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Hemicyanine *sec*-butyltriphenylborate salts as effective initiators of free radical polymerization initiated *via* photoinduced electron transfer process

Part II. KINETIC STUDIES AND APPLICATION OF ELECTRON TRANSFER THEORY**)

Summary — Ability of two groups of *sec*-butyltriphenylborate salts of hemicyanine dyes (HCBo), namely styrylpyridinium borates (ABo group) and styrylbenzoxazole borates (BBo group), to photoinitiation of radical polymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) was investigated. The effects of a dye structure and free energy of activation of electron transfer between the components of photoinitiator pair (ΔG_{el}) on the rate of photoinduced radical polymerization of TMPTA (R_p) were determined. The results have been analyzed on the basis of Marcus theory describing the kinetics of photoinduced electron transfer. The values of ΔG_{el} were previously calculated using Rehm—Weller equation [equation (2)]. Oxidation potential of borate was determined using cyclic voltammetry method. Monomer conversion, quantum yield of the polymerization process (Φ_{polym}) as well as photochemical bleaching yield (Φ_{bl}) dependently on chemical structure of HCBo investigated were also determined. It was found that the structure of initiator (dye) influenced R_p value. In case of use of ABo type initiators R_p values were similar — 3.24—4.88 while in case of BBo they were placed in wide range 1.00—5.05. The highest value has been reached for B3 dye. B3Bo initiator showed also the highest values of Φ_{polym}, Φ_{bl} and monomer conversion. Linear dependence between R_p and Φ_{bl} was observed only for ABo type initiators.

Key words: redox photoinitiators, hemicyanine dyes, *sec*-butyltriphenylborate salts, photoinduced radical polymerization, Marcus theory, polymerization rate.

Photoinitiated polymerization forms the basis of numerous applications in coatings, adhesives, inks, printing plates, optical waveguides and microelectronics. Almost all of the commercially significant photoinitiators are organic compounds that produce free radicals and/or cationic species upon irradiation. The most widely used free radical photoinitiators include benzoin and its derivatives, benzyl ketals, acetophenone derivatives, aromatic ketone/amine combinations, while onium salts belonging to iondonium, sulphonium and alkoxy pyridinium families represent a class of cationic photoinitiators [1].

Direct photoinduced polymerization reactions concern the creation of a polymer *via* a chain reaction initiated by light. Since a formation of reactive species from a monomer by direct light absorption is not an efficient route, the initiation step of the polymerization reaction requires the presence of a photoinitiator (PI) which, under light excitation is able to generate reactive species that can start polymerization chain reaction (see Scheme A).

The intrinsic reactivity of PI which plays an important role in curing speed is directly associated with its molecular structure, which governs the intensity of the light absorbed, the absorption wavelength range, the electron transfer reactions' ability and the efficiency of the photophysical and photochemical processes involved in the excited states deactivation (which deter-

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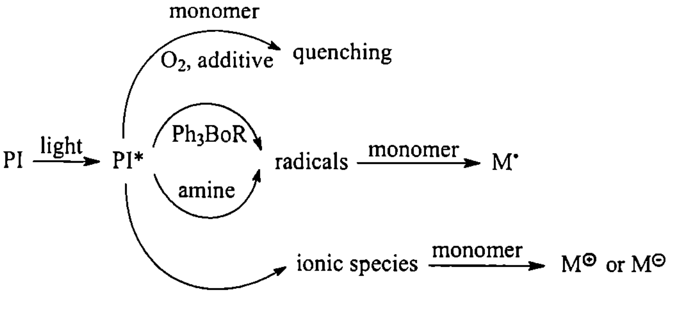
**) Part I — see [9].

mines the yield of cleavage reactions, the rate of electron transfer reactions, the yield of the quenching by monomer, oxygen or other additives such as hydrogen donors, light stabilizers, *etc.*) [2, 3].



where: Ph_3BoR — *sec*-butyltriphenylborate salts

Scheme A. Generation of reactive species during light excitation of photoinitiator

Generally, there are two types of initiators of free radical polymerization:

— Photofragmentable (photodecomposed). Photogeneration of free radicals occurs when a photoexcited molecule undergoes bond cleavage that gives a pair of such species. One or both of the resulting radicals can initiate free radical polymerization.

— Two components photoinitiation systems.

