aldrich Chemical Co. Solvents were of the spectroscopic grade.

Polymerization

The process of free radical polymerization was studied using a polymerization solution composed of 1 mL of 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). The diselenide concentration was $1 \cdot 10^{-2}$ M. The kinetic measurements — based on the heat evolution during polymerization in thin film cured sample — were carried out at an ambient temperature and the polymerizing mixture was not deaerated before curing.

They were performed by measuring photopolymerization exotherms using a homemade thin-film calorimeter constructed based on the design described by Hoyle et al. [34, 35]. The irradiation of the polymerization mixture was carried out using the emission of an Innova 90-4 argon-ion laser with intensity of light (measured with a Coherent Power Meter Type 543-500 mA) of 100 mW/cm² or 200 mW/cm². The light was absorbed by a sample 1 mm thick. As the results of kinetic measurements the polymerization rate values (R_p , *i.e.* slope of the initial part of kinetic curve) were received.

RESULTS AND DISCUSSION

The basic spectroscopic properties of diselenides tested are summarized in Table 1.

Table 1. Spectroscopic properties (λ_{\max}^{Ab} , ϵ) and relative rates (R_p values) of photopolymerization induced by organoselenium compounds

No	λ_{\max}^{Ab} , nm	ϵ^* , M ⁻¹ cm ⁻¹	R_p^{**} , au	R_p^{***} , au
Se1	333	1028	0.39	1.76
Se2	316	333	2.78	9.18
Se3	308	384	0.44	1.20
Se4	303	329	0.41	0.85
Se5	310	363	0.35	0.77
Se6	312	502	0.10	0.33

^{*)} λ_{\max}^{Ab} — wavelength in absorption maximum, ϵ (M⁻¹cm⁻¹) = ϵ (mol⁻¹dm³cm⁻¹) = molar absorptivity.

^{**)} Light intensity $I_0 = 100$ mW/cm².

^{***)} Light intensity $I_0 = 200$ mW/cm².

The analysis of these data shows that the novel photoinitiators absorb the UV light and their absorption

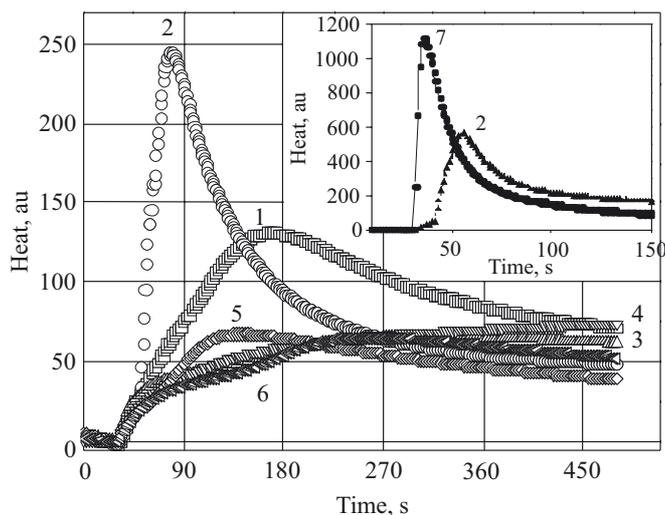


Fig. 1. Kinetic curves of TMPTA photopolymerization initiated by diselenides: 1 — Se1, 2 — Se2, 3 — Se3, 4 — Se4, 5 — Se5, 6 — Se6 ($I_0 = 200 \text{ mW/cm}^2$). Inset: comparison between the photoinitiation ability of Se2 (2) ($1.0 \cdot 10^{-2} \text{ M}$; $R_p = 47.68 \text{ au}$) and Irgacure 651 (7) ($1.0 \cdot 10^{-2} \text{ M}$; $R_p = 286.3 \text{ au}$) photoinitiation systems; $I_0 = 475 \text{ mW/cm}^2$

maxima are located in the range from 300 nm to 335 nm. The spectral properties of organoselenium compounds in low or medium polarity solvents such as *n*-hexane or esters indicate that the novel photoinitiating systems are perfect candidates for the initiation of polymerization reaction by an argon ion laser (351, 361 nm).

Figure 1 presents the kinetic curves observed during an argon ion laser initiated polymerization of TMPTA. All the results obtained during the measurements of polymerization kinetics are collected in Table 1. It is apparent, from the inspection of the initial rates of polymerization, that the photoinitiation ability of the organoselenium compound strongly depends on its structure. Among all compounds under the study the Se2 photoinitiator initiates the polymerization reaction with the highest rate. Its photoinitiation ability are compared to the efficiency of Irgacure 651 — commercial UV-initiator in free radical polymerization (see Figure 1 inset).

