

Silver MPC's Immobilized Co-initiators for Free Radical Polymerization

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Introduction

Photo initiated polymerization process can be started by a direct precursor photolysis. There are two ways of receiving free radicals: bond dissociation or electron or atom transfer [1, 2]. Free radicals which start chain can be formed by direct photolysis of a precursor (by direct bond scission) or can be formed in a sequence of reactions. Character of those reactions depends on both donor and acceptor type used in photoinitiation process. Reactivity of free radicals received in consequence of the PET processes and photoimitation system carriers i.e. polymer particles [3], can describe rate of polymerization. Silver nanoparticles of noble metal may be used as such specific carriers. There is no data in available literature describing influence of photochemical and photo physical nature of specific nano-carriers photoredox pair on free radical polymerization initiation abilities. This caused our scientific curiosity in silver nanoparticles of noble metal especially those which form cluster structures MPC's (monolayer protected clusters) [4÷7]. Phenomenon of the noble metal clusters immobilized by particles containing thiol group is well known in literature [8-10]. Schiffrin at al. [11] were the first to report a method of synthesis of thiol-immobilized gold nanoparticles. The main advantage of this method is the possibility of control the rate of complexing reaction, which determines that get obtain nanoparticles of small shape and sizes [12]. The presence of a metal in co-initiator molecule causes that the efficiency of quenching of the chromophore excited state is rather small [15÷17]. The main aim of this paper is to: (i) check the possibility of application of noble metal clusters MPCs as co-initiators of free radical polymerization and (ii) determinate kinetic parameters of these processes.

Experimental

All the solvents, monomer poly(ethylene glycol) diacrylate (PEGDA), substrates for preparation of MPCs and compounds used in experiments were purchased from Aldrich Chemical Co. with the best available purity grades and were used without further purification. The structure and spectral characteristics of both azoles and synthesized nanoparticles are described in Table I.

Absorption spectra of the synthesized silver nanoparticles: Ag-2-mercaptobenzimidazole (Ag-MBI), Ag-2-mercaptobenzothiazole (Ag-MBT), Ag-2-mercaptobenzoxazole (Ag-MBX) and Ag-2-thiouracyl (Ag-TU) were obtained using a Shimadzu MultiSpec-1501 photodiode array spectrophotometer.

FTIR spectra were measured using of a BrukerVector 22 spectrophotometer using KBr method. Thermogravimetric (TGA) analysis was performed with a Q-1500 D derivatograph.

The kinetics of PEGDA polymerization was studied by measuring the polymerization heat evolution in a sample irradiated with a Melles Griot system 543 argon-ion laser (488 nm lines). The measurements were performed based on the exotherms generated by photo-DSC apparatus constructed on the basis of TA Instruments DSC 2010 Differential Scanning Calorimeter and a homemade thin-film calorimeter constructed based on design described by Hoyle et al. [18]. The irradiation intensity was measured by a Coherent Power Meter Type 543-500 mA. During whole experiment was 100 mW/cm².

The kinetics of free radical polymerization was studied using a polymerization mixture composed of: monomer; (poly (ethylene glycol) diacrylate, PEGDA), initiator, (5,7-diiodo-3-butoxy-6-fluorene, DIBF ($c=4.5 \times 10^{-4} M$) [19]) and co-initiator (the MPCs of corresponding mercaptoazoles).

Results and discussion

Mercaptoazoles derivatives immobilized silver nanoparticles were synthesized based on modified procedure described by Kang and Kim [20]. The obtained family of silver nanoparticles clusters immobilized by appropriate mercaptoazole derivatives (MAz-MPCs—*Mercaptoazole-Monolayer Protected Clusters*) were used as coinitiators for free radical polymerization of PEGDA in presence of DIBF as primary absorber. Schematic diagram of the reaction leading to polymerization process is shown in Scheme I.

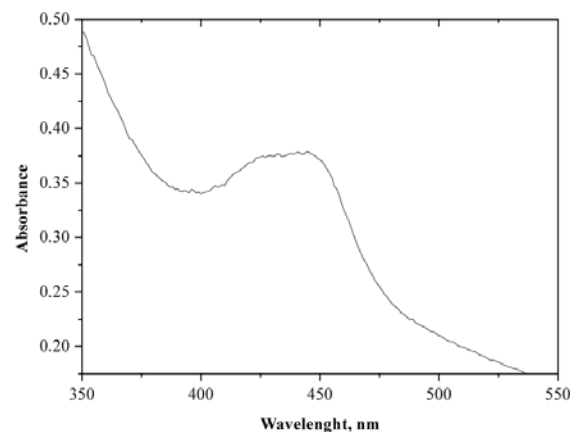
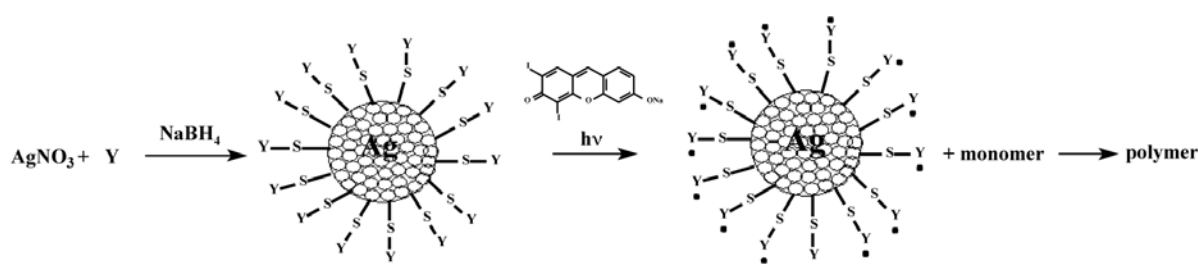