Photoinduced intermolecular electron transfer is an important process giving a free radical able to initiate polymerization chain reaction. The panchromatic sensitization of vinyl polymerization requires the presence of a suitable dye as a light absorber. For such a case, photophysical energy transfer between dye excited state and other chromophore which yields free radicals, is generally disfavored. As an alternative other processes avoiding typical energy restriction are usually considered. The photoinduced intermolecular electron transfer, which is nonclassical, endothermic energy transfer process, represents such an alternative. This process involves the use of light to initiate electron transfer from a donor to an acceptor molecule [4, 5].

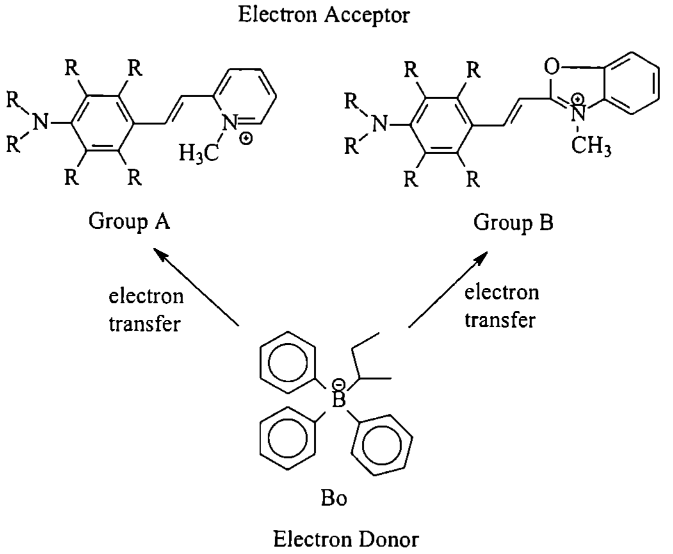
In recent years, there have been many new developments in the synthesis and photochemical studies of novel photoinitiating systems. Initiators possessing alkyltriphenylborate anion paired with symmetrical and unsymmetrical cation of cyanine dyes represent such a novel group. This group of photoinitiators has been synthesized and examined in terms of their efficiency as photoinitiators of free radical polymerization in our laboratory [6—8]. The ability of photoinitiation of multifunctional acrylate polymerization by *sec*-butyltriphenylborate salts of the styryl chromophoric groups is documented in this paper. In our previous paper we described the photoinitiating ability of *n*-butyltriphenylborate salts of hemicyanine dyes [9].

EXPERIMENTAL

Materials

Substrates used for the preparation of the dyes, monomers and solvents were purchased from Fluka, Merck and Aldrich. Hemicyanine dyes listed in Table 1 were obtained in our laboratory by the method described elsewhere [10—15].

The structures of the salts used in the study are shown in Scheme B.



Scheme B. Schematic presentation of electron transfer process between borate anion (Bo) and two groups of hemicyaniane cations

As electron acceptors hemicyanine dyes were used. These included:

— Styrylpirydinium dyes (group A),

— Styrylbenzoxazole dyes (group B).

As electron donor *sec*-butyltriphenyl borate was applied.

Methods

Absorption spectra were recorded using a Varian Cary 3E spectrophotometer and fluorescence spectra were obtained using a Hitachi F-4500 spectrofluorimeter. Absorption and emission spectra were recorded using a spectroscopic quality ethyl acetate (EtOAc) as a solvent. Fluorescence measurements were performed at an ambient temperature.

The reduction potentials of hemicyanine dyes and the oxidation potential of the tetramethylammonium *sec*-butyltriphenylborate were measured by cyclic voltammetry. An Electroanalytical MTM System model EA9C-4z (Cracow, Poland), equipped with a small volume cell, was used for measurements. A 1 mm platinum disc electrode was used as the working electrode, Pt wire constituted the counter electrode and Ag/AgCl electrode served as the reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate in dry acetonitrile [16].

The kinetics of free radical polymerization (ΔG_{el}) measurements were carried out by measuring the rate of heat evolution during polymerization [16—21]. Measurements were performed in a homemade microcalorimeter. A semiconducting diode immersed in 2 mm thick layer (0.25 mL) of a cured sample was used as a temperature sensor. Irradiation of the polymerization mixture was carried out using the emission of an Omnichrome model 543-500 MA argon-ion laser, which emits two wavelengths, at 488 and 514 nm. The power of irradiation, measured using a FieldMaster Power Meter, Coherent, 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 hemicyanine borate (HCBo) concentration was $1 \cdot 10^{-3}$ M. As a reference sample a polymerizing mixture containing hemicyanine iodides (dye without an electron donor) were used.

