JANINA KABATC[1)], JERZY PĄCZKOWSKI[1)], JERZY KAROLCZAK[2)]

What affects the rate of free radical polymerization of a multifunctional acrylate photoinitiated by cyanine borate salts?

Part II. APPLICATION OF ELECTRON TRANSFER THEORY[*)]

Summary — On the basis of Schuster's investigation, a mechanism of the processes going on during radical polymerization, photoinitiated by cyanine borate salts, has been proposed. As well the possibility of Marcus theory application to describe the kinetics of such polymerization, photoinitiated *via* electron transfer process, has been presented. It required the determination of the value of free energy of activation of electron transfer process (ΔG_{el}), using Rehm-Weller equation. Using cyclic voltammetry the reduction potentials of the dyes and oxidation potentials of borate salts were determined. Parabolic dependence between polymerization rate (R_p) and ΔG value has been obtained for all the salts tested. The lifetimes of excited singlet state of cyanine dye with and without quenching were determined and let calculate the rate constants of primary process of polymerization investigated, *i.e.* electron transfer from borate anion to excited state of the dye (k_{el}). According to the Scheme A, the effect of competitive process, *i.e.* cyanine and butyl radicals recombination on the photoinitiated polymerization rate was also determined. This process, which does not influence R_p value, leads to the dye bleaching what strongly depends on the structure of both dye cation and borate anion. There was stated that initiation rate of polymerization depends on the photoinitiator concentration and R_p value — on the co-initiator concentration.

Key words: dye photoinitiators, cyanine borate salts, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, radical polymerization, mechanism, kinetics, electron transfer process.

The initiation of polymerization *via* photoinduced intermolecular electron transfer process involves many steps, including photoinduced electron transfer from an electron donor to the singlet or triplet state of electron acceptor (usually dye) followed by secondary reactions, which yield a neutral radical initiating polymerization.

The kinetics of photoinduced electron transfer process is usually described using the Marcus theory [1]. However, the practical application of Marcus theory is commonly used for the study of only the primary photochemical processes. The description of the kinetics of the photoinduced polymerization *via* the intermolecular electron transfer is another example of this theory applying to practice [2, 3]. On the basis of this theory it was our intention to establish the kinetic and thermodynamic criteria of the cyanine borate redox pair (Cy^+Bo^-) selection as free radical polymerization initiating system. These compounds belong to the specific group of photoinitiating systems. Both components of the initiator exist as ions, therefore in nonpolar solvents they exist predominantly as ion pairs. After the electron transfer a radical pair $[Cy^{\cdot}][R^{\cdot}]$ is formed. Since these products are not stabilized by the electrostatic interaction they can easily diffuse from the initial solvent cage giving a separated free radical that can photoinitiate free radical polymerization. In particular, it was our intention to find the relationship between the primary process, *i.e.* the electron transfer process, and the rate of free radical polymerization, photoinitiated by cyanine borate salts, and to clarify the relationship between various parameters characterizing an initiating system and the rate of photoinitiated polymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). Our purposes were accomplished by:

[1)] University of Technology and Agriculture, Faculty of Chemical Technology and Engineering, ul. Seminaryjna 3, 85-326 Bydgoszcz, Poland.

[2)] Adam Mickiewicz University, Faculty of Physics, ul. Umultowska 85, 61-614 Poznań, Poland.

[*)] Part I — see [4].

(*i*) The study of the basic physical and chemical properties of the newly synthesized photoinitiating pairs [4] and the qualitative and quantitative analysis of the photochemical processes that occur during the polymerization reaction. This, in turn, allows to understand the mechanisms of the competitive reactions that reduce the quantum yield of the photoinitiated polymerization.

(*ii*) The study of the kinetics of the photoinitiated free radical polymerization in bulk using the calorimetric method.

(*iii*) The study of the influence of the rate of electron transfer process on the efficiency and rate of photoinitiated polymerization.

EXPERIMENTAL

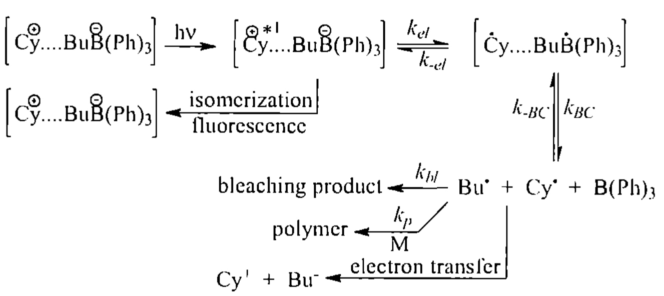
The kinetics of free radical polymerization was studied using a polymerization solution composed of 1 mL of 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). Cyanine borate concentration was $1 \cdot 10^{-3}$ M. As a reference sample a mixture containing monomer and cyanine iodides or ethyl sulfates (dye without an electron donor) was used. The methodology of measurements of the kinetics of free radical polymerization was described earlier [3, 5, 6]. The irradiation of the polymerization mixture was carried out using the emission of an Omnichrome argon ion laser Model 543-500 MA with the light intensity of 30 mW/0.78 cm^2.

The reduction potentials of the dyes were measured by cyclic voltammetry. An Electroanalytical MTM (Krakov) Model EA9C-4z was used for the measurements, and Ag-AgCl electrode served as a reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate.

