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Organosilicon sulfides as co-initiators in photoinduced free radical polymerization

Adam Leniec, Beata Jędrzejewska (✉), Jerzy Pączkowski

University of Technology and Agriculture, Faculty of Chemical Technology and Engineering
Seminaryjna 3, 85-326 Bydgoszcz, Poland
E-mail: beata@atr.bydgoszcz.pl; Fax: ++48 52 374 9009

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Summary

Three sulfur-containing silanes (organosilicon sulfides) were investigated as electron donors in photoinduced free radical polymerization, in conjunction with xanthene dye (5,7-diiodo-3-butoxy-6-fluorone, **DIBF**) as sensitizer. The results were compared with the nonsulfur-containing silane, N-((trimethylsilyl)methyl)aniline (**K1**) and thiophenoxyacetic acid (**TPAA**). The kinetic studies clearly showed that the **DIBF**-organosilicon sulfides exhibit a significant increase in the efficiency of free radical polymerization of TMPTA compared to nonsulfur-containing silane and that the efficiency of all tested electron donors is only slightly dependent on the structure of the sulfur-containing co-initiators.

Introduction

Photoinitiated polymerization is a technique, which allows using the energy of light for initiation of rapid conversion of liquid materials into solid polymeric products. This process is traditionally initiated by direct photolysis of a precursor to provide free radicals by bond photodecomposition. However, the bonds dissociation requires the energy of quanta associated with electromagnetic radiation, for most cases, in UV region. The shift of initiator sensitivity towards visible region requires panchromatic sensitization, and this in turn, requires the presence of suitable dye as a light absorber. For such case, photophysical energy transfer between dye excited state and other chromophore that yields free radicals, is generally disfavored. As an alternative other processes avoiding typical energy restriction should be considered. The photoinduced intermolecular electron (PET) transfer, which is nonclassical, endothermic energy transfer process, represents such as alternative [1,2].

There has been a number of studies on the dye photoinitiators that form a free radical *via* the photoinduced electron transfer process. These include the acridines, the xanthenes and the thiazines, first reported by Oster [3], a wide group of fluorone dyes [4-7], cyanine dyes [8-10], pyrene [11,12], safranine T [13], dyes based on quinaxolin-2-one residue [14,15] and many others [1,2]. Moreover, it is necessary to emphasize that the research related to the photochemistry of dying photoinitiators is mostly focused on the development of new light absorbers. However recently, more and more papers are focused on the effect of an electron-donating molecule structure on the efficiency of photoinitiation process.

In this presentation, we have compared the reactivity of new photoinitiation systems composed of xanthene dye acting as light absorber and a series of organosilicon sulfides functioning as the electron donors. For comparison, N-((trimethylsilyl)-methyl)aniline (**K1**) and thiophenoxyacetic acid (**TPAA**) as co-initiators of the free radical polymerization were tested as well.

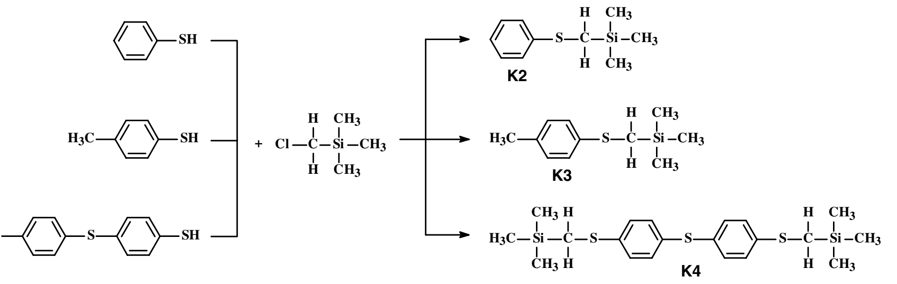
Experimental

Materials

2-Ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), thiophenoxyacetic acid (**TPAA**), tetrabutylammonium perchlorate, 1-methyl-2-pyrrolidinone (MP), methanol (MeOH), substrates for synthesis of the silanes and all spectroscopic grade solvents were purchased from Aldrich or Fluka Chemical Co.