The monomer conversion was determined as a ratio of the quantity of reacted double bonds to the total quantity of double bonds in monomer.

RESULTS AND DISCUSSION

Analysis of the kinetic scheme of photoinduced polymerization *via* intermolecular electron transfer process has shown [19—21] that for a negligible efficiency of the absorbing chromophore bleaching process (for very low quantum yield of the dye color loss process), and taking into account the Marcus relation [22—24], the following equation could be used for the description of the rate of polymerization (R_p) in viscous media:

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

where: A — *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, $[M]$ *and* I_a *have conventional meanings),* λ — *reorganization energy necessary to reach the transition states both of the excited molecule and the solvent molecules,* ΔG_{el} — *free energy change expressed by the Rehm—Weller equation (2) [25, 26].*

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

where: $E_{ox}(D/D^{\bullet+})$ — *oxidation potential of the electron donor,* $E_{red}(A^{\bullet-}/A)$ — *reduction potential of electron acceptor,* E_{00} — *excited state energy,* $Ze^2/\varepsilon a$ — *Coulombic energy, which is considered negligible to the overall magnitude of* ΔG_{el} *of analyzed synthesis.*

For the evaluation of ΔG_{el} the reduction potential of an electron acceptor is needed.

From the cyclovoltaic curve shown in Fig. 1 it is apparent that the electrochemical reduction of hemicyanine cation is reversible, therefore the reduction potentials values for novel dyes may have the thermodynamic meaning. Having known the reduction potentials of HC dyes and their singlet state energies (calculated basing on the fluorescence spectra, see Table 1) as well as the oxidation potential of tetramethylammonium *sec*-butyltriphenylborate (E_{ox} = 0.78 V) and using Rehm—Weller equation [25, 26] one can calculate the free energy change (ΔG_{el}) in the electron transfer process between HC cation and Bo anion. The structures of the hemicyanine dyes prepared, their electrochemical properties along with all calculated data are collected in Table 1.

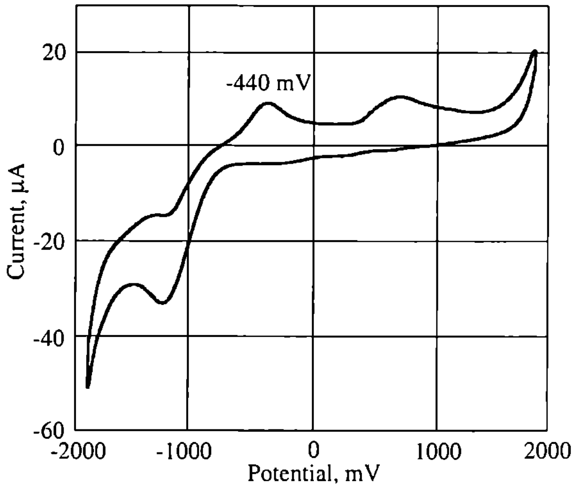


Fig. 1. Cyclic voltametric curve of hemicyanine dye B6 in electrolyte — 0.1 M tetrabutylammonium perchlorate in dry acetonitrile solution (for structure see Table 1)

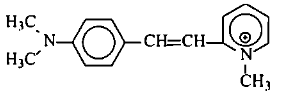
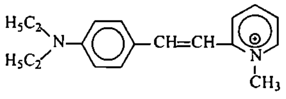
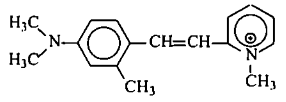
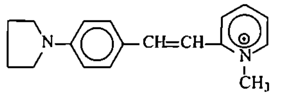
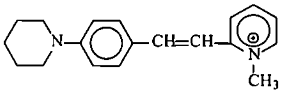
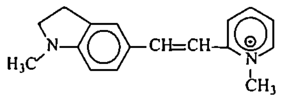
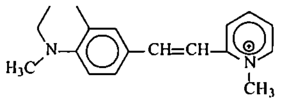
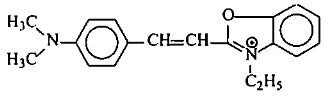
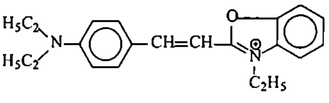
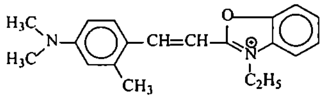
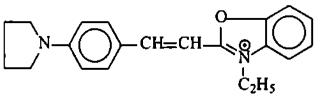
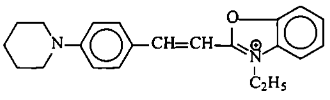
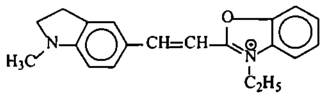
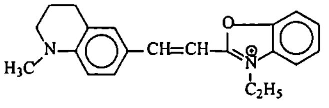
Negative values of ΔG_{el} indicate that for all combinations of HCBo pairs the electron transfer reaction yielding free radicals is thermodynamically allowed, and that the tested salts should initiate free radical polymerization of the vinyl monomers.