Fig. 1. Electronic absorption spectra of Ag-2-mercaptobenzoxazole (Ag-MBX) in water

Figure 1 presents the electronic absorption spectra of Ag-MBX in water. The spectroscopic, electrochemical and kinetic data are



Scheme I

collected in Table I. It can be noticed that for all obtained nanoparticles a strong broad band in the range of 400–550 nm can be found. This band is characteristic for the noble metal plasmon band which strongly depends on the surrounding and nanoparticle size [12, 21].

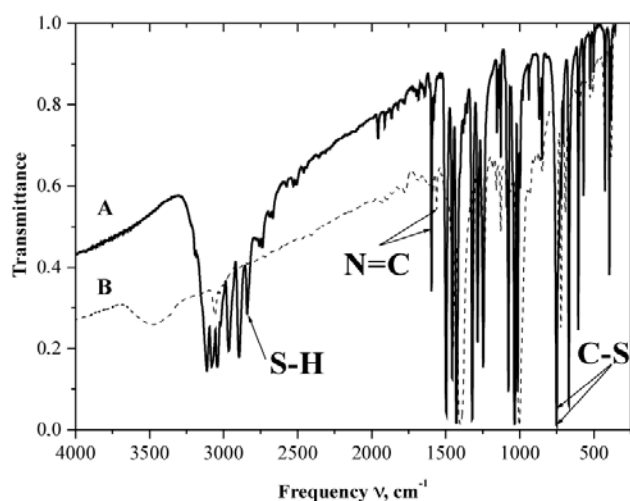


Fig. 2. FTIR spectrum: (A) 2-mercaptobenzothiazole (MBT), (B) immobilized nanoparticle (Ag-MBT)

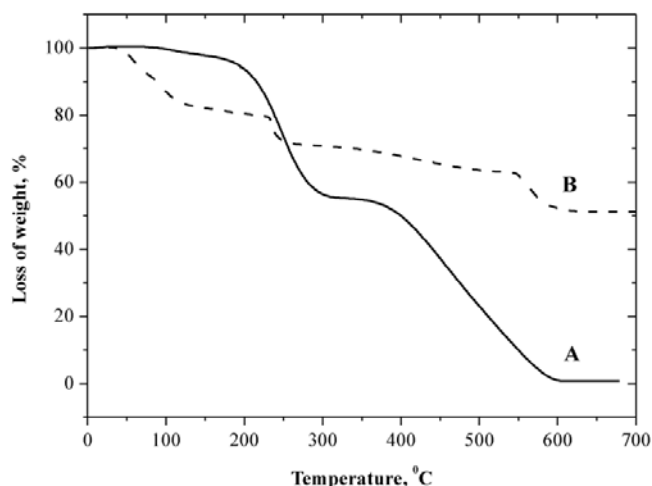


Fig. 3. Thermogravimetric curves for: (A) – 2-mercaptobenzoxazole (MBX); (B) – Ag-MBX nanoparticles

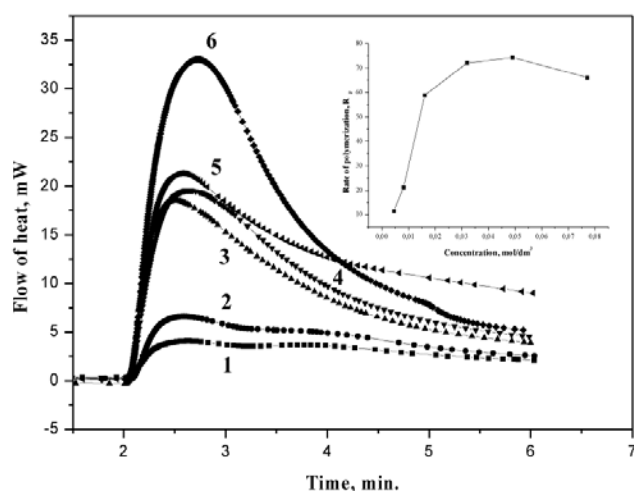


Fig. 4. The family of the photopolymerization kinetic traces recorded for polymerization mixture photo-initiated using DIBF and Ag-MBX as electron donors used various concentration respectively; (1)– $0,6 \times 10^{-6}$ g/dm³, (2)– $1,0 \times 10^{-6}$ g/dm³, (3)– $2,0 \times 10^{-6}$ g/dm³, (4)– $4,0 \times 10^{-6}$ g/dm³, (5)– $6,0 \times 10^{-6}$ g/dm³, (6)– $10,0 \times 10^{-6}$ g/dm³. Insert: The initial rate of polymerization vs. Ag-MBX concentration

FTIR spectrum of synthesized MAZ-MPC's characteristic for free mercaptoazoles groups (N=C; 1580cm^{-1} - 1650cm^{-1} , C-S; 730cm^{-1} - 760cm^{-1}) are presented in Figure 2. The analysis of the FTIR spectra (Fig. 2) revealed that characteristic for S-H group, band (2427cm^{-1} - 2841cm^{-1}) was not found for immobilized nanoparticles which confirms that free azoles particles was adsorbed on the surface of nanoparticles to form mercaptonic bond.