The fluorescence lifetime measurements were performed using pico/femtosecond spectrometer constructed at Adam Mickiewicz University, Poznań (Poland). The design and construction of a spectrometer for picosecond fluorescence decay measurements are described elsewhere [7, 8]. The apparatus utilizes for the excitation a pico/femtosecond tunable Ti:Sapphire laser generating pulses of about 1 ps. Short laser pulses in combination with a fast microchannel plate photodetector and ultrafast electronics make a successful analysis of fluorescence decay signals in the range of single picoseconds possible. The dyes were studied at the concentrations able to provide equivalent absorbances at 460 or 480 nm (0.2—0.4 in the 10 mm cell).

RESULTS AND DISCUSSION

The Schuster's study on the photochemistry of *N,N'*-dimethylindocarbocyanine borate salts [9, 10] allowed to describe the mechanism of free radical polymerization photoinitiated by cyanine borate salts. This is shown in Scheme A.



Scheme A

where: k_{BC} — rate constant of carbon-boron bond cleavage in boranyl radical (the opposite process is denoted as k_{-BC}); k_{bl} — rate constant of free radicals recombination process, leading to the bleaching of a dye.

The cyanine dye cation and borate anion exist as ion pair even in the solvents of medium polarity [9, 11]. Some of them even form the penetrating ion pairs of which the center-to-center distance between the ions is less than the sum of the individual ion radii [12—14]. Since, the lifetime of the excited singlet state of cyanine dye is too short (less than 0.5 ns) to let the efficient diffusive formation of encounter complex at achievable concentration of borate; the self-association of cyanine cation and borate anion in their ground state is a prerequisite for the effective photoinduced electron transfer process.

The irradiation of cyanine dye/borate anion ion pair with visible light generates the excited singlet state of cyanine chromophore, which can undergo three possible reactions:

(*i*) fluorescence process,

(*ii*) photoisomerization,

(*iii*) electron-transfer reaction.

The cyanine/boranyl radical pair formed after the photoinduced electron transfer process may undergo the back electron transfer process leading to the regeneration of substrates or it may undergo a carbon-boron bond cleavage to form an alkyl radical and triphenylboron. Formed in the latter process a radical pair $[Cy^{\cdot}][R^{\cdot}]$ might also undergo the electron transfer process leading to the formation of cyanine cation $[Cy^{+}]$ and alkyl anion $[R^{-}]$. The radicals formed might couple giving an alkylated cyanine [Cy-R] or might diffuse from the initial solvent cage.

It is known from the literature that the electron transfer process in the cyanine borate ion pair has two restrictions. Borate salts able to form the stabilized radicals (*e.g.* benzyl) give the cyanine radicals with high yields. In such cases the electron transfer process is faster than the back electron transfer process. In the case when borate salts are not able to generate the stabilized radicals (*e.g.* phenyl) the efficiency of the cyanine radicals formation is very low.

In the present paper it was our intention to present a possibility of the application of Marcus theory to the description of the kinetics of free radical polymerization photoinitiated *via* electron transfer process.

The relationship between the rate of polymerization, initiated *via* electron transfer process, and free energy of activation of the photoinduced electron transfer process

The discussion on the cyanine borate photochemistry should also include the estimation of the thermodynamic driving force of the photoinduced electron transfer (PET) process. It is well known that the main prerequisite of PET reaction is an equation described by Rehm—Weller, which states that free energy of activation of the PET process (ΔG_{el}) should have a negative value:

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

where: $E_{ox}(D/D^{\bullet+})$ — *oxidation potential of electron donor,* $E_{red}(A^{\bullet-}/A)$ — *reduction potential of electron acceptor,* E_{00} — *energy of electron acceptor (cyanine) excited state and* $Ze^2/\varepsilon a$ — *Coulombic energy gained by bringing the ions to an encounter distance in a solvent with relative permittivity* ε.

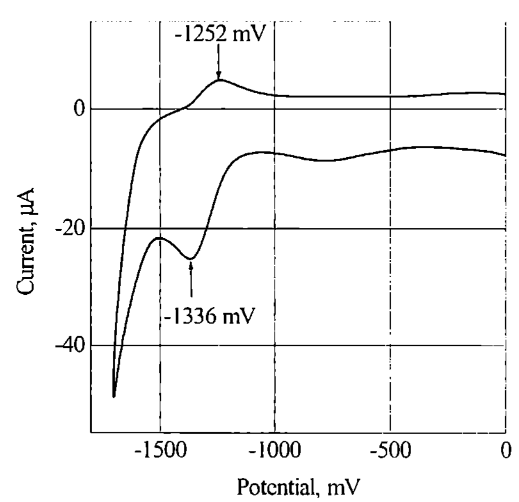
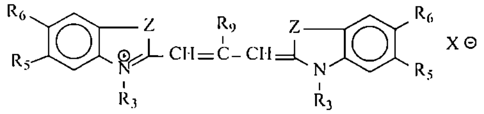


Fig. 1. Illustrative cyclic voltametric curve of selected dye (3,3'-diethyl-5,5'-diphenyl-9-methylcarbocyanine iodide)

