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Hexaarylbisimidazoles and ketocyanine dyes as effective electron transfer photoinitiating systems

RAPID COMMUNICATION

Summary — Four different hexaarylbisimidazoles (HABIs) and 5 ketocyanine dyes (JAWs) have been synthesized. Chemical structures and basic spectroscopic properties of JAWs obtained have been characterized. Free energy changes (ΔG_{el}) of the process of electron transfer between HABIs and JAWs tested have been experimentally determined for 20 pairs of HABI + JAW. The dependence of the rate of 1,1,1-tri(acryloxymethyl)propane photopolymerization, initiated with HABI + JAW systems in the presence of mercaptobenzoxazole, on the ΔG_{el} value and on the radiation wavelength (488 nm and 355 nm or 365 nm, Fig. 1) has been determined. It was found that chemical structures of HABI and JAW do not affect considerably the rate of polymerization.

Key words: photoinitiators, electron transfer mechanism, hexaarylbisimidazole + ketocyanine dye systems, photopolymerization, 1,1,1-tri(acryloxymethyl)propane.

2,2',4,4',5,5'-Hexaarylbisimidazoles (HABIs) are one of the most widely patented photoinitiators [1]. HABIs are both thermochromic and photochromic and are cleaved either thermally or photochemically (when irradiated in the 255–275 nm or 300–375 nm regions) into a pair of tetraarylimidazolyl radicals (lophyl radicals = *L*). These radicals recombine in the dark to form the starting HABI. The *L* radical generated in the photodecomposition process can interact with chain-transfer agent either by direct hydrogen atom abstraction or by electron transfer to produce an initiating species capable to addition to the monomer.

Photoinitiated polymerization with HABI systems can occur under the visible light in the presence of absorbing dyes that are good electron donors [2]. Reaction between the HABI and sensitizer involves the singlet excited state [3, 4]. A combination of ESR [5] and laser flash photolysis [5, 6] has established an electron transfer mechanism for the reaction between HABI and sensitizer {2,5-bis(1*H*,5*H*-benzo[*i,j*]-quinolizin-1-yl)methylene)cyclopentanone (JAW).

The mechanism proposed for the photoinitiation of acrylates with HABI takes into account that, after electron transfer, HABI dimer dissociates yielding free radical and HABI/JAW radical ion pairs. The lophyl radicals then leave the solvent cage and react with good hydrogen donors thus producing the initiating radicals. The components that remain in the solvent cage produce a radical ion pair (stabilized by electrostatic interaction) that subsequently undergoes a proton transfer to form two radicals; one from JAW and the other from HABI. The lophyl radical behaves as mentioned earlier, and the radical resulting from JAW likely reacts with a monomer to start polymerization [7, 8].

One other important difference between commonly dye sensitized initiators and HABI/JAW pair should be emphasized. For traditional dye/amine systems electron transfer occurs from the ground state of amine donor to the excited state of the dye. For the HABI/JAW system the electron transfer occurs from the excited state of amine (JAW) to the ground state of HABI. This specific behavior significantly differentiates this system from other dye/amine systems.

Analysis of the kinetic scheme of photoinduced polymerization *via* intermolecular electron transfer process [9–11] has shown that for a negligible efficiency of the absorbing chromophore bleaching process and taking into account the Marcus relation [12, 13], the following

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equation can describe the rate of the polymerization in viscous media:

$$\ln R_p = A - (\lambda + \Delta G_{el})^2 / 8\lambda RT \quad (1)$$

where: A — for the initial time of polymerization is the sum: $\ln k_p - 0.5 \ln k_t + 1.5 \ln [M] + 0.5 \ln I_a$, where k_p , k_t , $[M]$ have conventional meanings; I_a — intensity of absorbed UV light; λ — reorganization energy necessary to reach the transition states both of excited molecule and solvent molecules; ΔG_{el} — free energy change expressed by the Rehm-Weller equation [14].

$$\Delta G_{el} = E_{ox}(D/D^{*+}) - E_{red}(A^{*}/A) - Z e^2 / \epsilon a - E_{00} \quad (2)$$

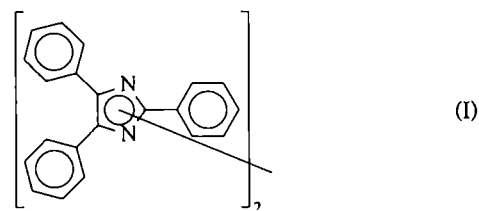
where: $E_{ox}(D/D^{*+})$ — oxidation potential of the electron donor, $E_{red}(A^{*}/A)$ — reduction potential of the electron acceptor, E_{00} — excited state energy, $Z e^2 / \epsilon a$ — Coulombic energy of the reaction (considered negligible with respect to the overall magnitude of ΔG in the present system).

Using the Rehm-Weller equation [14] and knowing the oxidation potentials of JAWs (measured using cyclovoltamperometry), knowing their singlet state energy (established based on the fluorescence spectra, see Table 1) and knowing the reduction potential of HABI (measured using cyclovoltamperometry), one can calculate the free energy change (ΔG_{el}) for the electron transfer process between tested HABIs and JAWs.

EXPERIMENTAL

HABIs were prepared by oxidation of the corresponding triarylimidazoles [15–20]. The ketocyanine dyes, 2,5-bis[[4-dialkylamino)phenyl]methylene]cyclohexanone derivatives (JAWs) were synthesized according to known procedures [21].