Thermal decomposition of MAZ-MPCs (Fig. 3) shows that organic fraction was volatilized from the sample, only residue of silver can be found. Based on this experiment the combining proportion between mercaptoazoles and nanoparticles can be estimated. Different attaching values for Ag-MBI, Ag-MBO, Ag-MBX oscillate in the range of 30-55% depending on free mercaptoazoles used.

Table I
Spectral characteristics and rate of polymerization values (R_p) for nanoparticles and unbound ligands

L.p.	Structural formula of ligand	Ligand Nanoparticle	λ_{max} , nm	IR Frequency, cm^{-1}			Rate of polymerization, R_p
				S-H	N=C	C-S	
1		MBI Ag-MBI	455	2573	1626	743	19.00
				-	1617	735	21.12
2		MBT Ag-MBT	445	2841	1589	749	10.62
				-	1597	752	19.11
3		MBX Ag-MBX	540	2427	1633	739	23.93
				-	1619	728	74.37
4		TU Ag-TU	404	2665	1628	737	17.58
				-	1635	756	34.00

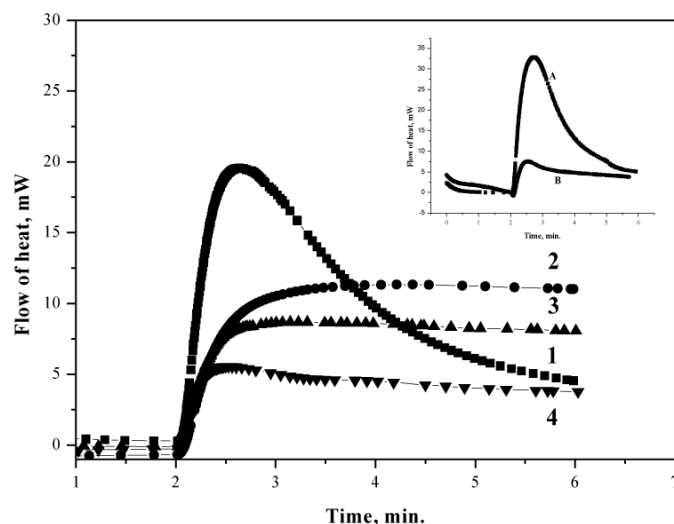


Fig. 5. The family of the photopolymerization kinetic traces recorded for polymerization of PEGDA using; (1) Ag-MBX, (2) Ag-TU, (3) Ag-MBI, (4) Ag-MBT as co-initiator and DIBF as initiator. Insert: using (A) – Ag-MBX and (B) – MBX as co-initiators

Figure 4 shows the kinetic curves of polymerization photoinduced by Ag-MBX as electron donor. Analysis of those data suggests that the rate of polymerization increases as the electron donors concentration

increases. The initial rate of polymerization (R_p) was estimated as the tangents of the slope of the straight line of the kinetic curves for the initial time.

Analysis of the data presented in Table I and revealed that the rate of PEGDA polymerization depends on the Ag-MPCs structure. The Ag-MBX is better co-initiator than the other Ag-MPCs at the same initiator concentration and irradiation conditions. It should be added however, that those co-initiators have a comparable electron donating ability (Tab. I, Fig. 5).

Comparison of co-initiating abilities of silver nanoparticles immobilized by mercaptoazoles and free mercaptoazoles derivatives show that the rate of polymerization and the maximal heat flow during polymerization are higher for Ag-MBX than for MBX.

Summary

Performed experiments prove that mercaptoazole derivatives immobilized silver nanoparticles can be used as co-initiator for free radical polymerization process. The rate of PEGDA polymerization depends on the co-initiator concentration and structure. The co-initiation process by mercaptoazole-MPCs is more efficient than co-initiation observed for mercaptoazoles acting as free molecule. This behaviour can be attributed to: (i) specific interaction of sulfur electrons with surface plasmon electrons that make an electron transfer from mercaptoazole to excited electron acceptor more efficient, or (ii) to a high concentration of electron donor in the ligand shell.

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Translation into English by the Author

Literature

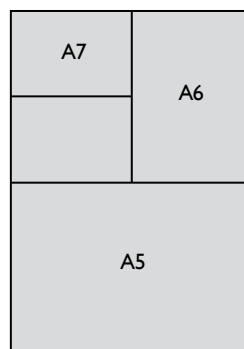
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