The electrochemical reduction of cyanine dyes in acetonitrile solution is reversible (Fig. 1), however, the oxidation process of borate anion, as is shown in Fig. 2, is irreversible. The values of the oxidation potential of

T a b l e 1. Thermodynamic characteristics of cyanine borates tested*)



Cy	Z	R_5	R_6	R_9	R_3	E_{red}, V CyX	ΔG_{el}, eV CyB2	ΔG_{el}, eV CyB3	ΔG_{el}, eV CyB4	ΔG_{el}, eV CyB5
Cy22	O	Cl	H	H	C_2H_5	-1.35	-0.054	-0.12	-0.168	-0.36
Cy48	O	Cl	H	CH_3	C_2H_5	-1.074	-0.320	-0.384	-0.432	-0.694
Cy49	O	Cl	H	C_2H_5	C_2H_5	-1.356	-0.044	-0.085	-0.135	-0.393
Cy23	O	CH_3	H	H	C_2H_5	-1.279	-0.134	-0.143	-0.240	-0.444
Cy51	O	CH_3	H	CH_3	C_2H_5	-1.19	-0.191	-0.217	-0.254	-0.527
Cy53	O	CH_3	H	C_2H_5	C_2H_5	-1.383	0.003	-0.011	-0.056	0.347
Cy19	O	H	H	H	C_2H_5	-1.196	-0.212	-0.304	-0.352	-0.568
Cy41	O	H	H	CH_3	C_2H_5	-1.334	-0.065	-0.118	-0.161	-0.411
Cy45	O	H	H	C_2H_5	C_2H_5	-1.295	-0.120	-0.147	-0.189	-0.484
Cy25	O	C_6H_5	H	H	C_2H_5	-1.21	-0.178	0.218	-0.270	-0.475
Cy52	O	C_6H_5	H	CH_3	C_2H_5	-1.251	-0.095	-0.143	-0.206	-0.473
Cy28	O	C_6H_5	H	C_2H_5	C_2H_5	-1.378	0.050	-0.033	-0.081	-0.286
Cy27	O	CH_3O	H	C_2H_5	C_2H_5	-0.421	-0.917	-0.979	-1.040	-1.192
Cy24	O	CH_3O	H	H	C_2H_5	-1.389	0.029	-0.078	-0.074	-0.307
Cy9	S	CH_3	H	H	C_2H_5	-1.229	0.121	0.063	0.008	-0.167
Cy46	S	CH_3	H	CH_3	C_2H_5	-1.284	0.139	0.097	0.055	-0.195
Cy47	S	CH_3	H	C_2H_5	C_2H_5	-1.160	0.024	0.011	-0.050	-0.316
Cy3	S	H	H	H	C_2H_5	-1.240	0.169	0.046	0.002	0.210
Cy4	S	H	H	CH_3	C_2H_5	-1.268	0.167	0.059	0.014	-0.203
Cy50	S	H	H	C_2H_5	C_2H_5	-1.389	0.230	0.189	0.095	-0.134
Cy10	S	H	CH_3O	H	C_2H_5	-1.224	0.156	0.093	0.043	-0.189
Cy11	S	CH_3O	H	C_2H_5	C_2H_5	-1.229	0.017	0.012	0.069	-0.186
Cy61	S	CH_3O	H	H	C_2H_5	-0.917	-0.149	0.186	-0.244	-0.507
Cy33	S	H	C_2H_5O	H	C_2H_5	-0.817	-0.250	-0.310	-0.360	-0.589
Cy58	S	OH	H	H	C_2H_5	-1.147	0.100	0.053	-0.005	-0.391
Cy59	S	OH	H	CH_3	C_2H_5	-1.268	0.190	0.188	0.109	-0.323
Cy60	S	OH	H	C_2H_5	C_2H_5	-1.356	-0.049	-0.109	-0.140	-0.400
Cy36	S	NO_2	H	H	C_2H_5	-1.081	-0.082	-0.117	-0.161	-0.374

*) The meaning of X — see text.

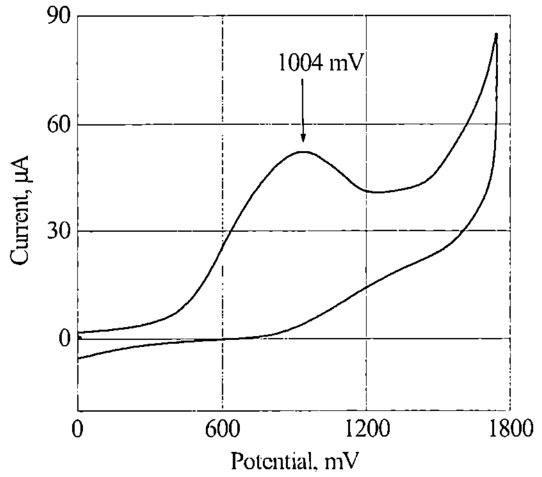


Fig. 2. Cyclic voltametric curve of tetramethylamino-n-butyltriphenylborate

tested borates and values of E_{00} were published earlier [15, 16].

On the basis of electrochemical as well as fluorescence measurements and using the Rehm—Weller equation, the values of the free energy of the electron transfer process were estimated for cyanines possessing four different borate anions. They are presented in Table 1 (symbols B2, B3, B4 and B5 denote *n*-, *sec*-, *tert*-butyltriphenylborate salts and tetra-*n*-butylborate, respectively).