The relative rates of the initial rates of photoinitiated polymerization measured for all the tested photoredox pairs are collected in Table 2.

The analysis of the initial R_p (Fig. 2, Table 2) shows that the photoinitiation efficiency of tested initiators strongly depends on the structure of HCBo photoredox pair. It is obvious that the initiators form group A, possessing only an alkyl substituent at amino group, initiate polymerization of TMPTA of about one order of magnitude faster than initiators with substituents making the rotation about C-N bond difficult. It is surprising that the photoinitiator possessing methyl group in styryl moiety (A3) in ortho position with respect to C=C bond in general does not initiate the polymerization. However, dye B3 initiates the polymerization with the highest observed rate.

It is clear that the exchange of the pyridinium moiety with benzoxazole ring changes the photoinitiator sensitivity. The rates of polymerization observed for initiators from group A are comparable, while in group B only three of tested compounds are good photoinitiators (B3,

Table 1. Structures, basic electrochemical and thermodynamical properties of hemicyanine (HC) dyes tested

Dye	Structure of acceptor cation	E_{red} V*)	E_{00} eV**)	ΔG_{el} eV***)
A1		-0.586	2.390	-1.014
A2		-0.597	2.380	-0.993
A3		-0.602	2.362	-0.970
A4		-0.581	2.376	-1.005
A5		-0.544	2.380	-1.046
A6		-0.596	2.275	-0.889
A7		-0.600	2.319	-0.929
B1		-0.575	2.314	-0.857
B2		-0.550	2.309	-0.877
B3		-0.445	2.276	-0.949
B4		-0.470	2.249	-0.989
B5		-0.360	2.288	-1.046
B6		-0.440	2.271	-0.949
B7		-0.460	2.247	-0.951

*) Measured in MeCN. **) Measured in EtOAc.
***) Calculated using Rehm—Weller equation: E_{ox} (D/D$^{\bullet}$) = 0.790 V.

B4 and B7). The others do not initiate the polymerization at all.

Table 2. Measured relative rates of polymerization (1 + lnR_p), degrees of monomer conversion and quantum yields of photopolymerization (Φ_{polym}) and of photobleaching process (Φ_{bl}) for tested HCBo salts processes

Dye	1 + lnR_p a.u.	Monomer conversion, %	Φ_{polym}	Φ_{bl}	tgα*) · 10^3
A1	4.88	15.24	37.57	0.232	3.34
A2	4.74	11.38	29.92	0.300	2.90
A3	—	—	—	0.457	—
A4	4.50	5.80	16.95	0.245	2.29
A5	4.69	11.16	27.50	0.374	2.75
A6	3.24	1.90	6.51	0.014	0.65
A7	3.45	3.06	8.04	0.042	0.80
B1	1.00	0.11	0.69	0.280	0.069
B2	1.40	0.26	1.08	0.710	1.03
B3	5.03	27.78	64.43	0.135	3.901
B4	5.05	15.60	36.18	—	3.971
B5	1.04	0.21	0.84	0.697	0.072
B6	1.14	0.08	0.40	0.849	0.079
B7	4.71	6.66	27.67	—	2.825

*) Slope of the linear part of photoinitiated polymerization kinetic curve for the initial time of polymerization.

From the data obtained during the measurements it was also deduced that the conversion of monomer is ranging from 5 % to 28 %, while the quantum yields of photopolymerization oscillates between 20 and 30 (Table 2) for the almost all active photoinitiating pairs. It is noteworthy that the ion pair marked as B3Bo shows the best photoinitiation ability with quantum yield of polymerization of *ca.* 64. It was also found that the degree of monomer conversion depends on the structure of the photoinitiating pair.