Synthesis

5,7-Diiodo-3-butoxy-6-fluorone (**DIBF**) was synthesized according to the method of Shi and Neckers [16,17]. A general route for synthesis of the organosilicon sulfides prepared by Cooper's method [18] is shown in Scheme 1.



Scheme 1. A general route for the synthesis of organosilicon sulfides

*Trimethyl-(benzenethiomethyl)silane (**K2**)*

A solution of 2.44 g. (0.02 mole) of chloromethyltrimethylsilane was added to a solution of 2.2 g. (0.02 mole) of thiophenol in 10 mL of 10% sodium hydroxide solution. The mixture was stirred and heated under reflux for four hours. The mixture was cooled to a room temperature and then 30 mL of water was added to the resulting mixture. The organic layer was separated, washed with 10% sodium hydroxide solution and with water and dried over anhydrous calcium chloride [18]. The desired sulfide was obtained by distillation. This methodology was applied for the synthesis of the other organosilicones.

The purity of the co-initiators was controlled with the use of TLC, which confirmed high purity of the compounds synthesized. The chemical structures of the synthesized compounds were confirmed by ^{1}H NMR spectroscopy (The ^{1}H NMR spectra were recorded with the use of a Varian spectrometer Gemini 200 operating at 200 MHz. Dimethylsulfoxide (DMSO-d6) was used as the solvent and tetramethylsilane (TMS) as internal standard). The yields of synthesis of the sulfides tested were about 40 %.

*Trimethyl-(benzenethiomethyl)silane (**K2**)*
^{1}H NMR (DMSO-d6) δ (ppm): 0.161-0.177 (9H, SiCH_3); 2.152 (s, 2H, SiCH_2); 7.206-7.256 (5H, Ph).

*Trimethyl-(4-methyl-benzenethiomethyl)silane (**K3**)*
^{1}H NMR (DMSO-d6) δ (ppm): 0.149-0.178 (9H, SiCH_3); 2.156 (s, 2H, SiCH_2); 1.542-1.547 (3H, CH_3); 7.209-7.26 (4H, Ph).

*4,4'-Thiobis-[S-(methylthiobenzyl)-trimethylsilyl] (**K4**)*
^{1}H NMR (DMSO-d6) δ (ppm): 0.140-0.171 (18H, SiCH_3); 2.17-2.183 (s, 2H, SiCH_2); 2.3-2.317 (s, 2H, SiCH_2); 7.055-7.120 (4H, Ph); 7.176-7.258 (4H, Ph).

Nanosecond laser flash photolysis

Nanosecond laser flash photolysis experiments were performed using a LKS.60 laser flash photolysis apparatus (Applied Photophysics), applying a laser irradiation at 355 nm from the third harminic of the Q-switched Nd:YAG laser from a Lambda Physik/model LPY 150 operating at 65 mJ/pulse (pulse width about 4-5 ns). The rate **DIBF** triplet state quenching was measured for 1×10^{-5} M solution in acetonitrile.

Electrochemical measurements

The reduction potentials of tested dye (**DIBF**) and the oxidation potentials of organosilicon sulfides were measured by cyclic voltammetry. An Electroanalytical Cypress System Model CS-1090, equipped with a small volume cell, was used for the measurements. A 1-mm platinum disc electrode served as a working electrode, a Pt wire constituted the counter electrode and an Ag-AgCl electrode was used as the reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate in dry acetonitrile [10,14,15].

Polymerization procedure

The kinetics of the free radical polymerizations were determined by measuring the polymerization heat evolution of the sample irradiated with a laser beam through an optical system, in a homemade micro-calorimeter. A semiconducting diode immersed in a 2 mm thick layer (0.25 mL) of a cured sample was used as a temperature sensor. The irradiation of the polymerization mixture was carried out using the emission of an Omnichrome model 543-500 MA argon-ion laser, which emits two visible light wavelengths at 488 and 514 nm. The irradiation intensity was measured with a Coherent Power Meter Type 543-500 mA and was 64 mW/cm^2.