It should be noted that according to the Schuster's studies the oxidation potentials of the tested borate salts determined by electrochemical method have only rough meaning. This is because of a very short lifetime (about 250 fs) of the boranyl radical formed as a result of the photoinduced electron transfer process [17]. The values of ΔG_{el} of tested photoredox pairs oscillate in the range from -0.7 to 0.36 eV (-67.1 to 34.73 kJ/mol).

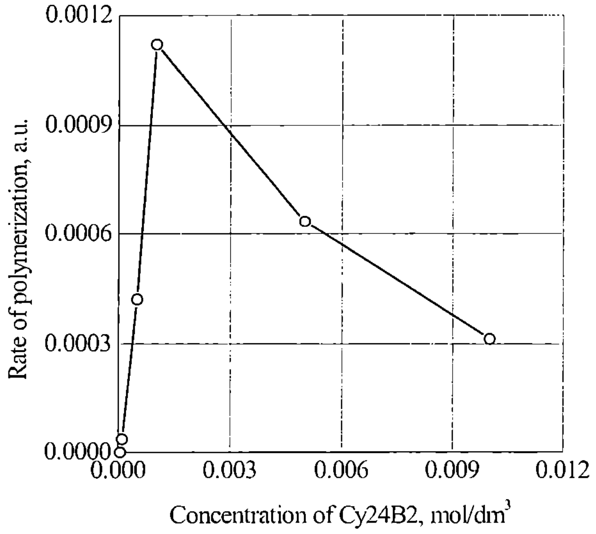


Fig. 3. The influence of donor/acceptor concentration (Cy24B2) on the rate of photoinitiated polymerization of MP:TMPTA mixture in vol. ratio 1:9

The influence of a donor-acceptor concentration on the rate of free radical polymerization

The plot illustrated the relationship between the rate of photoinitiated free radical polymerization and the photoinitiator concentration [*n*-butyltriphenylborate salt of dye Cy24 (Cy24B2)] is shown in Fig. 3.

It is apparent from the data shown in this figure that at low concentration range one observes an increase in the rate of polymerization with the increasing of initiator concentration. The further increase in cyanine borate salts concentration causes the decrease in the rate of the polymerization. Basing on the experimental data, one can conclude that, for the thickness of polymerizing sample about 3 mm, the optimal initiator concentration is about $1 \cdot 10^{-3}$ M. On this condition the incident light is absorbed by the whole volume of the sample.

The influence of an electron donor (co-initiator) concentration on the rate of free radical polymerization of TMPTA

The electron donor (co-initiator) concentration affects also the rate of free radical polymerization. Since the lifetime of the excited singlet state of cyanine dye is less than 0.5 ns, high electron donor concentration is needed to achieve an effective electron transfer process. In this case, high concentration of borate ions in close approach to the absorbing dye is gained by the association of the dye cation and borate ion as the ion pair. The dye concentration and electron donor concentration are equal if we used them as the salts. An interesting question arises whether additional amount of borate anion affects the rate of polymerization? The experimental results are shown in Fig. 4, where an increase in the rate of polyme-

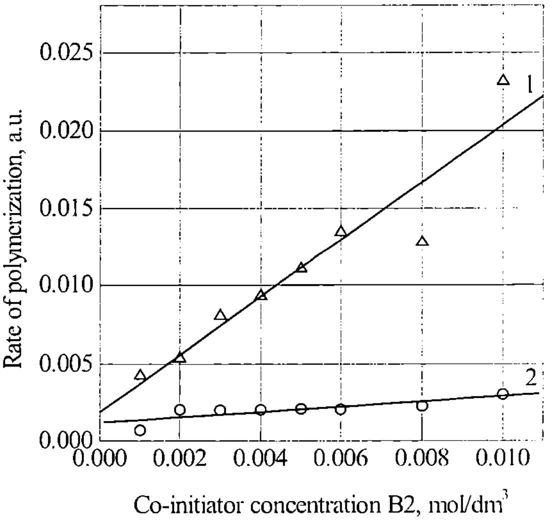


Fig. 4. The influence of the electron donor (co-initiator) concentration — B2 on the rate of photoinitiated polymerization of MP:TMPTA mixture in vol. ratio 1:9; 1 — Cy23, 2 — Cy33

rization with the increase in co-initiator concentration is distinctly visible.

However, it is worth to note that, for the cyanine borate salts tested, the influence of an additional amount of borate anion on the rate of photoinitiated polymerization is different and depends on the type of the dye cation. The obtained results suggest that the borate cyanine salts in the tested polymerizable formulation do not exist exclusively as ion pairs and that they are partially dissociated. The increase in the co-initiator concentration shifts the equilibrium constant of cyanine cation/borate anion system towards the ion pair formation. This leads to the acceleration of the electron transfer process and this, in turn, causes the rise of free radical polymerization rate.