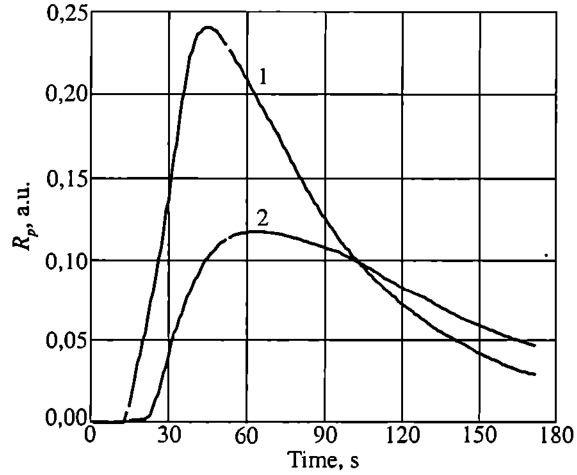


Fig. 2. Influence of the photoinitiation type on the rate of photoinitiated polymerization (R_p) of TMPTA:MP (9:1) (I_a = 64 mW/cm^2, argon-ion laser irradiation). Photoinitiators: 1 — B3Bo, 2 — A2Bo (for symbols and structures see Table 1)

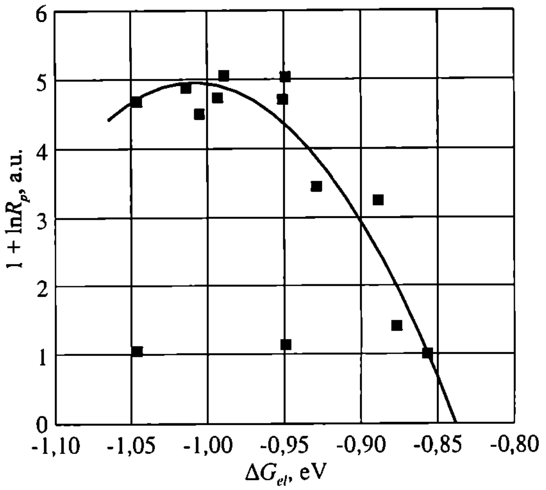


Fig. 3. Marcus plot of the rate of polymerization of TMPTA:MP (9:1) mixture initiated by HCBo photoredox pairs (dyes listed in Table 1)

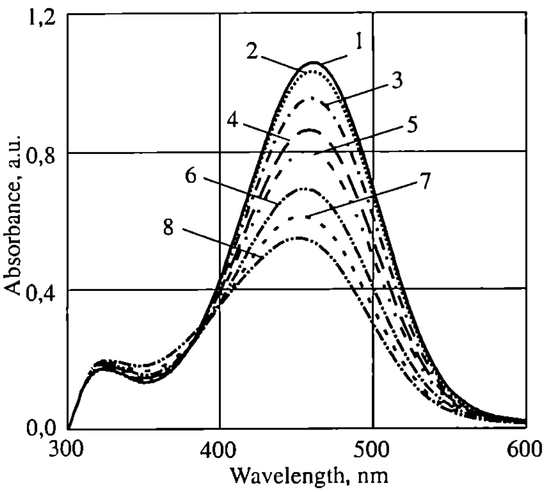


Fig. 4. Electronic absorption spectra of A6Bo during an argon-ion laser irradiation (I_a = 50 mW/cm^2) in EtOAc solution. Time of irradiation: 1 — 0 s, 2 — 2 s, 3 — 20 s, 4 — 50 s, 5 — 90 s, 6 — 210 s, 7 — 510 s, 8 — 1110 s

It is apparent from the inspection of the data presented in Fig. 3 that the rate of polymerization initiated by HCBo increases as the driving force of electron transfer reaction increases. This behavior is predicted by the classical theory of photoinduced electron transfer [22—24].

Irradiation of hemicyanine borates causes a bleaching of the dye (Fig. 4). According to the general kinetic scheme of polymerization photoinduced by cyanine dyes in the presence of alkyltriphenylborate salts, the colorless product obtained during the polymerization originates from cross-coupling reaction between an alkyl radical and a cyanine radical formed from both electron donor and electron acceptor [16, 18, 27—29]. The analysis of the bleaching process shows that the quantum yields of these reactions for radicals pairs under study oscillate between 0.014 and 0.849. For initiators A3, B5, B6 the values of the quantum yields of the bleaching process (Φ_{bl}) is close to the value of the quantum yield of *sec*-butyl radical formation (Φ_{bl} = 0.78), determined for the symmetrical cyanine dyes [28] (see Table 2). This observation allow to conclude that the bleaching process might decrease the efficiency of free radical polymerization. From the inspection of the data presented in Table 2 one can also conclude that the styrylbenzoxazole borate salts (group B) are characterized by the highest value of Φ_{bl} and are rather poor photoinitiators of free radical polymerization of TMPTA. On the other hand, for the styrylpyridinium borate salts (group A) the highest rate of photoinitiated polymerization is observed for HCBo pair showing the highest quantum yield of the color loss. Concluding, there is no general relationship between the rate of photoinitiated polymerization and the bleaching reaction for the photoinitiating pairs under study.