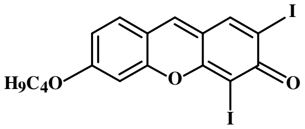
A polymerization solution was composed of 1 mL of 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). The concentration of 5,7-diiodo-3-butoxy-6-fluorone (**DIBF**) was 1×10^{-3} M. The concentration of silanes studied in the tested formulations was 1×10^{-2} M. As a reference sample, a polymerizing mixture containing dye without an electron donor was used.

Results and Discussion

The studied photoinitiating systems contain both components that are neutral in a ground state and form radical-ion pair after electron transfer process. In such a photoinitiating donor-acceptor system there is no electrostatic interaction in ground state. However, such an interaction occurs after electron transfer process. This kind of photoinitiating donor-acceptor pair effectively initiates free radical polymerization only when the lifetime of the excited state of the absorbing dye is long enough to allow an efficient diffusive encounter.

The photoinitiating systems tested in this work consist of organosilicon sulfides acting as an electron donor and neutral xanthene dye acting as electron acceptor (Chart 1). Irradiation of these photoredox pairs leads to the formation of a free radical, which is capable of initiating polymerization.

Chart 1



DIBF: $E_{red}\left(A^{\bullet-}/A\right)$= -0.9 V, $E_{00}^{(T)}$ = 222 kJ mol^{-1} (2.3 eV) [19], τ_T=15 μs [7]

It is well known that the main prerequisite for the electron transfer (PET) reaction, vital for free radicals formation, states that the thermodynamic driving force of the electron transfer reaction between the triplet excited state of the **DIBF** and organosilicon sulfides should have negative value. The free energy of activation for the PET (ΔG_{el}) process can be easily estimated on the basis of the Rehm-Weller [20,21] equation (1):

$$\Delta G_{el} = E_{ox}\left(D/D^{\bullet+}\right) - E_{red}\left(A^{\bullet-}/A\right) - E_{00} - Ze^2/\varepsilon a \qquad \mathbf{(1)}$$

where: $E_{ox}\left(D/D^{\bullet+}\right)$ is the oxidation potential of the electron donor, $E_{red}\left(A^{\bullet-}/A\right)$ is the reduction potential of the electron acceptor, E_{00} is the energy of the excited state involved in electron transfer reaction and $Ze^2/\varepsilon a$ is the Coulombic energy associated with the process. Since the last term is relatively small in polar or medium polarity media, it can be neglected in the estimation of ΔG_{el}. The E_{ox} and E_{red} of both photoredox pair components were determined from the cyclovoltameric measurements (Table 1). The electrochemical reduction of the **DIBF** is, as it is shown in Figure 1A, reversible. However, the oxidation of the selected organosilicon sulfide is semireversible (see Figure 1B). This behavior indicates that the oxidation products of tested electron donor in part undergo secondary reactions.

Using the Rehm-Weller equation [20,21], knowing the oxidation potentials of organosilicon sulfides, the reduction potential of **DIBF** (E_{red} = -0.9 V) and knowing its triplet energy ($E_{00}^{(T)}$ = 2.3 eV [19]), one can calculate the free energy change (ΔG_{el}) for electron transfer process (Table 1). According to the Rehm-Weller model, significant quenching rate constant through electron transfer mechanism (>10^9 M^{-1}s^{-1}) should be observed when ΔG values is negative. Data summarized in Table 1 indicates that the reaction between the excited state of the dye and the organosilicon sulfides is thermodynamically favorable for all tested electron donors, for the triplet state of the absorbing dye.