The influence of the bleaching process of cyanine dye on the rate of polymerization

The general equation describing the rate (R_p) of the photoinitiated free radical polymerization *via* the intra- or intermolecular electron transfer process can be presented as follows [3]:

$$R_p = -\frac{\mathrm{d}[M]}{\mathrm{d}t} = k_p[M]\cdot\left[\frac{I_a(k_{obs}-k_{bl})}{k_t}\right]^{1/2} \qquad (2)$$

where: I_a — *light intensity, [M] — monomer concentration,* k_{obs} — *rate constant of the primary photochemical process (in this case the electron transfer process),* k_{bl} — *rate constant of the bleaching process (rate constant of the cyanine and butyl radicals recombination process),* k_t — *rate constant of the termination of the macroradicals,* k_p — *rate constant of propagation.*

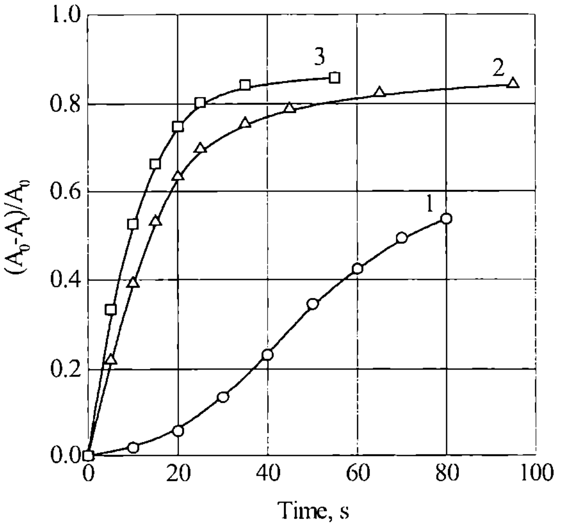


Fig. 5. Changes in the absorption intensity [(A0 - At)/A0] of the dyes Cy27B2 (curve 1), Cy28B2 (curve 2) and Cy29B2 (curve 3) with one type of counter-ion (B2) during argon-laser irradiation (I_a = 20 mW/cm^2) in ethyl acetate (EtAc) solution (V = 4.0 mL, c = 1 · 10^{-5} M)

The equation (2) contains the rate constant of the process (bleaching) that is competitive to photoinitiated polymerization. This is why it was very important to establish the possible influence of the bleaching process on the rate of free radical polymerization. The simplest method allowing to follow the colour loss of the photoinitiating system was based on the measurement of the changes of the electronic absorption spectrum intensity. On the basis of these experiments it appears that, as in the case of the kinetics of the photopolymerization, the rate of the bleaching process strongly depends on the structure of both the dye cation and borate anion (Figs. 5 and 6).

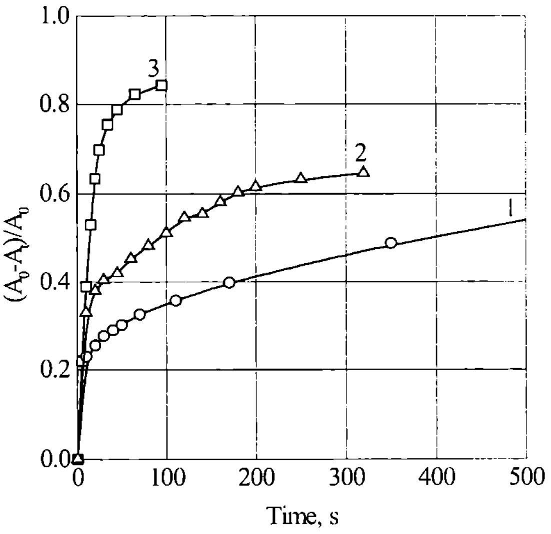


Fig. 6. Changes in the absorption intensity [(A0 - At)/A0] of Cy28 dye with various counter-ions (B2, B3, B4) during argon-laser irradiation (conditions as in Fig. 5); 1 — Cy28B3, 2 — Cy28B4, 3 — Cy28B2

On the basis of the spectroscopic measurements the quantum yields of the bleaching process of the tested photoinitiating systems were calculated. The quantum yields of this reaction oscillates in the range from 0.0005 to 0.04. These results are at least one order of magnitude lower than the quantum yield of *n*-butyl radical formation (ϕ = 0.73) [9]. It allows to conclude that the bleaching process is slow and it does not influence the overall efficiency of photoinitiated free radical polymerization.

The influence of the free energy of electron transfer process on the rate of free radical polymerization

Taking into consideration the Marcus theory, the rate of free radical polymerization photoinitiated by cyanine borate salts can be expressed by the following equation:

$$R_p = -\frac{\mathrm{d}[M]}{\mathrm{d}t} = k_p[M]\sqrt{\frac{I_a\chi Z\exp[-(\lambda+\Delta G_{el})^2/4\lambda RT]}{k_t}} \qquad (3)$$

where: χ — *transmission coefficient, Z — universal frequency factor* ($6 \cdot 10^{12}$ s^{-1}) *at* $25^{o}C$, λ — *total reorganization energy,* ΔG_{el} — *free energy of the electron transfer process, described by earlier mentioned Rehm—Weller equation [eq. (1)].*

The rate of free radical polymerization can also be described in the simpler logarithmic form:

$$\ln R_p = A - (\lambda + \Delta G_{el})^2 / 8\lambda RT \qquad (4)$$

where: *A combines all the constant data of initial time of polymerization.*

From the analysis of the equation describing the rate of the photopolymerization one can conclude that for the polymerization initiated *via* electron transfer process the relationship between $\ln R_p$ and ΔG_{el} should present the classical Marcus parabolic relation. This type of dependence for the selected photoinitiating salts is shown in Fig. 7.