The photoreduction of the dyes, in the absence of monomers, should show characteristics indicating the link between the rate of the photoinduced intermolecular electron transfer and the quantum yield of the bleaching process. For *sec*-butyltriphenylborate salts of hemicyanine dyes this type of relationship is shown in Fig. 5.

It is evident that the efficiency of the bleaching process of the initiator can be also described using the Marcus relationship.

The kinetic analysis of the dyes photobleaching process in an inert solvent indicates that, for a dye from group A, R_p is proportional to Φ_{bl} (Fig. 6). Such a relationship is not observed for initiators from group B. The presence of a linear relationship between R_p and Φ_{bl} observed only for pairs from group A indicates that the formation of free radicals is followed by two parallel reactions. This conclusion allows to anticipate that for the selected groups of photoredox pairs, which form the bleached products *via* free radicals cross-coupling reaction, the rate of polymerization can be presented in a form similar to

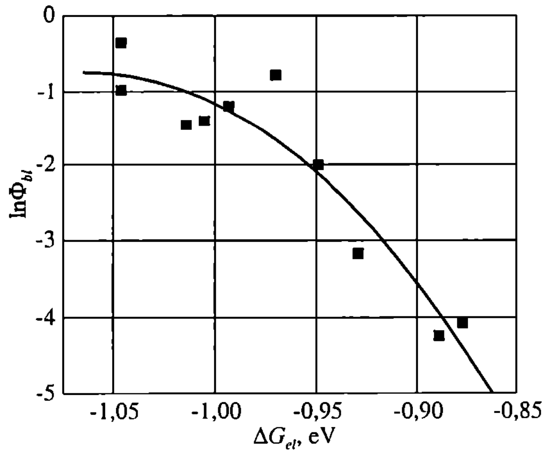


Fig. 5. Dependence of quantum yield of photobleaching process (Φ_{bl}) of HCBo salts on free energy changes of electron transfer process (ΔG_{el}). The reaction was carried out in EtOAc

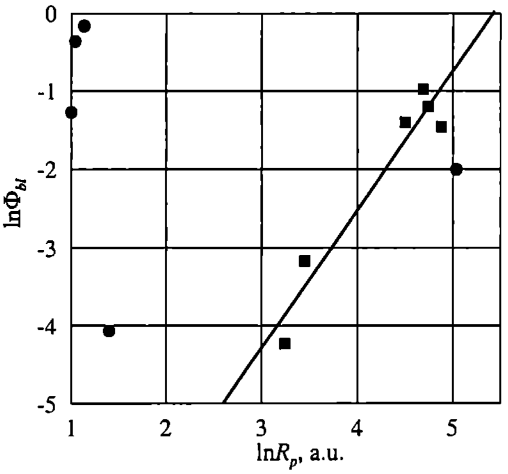


Fig. 6. Dependence of quantum yields of photobleaching process (Φ_{bl}) on rate of polymerization of TMPTA:MP (9:1) mixture initiated by HCBo photoredox pairs. Type of salts: ■ *— group A,* ● *— group B*

that describing the rate of polymerization occuring without the bleaching reaction [19, 20]. It is obvious that the coupling of *sec*-butyl radical with styrylpyridinium (group A) radical can compete with the initiation of free radical polymerization and that the beaching reaction can significantly affects the final photoinitiation ability and cannot be neglected in many cases.

CONCLUSIONS

Polymerization photoinitiated by HCBo pairs occurs *via* the electron transfer process. The efficiency of the polymerization significantly depends on the structure of the hemicyanine cation used as an electron acceptor. It was found that B3Bo initiator showed the highest values of rate of polymerization, quantum yields of photopolymerization and photobleaching, and monomer conversion. Linear relationship between the rate of polymerization and quantum yields of photobleaching were observed only for ABo initiators. Described in this work results are in contrast to those obtained recently for the same hemicyanine dyes pared with *n*-butyltriphenylborate anion [9].

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