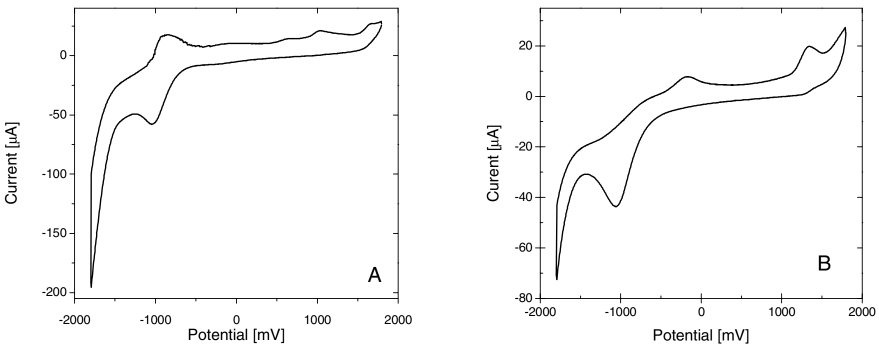
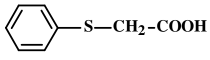
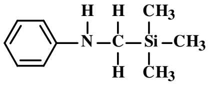
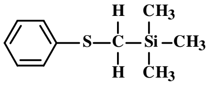
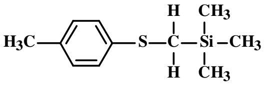
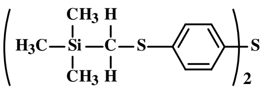


Figure 1. Cyclic voltammograms of **DIBF** (A) and **K4** (B) in 0.1 M tetrabutylammonium perchlorate solution in dry acetonitryle as the supporting electrolyte

Table 1. Characteristics of the co-initiators tested. Oxidation potential data, calculated free energies (ΔG_{el}) of the electron transfer reaction between the triplet excited state of the **DIBF** and co-initiators used and initial polymerization rates of TMPTA photoinitiated by photoredox pairs tested

No.	Co-initiators Structure	E_{ox} (V)	${}^{T}\Delta G_{el}$ (eV)	Time (s)[1]	R_p (μmol/s)	Monomer conversion (%)	Φ_{polym}
TPAA		1.097	-0.303	42	1.27	3.2	5.9
K1		0.798	-0.602	100	0.45	2.7	2.1
K2		1.115	-0.285	14	9.43	7.8	44.0
K3		1.140	-0.260	14	12.49	10.3	58.2
K4		1.149	-0.251	14	13.07	10.8	60.9

E_{ox} measured in 0.1 M tetrabutylammonium perchlorate in dry acetonitryle, ΔG_{el} calculated using Rehm-Weller equation (1), the coulombic stabilization term is negligible in polar solvents like MeCN, [1]the irradiation time for the initial rates of photoinitiated polymerization.

The triplets of **DIBF** are effectively quenched by organosilicon sulfides. Figure 2 presents the Stern-Volmer relationship obtained for **DIBF** triplet state quenching by selected organosilicon sulfides.

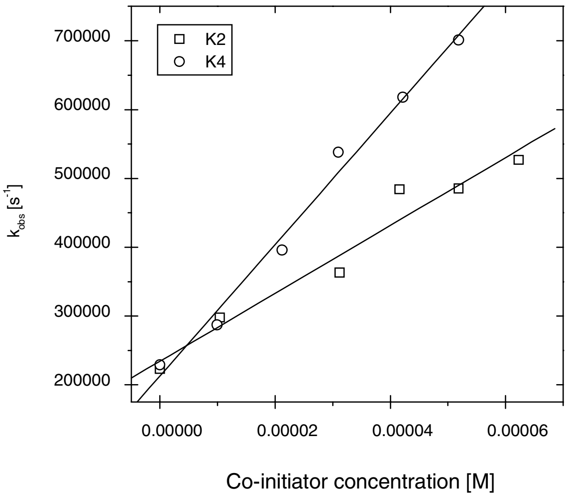


Figure 2. Plots for **DIBF** triplet quenching by organosilicon sulfides. Type of the electron donors marked in the Figure

The **DIBF** triplet state quenching by organosilicon sulfides suggests the mechanism of free radical generation. The mechanism, by analogy to other sulfur-containing compounds [22], involves probably the photoinduced electron transfer process.