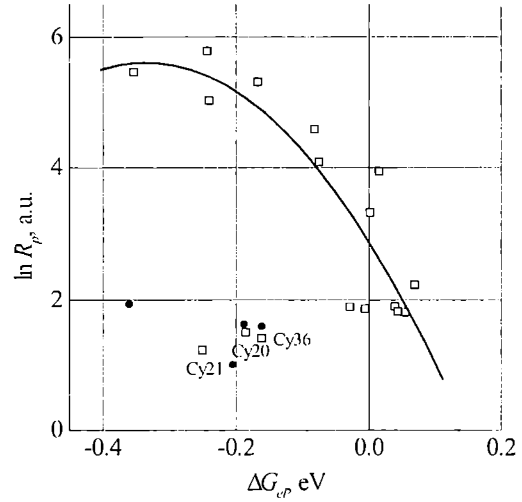


Fig. 7. Marcus plot of the rates of polymerization (a.u.) of TMPTA:MP (9:1 by volume) mixture for cyanine-tert-butyltriphenylborate photoinitiating systems; □ — *cyanines,* ● — *meso-cyanines*

It is apparent that the experimental data show, for almost all the cases, the relation consistent with Marcus theory. It is worth to note that in the series of both *sec*-butyltriphenylborate and *tert*-butyltriphenylborate as the electron donors, the rate of free radical polymerization increases when the driving force of the electron transfer process (free energy of activation, ΔG_{el}) becomes more negative.

For the series with tetra-*n*-butylborate as the electron donor, in the area of free energy change of electron transfer process from -0.6 eV to -0.3 eV, while the driving force of the electron transfer process increases, the rate of the polymerization decreases. In the literature this type of behavior is called "the inverted Marcus region".

There are two types of the electron donors that form identical initiating radical after the electron transfer reaction. These are *n*-butyltriphenylborate and tetra-*n*-butylborate salts. Since for these types of the electron donors the values of ΔG_{el} exhibit different values, therefore it was interesting to see the Marcus relationship for these two types of donors displayed on one plot. It is shown in Fig. 8.

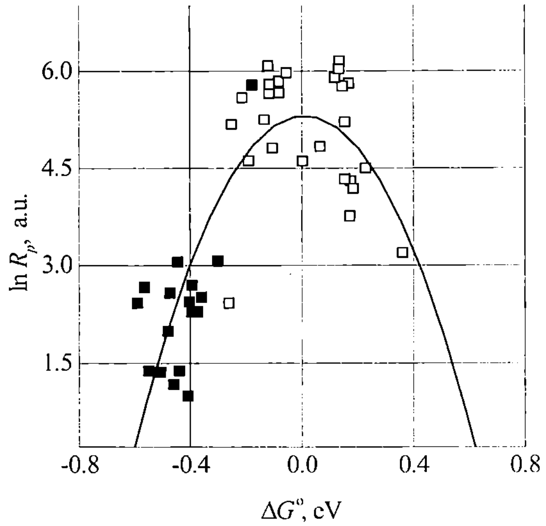


Fig. 8. Marcus plot of the rates of polymerization (a.u.) of TMPTA:MP (9:1 by volume) mixture for cyanine-n-butyltriphenylborate (□) *and cyanine-tetra-n-butylborate* (■) *photoinitiating systems*

The experimental data covers practically the whole parabola. This observation allows to conclude that the tested systems behave as predicted by Marcus theory, including the presence of so-called "the inverted Marcus region".

The photophysics of the cyanine dyes. The kinetics of the quenching of the cyanine dyes excited singlet state

The kinetics of the quenching of the excited singlet state was studied using the measurements of the fluorescence lifetime of the selected cyanine dyes, namely the dyes with iodine, ethyl sulfate and simultaneously with borate ions as counter-ion. The examples of the fluorescence decay curves are shown in Fig. 9.

The analysis of the experimental data shows that there is a significant difference between the singlet state lifetime of cyanine dye with and without an alkyl group in the *meso* position of the polymethine chain. The alkyl substitution in the *meso* position of the polymethine chain (Cy54, O) dramatically decreases the fluorescence lifetime. This behavior is attributed to the faster torsional, non-radiative relaxation of the excited state of the dye to the ground state.

The effect of ethylsulfate anion exchange to *n*-butyltriphenylborate anion is shown in Fig. 10. It is clear from

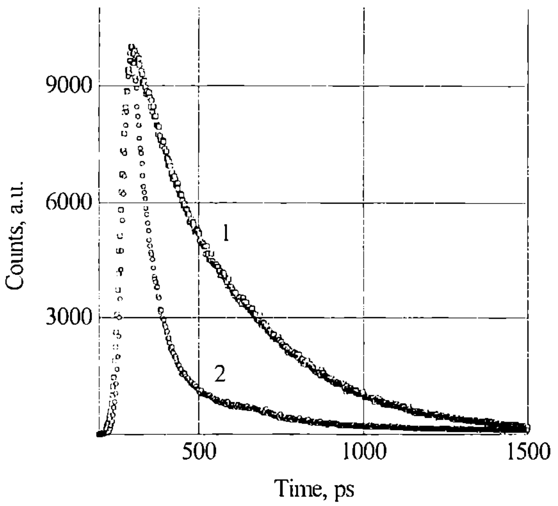


Fig. 9. The influence of the substitution in meso position (Cy54 vs. Cy6, see Table 1 in [4]) on the fluorescence lifetime of cyanine borates tested. Fluorescence measurements performed in MP:ethyl acetate (EtAc) solution (1:9); 1 — Cy6, 2 — Cy54

the data shown in Fig. 10 that borate ion strongly decreases cyanine ion fluorescence lifetime and this, in turn, suggests that borate ion quenches the singlet excited state of the cyanine dye.