Four different HABIs as follows: 2,2',4,4',5,5'-hexaphenylbisimidazole [HABI-1, $E_{red}(A^{*}/A) = -1.2849$ V, Formula I]; 2,2',4,4',5,5'-hexa(4-fluorophenyl)bisimidazole [HABI-2, $E_{red}(A^{*}/A) = -0.6542$ V]; 2,2',4,4',5,5'-hexa(4-methoxyphenyl)bisimidazole [HABI-3, $E_{red}(A^{*}/A) = -1.2744$ V] and 2,2',4,4',5,5'-hexa(4-bromophenyl)bisimidazole [HABI-4, $E_{red}(A^{*}/A) = -1.2533$ V]



were synthesized in our laboratory. The structures of five ketocyanine dyes prepared along with their spectroscopic and electrochemical properties are collected in Table 1.

Table 1. Structures and basic spectroscopic and electrochemical properties of ketocyanine dyes tested

Structure	Symbol	λ_{max}^{abs} , nm	ϵ_{max} , $dm^3 \cdot mol^{-1} \cdot cm^{-1}$	λ_{max}^{Fl} , nm	E_{ox}^{*} , V
	JAW-1	424	32 500	525	0.686
	JAW-2	431	20 470	520	0.786
	JAW-3	434	25 500	541	0.560
	JAW-4	432	70 700	529	0.371
	JAW-6	438	39 200	564	0.297

^{a)} Measured using cyclic voltammetry.

The present study uses the relationship between the structures of HABI/JAW pairs and the rate of polymerization photoinitiated by this system. Since tested ketocyanine dyes absorb in a blue region of visible light, initiation systems described in this contribution may play an important role in dentistry as initiating systems for dental fillings materials.

The photopolymerization rate (R_p) was measured for a solution composed of 1 mL of 1-methylpyrrolidine-2-one (MP), 9 mL of 1,1,1-tris(acryloxymethyl)propane (TMPTA), corresponding HABI/JAW pair ($c \approx 0.5 \cdot 10^{-2}$ M) and mercaptobenzoxazole (MBO) ($c \approx 3 \cdot 10^{-2}$ M). Since the absorption band of JAWs covers the range from 330 to 510 nm for the initiation of polymerization the

emission of argon-ion lasers emitting at 488 (Omnichrome) and emitting lines at 355 and 365 nm (Innova 90-4, Coherent, USA) were used.

RESULTS AND DISCUSSION

The experimentally established data are summarized in Table 2.

Table 2. The experimentally established thermodynamical properties of HABI/JAW initiating pairs tested

JAW	E_{00} , eV	ΔG_{el} , eV			
		HABI-1	HABI-2	HABI-3	HABI-4
JAW-1	2.363	-0.382	-1.023	-0.403	-0.424
JAW-2	2.386	-0.305	-0.946	-0.326	-0.347
JAW-3	2.293	-0.439	-1.080	-0.459	-0.480
JAW-4	2.345	-0.680	-1.320	-0.700	-0.720
JAW-6	2.199	-0.608	-1.248	-0.628	-0.649

Negative values of ΔG_{el} indicate that for all combinations of HABI/JAW pairs the electron transfer reaction is thermodynamically allowed, and that tested pairs, in the presence of MBO as hydrogen atom donor, should initiate free radical polymerization.

The inspection of the initial rates of polymerization shows that the photoinitiation efficiency of tested initiators only slightly depends on the structures of both components of HABI/JAW photoredox pair (Figure 1). The explanation of this phenomenon may come from the additional experiments that clarified behaviors observed.

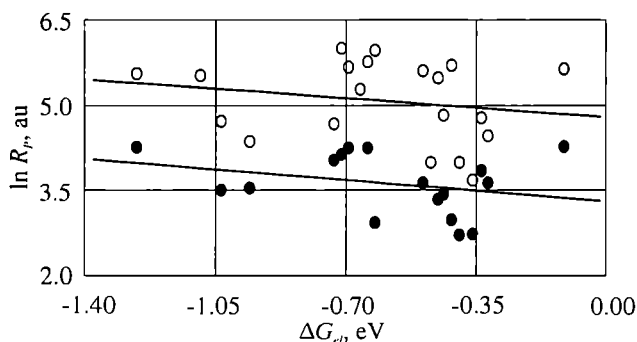


Fig. 1. The relationship between the rate of photoinitiated polymerization (R_p) and free energy (ΔG_{el}) of activation of photoinduced electron transfer process for HABI/JAW photoredox pairs. The intensities of light are: ○ — $8.15 \cdot 10^{16}$ photons \cdot sec^{-1} in UV area (355 and 365 nm); ● — $6.14 \cdot 10^{16}$ photons \cdot sec^{-1} at 488 nm

First comes from the fluorescence quenching experiments, which show that the quenching rate of singlet excited state of JAWs by HABIs is diffusion controlled;

the second is that the initiating radical is identical for all tested HABI/JAW pairs; and finally, the absorption bands for all tested photoinitiating system are located in the some spectral region. All these observations clearly indicate that the structure of both HABI and JAW essentially has no effect on the rate of electron transfer process, and these in turn, can not affect the rate of photoinitiated polymerization.

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