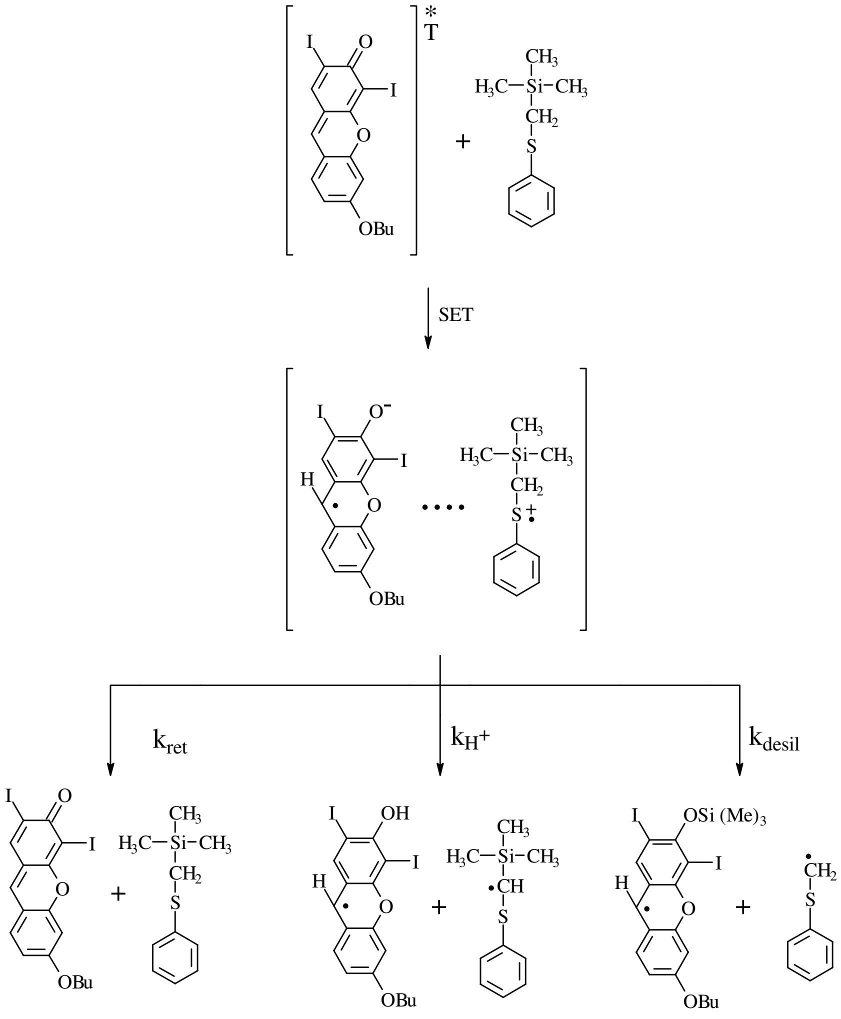
Electron donor reaction in α–silyl donor-**DIBF** pair results in initial formation of ion radical pair. On the basis of the Mariano et al. research, one can conclude that the radical cation generated from silyl derivative (silyl tioether) undergoes efficient desilylation and trimethylsilane cation transfer to **DIBF** radical anion that serves as the nucleofile in the desilylation reaction [23-25]. Desilylation process additionally yields α–akylthio-type radical ($R\text{-}S\text{-}CH_2^{\bullet}$) that is able to initiate free radical polymerization.

Based on the well-established mechanism of the photooxidation of sulfur-containing similar types of molecules, one can propose the scheme that describes possible secondary reactions that follow the electron transfer in tested photoredox pairs.

The processes shown in Scheme 2 involve: (i) the back electron transfer to reproduce the reactants in the ground state (ii) the formation of the α–akylthio-type radical ($R\text{-}S\text{-}CH_2^{\bullet}$) produced from the free radical cation of sulfur-contaning silane as a result of the desilylation and (iii) the formation of α–(akylthio)trimethylsilane radical ($R\text{-}S\text{-}CH^{\bullet}\text{-}Si(CH_3)_3$) being the result of the fast proton transfer between **DIBF** radical anion and sulfur-contaning silane radical cation.