The lifetime of the excited singlet state of the cyanine dye strongly depends on the structure of the dye and the type of borate ion. The results obtained during fluorescence lifetime measurements show that the lifetimes of the tested thiacarbocyanine dyes are in the range from 3 to 595 ps. The lifetimes of the excited singlet state of the carbocyanine dyes are shorter and are in the range from 7 up to 399 ps.

The relationship between the rate constant and free energy of the electron transfer process

The electron transfer process between the cyanine and borate ions causes the quenching and simultaneous shortening of the fluorescence lifetime of the cyanine dye. Assuming that the electron transfer is the only one quenching route, one can calculate the rate of the electron transfer for the tested ion pairs. The calculated rate constants for the selected tested dyes are listed in Table 2.

Analysis of the data collected in Table 2 shows that the rate constants of the electron transfer ranging from $1.9 \cdot 10^{8}$ to $1.6 \cdot 10^{11}$ s^{-1} and are lower than those measured for the borate salts of *N,N'*-dimethylindocarbocyanine dyes in benzene solution (about 10^{13} s^{-1}) [9, 18]. The introducing of methyl or ethyl group to the polymethine chain increases, in the majority of cases, the rate constant of the electron transfer process by about two orders of magnitude.

The classical Marcus equation combines the rate constant of the electron transfer process with free energy

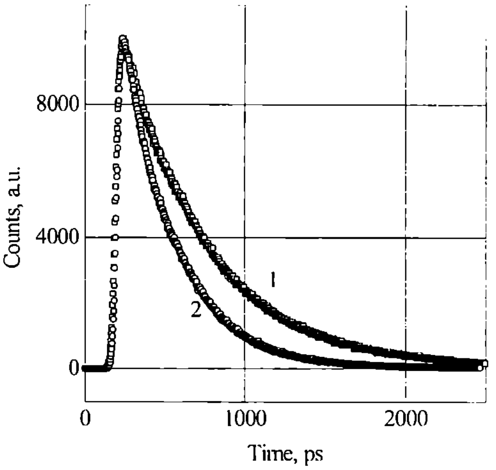


Fig. 10. The influence of the borate ion on the fluorescence decay of Cy9. Fluorescence measurements performed in MP:EtAc solution (1:9); 1 — ethylsulfate anion, 2 — n-butyltriphenylborate anion

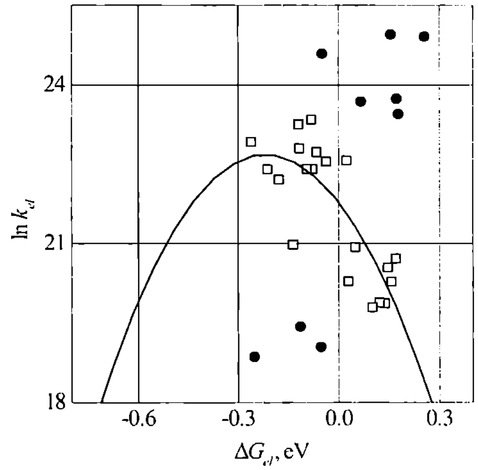


Fig. 11. The dependence of the rate constant of electron transfer (k_{el}) on free energy of electron transfer (ΔG_{el}) from n-butyltriphenylborate ion (B2) to the cyanine dyes tested; □ — cyanines, ● — meso-cyanines

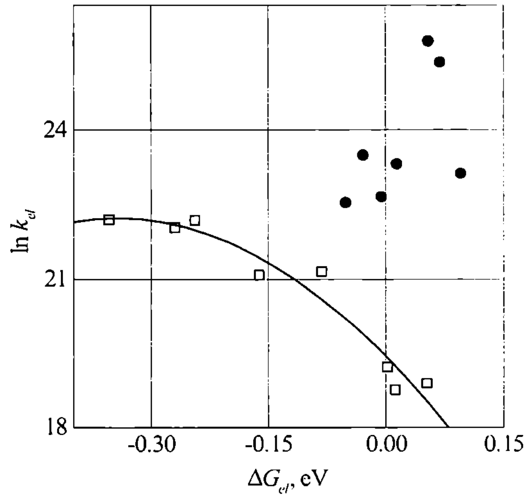


Fig. 12. The dependence of the rate constant of electron transfer (k_{el}) on free energy of electron transfer (ΔG_{el}) from tert-butyltriphenylborate ion (B4) to the cyanine dyes tested; □ — cyanines, ● — meso-cyanines

T a b l e 2. Calculated rate constants (k_{el}) of electron transfer process for selected tested dyes*)