The mechanism causing the starting free radical polymerization is not clear. Probably irradiation of selenides leads to a homolytic photodissociation of the compounds tested giving radicals which react with monomer, starting polymerization chain reaction. However, the confirmation of the mechanism initiating the polymerization chain reaction requires more research using a combination of ESP and picosecond flash photolysis.

The concentration of photoinitiator plays a key role in the photopolymerization. An increase in the photoinitiator concentration according to [36], leads to:

- an increase in the absorbed light intensity (I_a) (through an increase in the optical density) and consequently an increase in a rate of polymerization (R_p) up to a constant value,

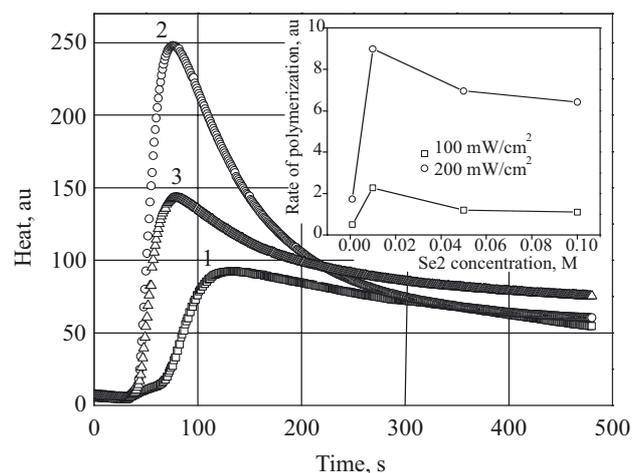


Fig. 2. Kinetic curves recorded during the polymerization of TMPTA, photoinitiated by Se2 at different concentrations: 1 — 0.001 M, 2 — 0.01 M, 3 — 0.05 M ($I_0 = 200 \text{ mW/cm}^2$). Inset: the dependence of the rate of photoinitiated polymerization on Se2 concentration

- an increase in the concentration of initiating radicals which tends to favor a decrease in an induction period and an increase in the recombination reactions of these radicals,

- an increase in product hardness [36].

As we can see in Fig. 2, R_p increases when more initiator is used, up to a certain level and then rapidly decreases when too much initiator is added to a polymerizing formulation which is common feature of the conventional UV-vis photopolymerization [36]. The reduction of the photoinitiated polymerization rate at higher initiator concentration (for applied technique of polymerization rate measurement) can be easily understood taking into account the decrease in penetration depth of the laser beam. For the tested novel initiators, the highest R_p values for 1 mm thick samples (Fig. 2) were achieved for initiator concentration about $1 \cdot 10^{-2} \text{ M}$.

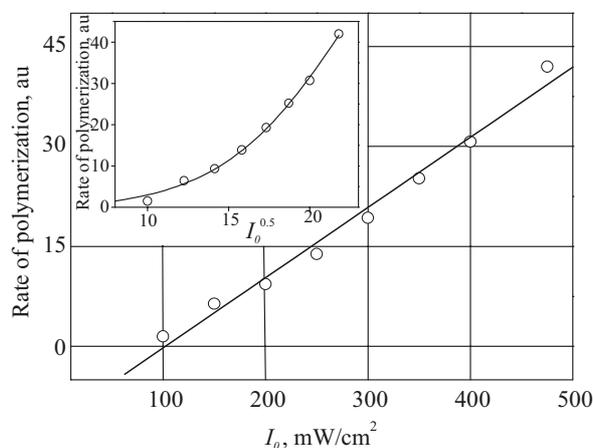


Fig. 3. Dependence of the rate of polymerization of TMPTA on the light intensity (I_0); process initiated by Se2 compound. Inset: rate of polymerization versus $I^{0.5}$

The study of a light intensity effect on the rate of TMPTA photopolymerization induced by Se₂ revealed linear dependence as it is shown in Fig. 3, what is different from the usual behavior expressed by a polymerization kinetic law $R_p = kI_a^{0.5}$ and presents a first-order or rather pseudo first-order dependence. In isothermal conditions, typical unimolecular termination reactions are: the inclusion of the polymer radical, diffusion controlled termination, and pseudo first-order termination with oxygen [37–39]. The observed linear relation between the rate of polymerization and the light intensity in the tested photoinitiating system can result from the pseudo adiabatic conditions of polymerization process conducting.

Summarizing, our study revealed that the diselenides tested seemed to be good candidates as photoinitiators for acrylates.

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