Figure 3 presents the kinetic traces recorded during an argon ion laser photoinitiated polymerization of TMPTA in the presence of 5,7-diiodo-3-butoxy-6-fluorone (**DIBF**) as the light absorber and organosilicon sulfides functioning as the electron donating molecules.

Scheme 2. Possible processes, which may occur during the free radical photoinitiated polymerization with the use of **DIBF**-organosilicon sulfide initiating system



It is apparent from the inspection of the data shown in Figure 3 that the structure of the organosilicon sulfides does not significantly affect the ability to the photoinitiation of free radical polymerization. More distinct differences are observed in the rates of polymerization when one compares the rate of polymerization photoinitiated by **DIBF**-trimethyl-(benzenethiomethyl)silane (**K2**) and **DIBF**-N-((trimethylsilyl)-methyl)aniline (**K1**). The results of polymerization kinetics measurements obtained for all tested photoinitiating systems are listed in Table 1. Two more electron donors (N-((trimethylsilyl)methyl)aniline (**K1**) and thiophenoxyacetic acid (**TPAA**)) were tested as co-initiators for comparison. On the basis of the data in Table 1 and results shown in Figure 3, one can conclude that the exchange of nitrogen atom on sulfur in silane molecule increases the sensitivity of the photoinitiating system more than 1 order of magnitude.

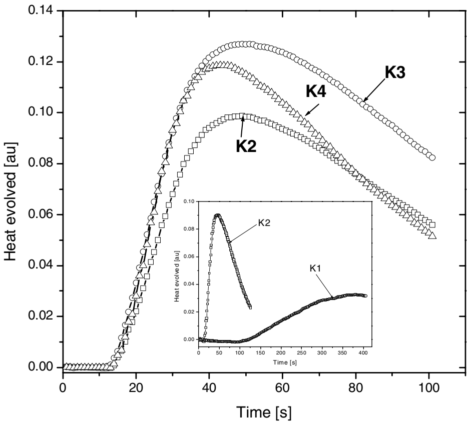


Figure 3. The rate of heat evolution during an argon ion laser photoinitiated polymerization of 1 mL 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymehyl)-1,3-propanediol triacrylate (TMPTA) mixture. The dye (**DIBF**) and the co-initiator concentration are: 1×10^{-3} M and 1×10^{-2} M, respectively. The electron donors tested are marked in the Figure. Inset: Family of the kinetic curves recorded during the measurements of the flow of heat for the photoinitiated polymerization of the TMPTA/MP (9/1) mixture initiated by **DIBF-K2** and **DIBF-K1** pairs illustrating the effect of the co-initiator structure on the polymerization rate

From the data, obtained during the polymerization kinetics measurements, it was also deduced that the conversion of monomer at initial time of polymerization is ranging from 2.7% to 10.8%, while the quantum yield of photoinitiated polymerization oscillates between 2.1 and 61 (Table 1). It is noteworthy that the photoinitiating systems composed of **DIBF**-organosilicon sulfides exhibit better photoinitiating ability and higher quantum yield of polymerization (about 60) in comparison to **DIBF**-nitrogen-containing silanes. Additionally, it was found that the degree of monomer conversion only slightly depends on the structure of the co-initiators. However, the change of the sulfur atom on the nitrogen in co-initiator molecule results in sharp decrease in the initiating ability of the photoredox pair.

It is also obvious that **DIBF**-silane photoredox pairs initiate free radical polymerization with the rate higher than the **DIBF**-thiophenoxyacetic acid (**TPAA**) initiating photoredox pair [26]. Figure 4 presents the kinetic traces recorded during an argon ion laser photoinitiated polymerization of TMPTA in the presence of 5,7-diiodo-3-butoxy-6-fluorone (**DIBF**) as the light absorber and either organosilicon sulfide (**K3**) or thiophenoxyacetic acid (**TPAA**) functioning as the electron donating molecule.

The rate of photoinitiated polymerization can be controlled by any of the processes that limit the formation of free radicals. These processes could include the rate of the primary process, e.g. the rate of the photochemical electron transfer (PET) process and consequences related to this phenomenon. Analyzing the rate of **DIBF** triplet-state quenching, one can conclude, that for these **DIBF**-silane systems, the rates of quenching are equal 1.8×10^9, $4,9\times10^9$ and $9,6\times10^9$ $M^{-1}s^{-1}$ for **K1**, **K2** and **K4** quenchers, respectively. The results show that the main photochemical channel that controls the rate of initiation is the diffusion. This suggests that the primary process does not limit the observed rate of the photoinitiated polymerization. Therefore, the differences in the measured rates of the polymerizations are likely affected by the yields of secondary processes that followed PET, e.g. decarboxylation or deprotonation, and/or by the reactivity of the free radicals [1,22,26,27].

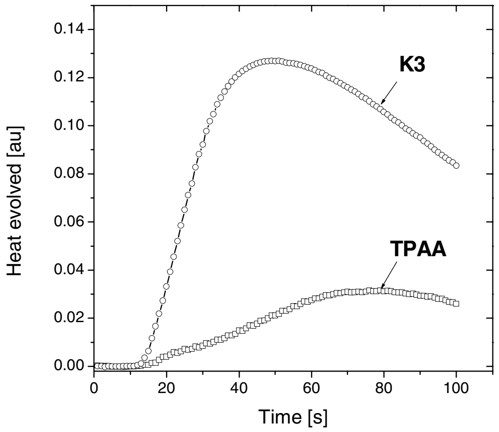


Figure 4. The rate of heat evolution during an argon ion laser photoinitiated polymerization of 1 mL 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymehyl)-1,3-propanediol triacrylate (TMPTA) mixture. The dye (**DIBF**) and the co-initiator concentration are: 1×10^{-3} M and 1×10^{-2} M, respectively. The electron donors marked in the Figure

Measurements of photoinitiated polymerization showed that the rate of the polymerization of TMPTA is depended on the co-initiator concentration. Figure 5 illustrates this relationship.

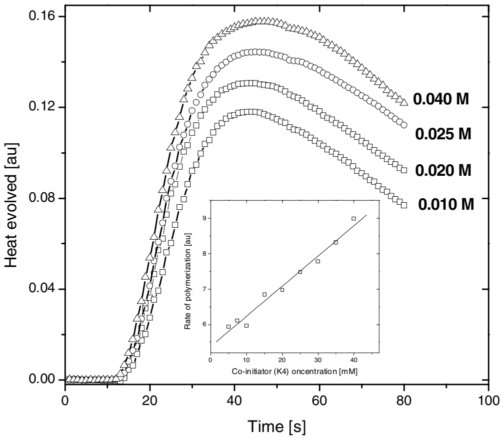


Figure 5. Family of the kinetic curves recorded during the measurements of the flow of heat for the photoinitiated polymerization of the TMPTA/MP (9/1) mixture initiated by **DIBF**-**K4** system. The **DIBF** concentration equal 1×10^{-3} M. Inset: Relationship between the rate of photoinitiated polymerization and the co-initiator (**K4**) concentration

Conclusions

Organosilicon sulfides are efficient co-initiators of the photoinitiated free radical polymerization. The inspection of the initial rates of polymerization showed that the photoinitiation efficiency of tested **DIBF**-organosilicon sulfide systems only slightly depends on the structures of co-initiator. The explanation of this observation may come from the additional experiments that clarified observed behaviors. First comes from the triplet state quenching experiments which show that the rate of **DIBF** triplet state quenching by organosilicon sulfides is diffusion controlled, the second, is that the initiating radical is almost identical for all tested donor-acceptor pairs. The change of the sulfur atom on the nitrogen in co-initiator molecule results in sharp decrease of the photoinitiating ability of the **DIBF**-co-initiator pair. Variation in reactivity of the photoinitiation system containing sulfur- and nitrogen-containing silanes is probably caused by different reactivity of radicals resulting from photoinduced electron transfer process.

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