Dye	k_{el}, s^{-1} CyB2		k_{el}, s^{-1} CyB3		k_{el}, s^{-1} CyB4		k_{el}, s^{-1} CyB5	
Cy3	$9.84 \cdot 10^{8}$	$1.48 \cdot 10^{9}$	$5.27 \cdot 10^{8}$	$1.07 \cdot 10^{9}$	$2.23 \cdot 10^{8}$	$9.97 \cdot 10^{8}$	—	—
Cy4	$1.55 \cdot 10^{10}$	—	—	—	$1.34 \cdot 10^{10}$	—	—	—
Cy50	—	—	$5.98 \cdot 10^{9}$	—	$1.1 \cdot 10^{10}$	—	—	—
Cy6	$8.28 \cdot 10^{8}$	$4.45 \cdot 10^{8}$	—	—	—	—	—	—
Cy54	$6.8 \cdot 10^{10}$	—	—	—	$1.59 \cdot 10^{11}$	—	$7.14 \cdot 10^{10}$	—
Cy8	$4.21 \cdot 10^{8}$	$4.39 \cdot 10^{8}$	—	—	$1.41 \cdot 10^{8}$	$3.33 \cdot 10^{8}$	$2 \cdot 10^{8}$	—
Cy56	$1.97 \cdot 10^{10}$	—	—	—	$1.6 \cdot 10^{10}$	—	$1.59 \cdot 10^{10}$	—
Cy9	$4.26 \cdot 10^{8}$	$1.03 \cdot 10^{9}$	—	—	—	—	—	—
Cy47	$6.5 \cdot 10^{9}$	—	$6.33 \cdot 10^{8}$	—	$6.09 \cdot 10^{9}$	—	—	—
Cy10	$6.31 \cdot 10^{8}$	—	—	—	—	—	$1.59 \cdot 10^{9}$	$1.09 \cdot 10^{9}$
Cy11	$2.06 \cdot 10^{10}$	$3.67 \cdot 10^{9}$	—	—	$1.05 \cdot 10^{11}$	$4.7 \cdot 10^{9}$	—	—
Cy33	—	$1.55 \cdot 10^{8}$	—	—	—	—	—	—
Cy36	$1.4 \cdot 10^{10}$	$2.93 \cdot 10^{9}$	—	—	$1.44 \cdot 10^{9}$	$2.84 \cdot 10^{9}$	—	—
Cy58	$3.9 \cdot 10^{8}$	$2.05 \cdot 10^{9}$	—	—	$6.85 \cdot 10^{9}$	$3.63 \cdot 10^{9}$	—	—
Cy59	$6.57 \cdot 10^{10}$	—	—	—	—	—	$2.83 \cdot 10^{9}$	$2.35 \cdot 10^{9}$
Cy60	$4.77 \cdot 10^{10}$	—	—	—	—	—	—	—
Cy63	—	—	—	—	—	$1.6 \cdot 10^{8}$	—	—
Cy65	—	—	—	—	—	—	$8.97 \cdot 10^{9}$	—
Cy66	—	—	$5.31 \cdot 10^{9}$	—	—	—	—	—
Cy18	$8.14 \cdot 10^{9}$	$7.36 \cdot 10^{8}$	$9.94 \cdot 10^{9}$	$9.89 \cdot 10^{8}$	$4.31 \cdot 10^{9}$	$1.07 \cdot 10^{9}$	—	—
Cy19	$5.45 \cdot 10^{9}$	$1.41 \cdot 10^{9}$	—	—	$4.34 \cdot 10^{9}$	$1.45 \cdot 10^{9}$	—	—
Cy41	$7.59 \cdot 10^{9}$	—	—	—	—	—	—	—
Cy45	$1.27 \cdot 10^{10}$	—	$9.38 \cdot 10^{9}$	—	—	—	$4.62 \cdot 10^{9}$	$1.16 \cdot 10^{11}$
Cy20	$5.49 \cdot 10^{9}$	$1.09 \cdot 10^{9}$	—	—	—	—	—	$2.06 \cdot 10^{8}$
Cy21	$2.74 \cdot 10^{8}$	—	—	—	—	—	—	—
Cy22	—	$1.86 \cdot 10^{8}$	$5.18 \cdot 10^{9}$	—	—	—	—	—
Cy48	$9.22 \cdot 10^{9}$	$4.56 \cdot 10^{9}$	—	—	—	—	—	—
Cy23	$1.28 \cdot 10^{9}$	$1.86 \cdot 10^{8}$	$1.09 \cdot 10^{9}$	$3.77 \cdot 10^{8}$	—	—	$2.12 \cdot 10^{9}$	—
Cy24	$6.38 \cdot 10^{8}$	$2.21 \cdot 10^{8}$	$1.05 \cdot 10^{9}$	$3.94 \cdot 10^{8}$	—	—	—	—
Cy27	$6.31 \cdot 10^{9}$	—	—	—	—	—	—	—
Cy25	$4.48 \cdot 10^{9}$	$2.55 \cdot 10^{8}$	$2.02 \cdot 10^{9}$	$2.83 \cdot 10^{8}$	$3.7 \cdot 10^{9}$	$1.91 \cdot 10^{8}$	—	—
Cy52	—	$5.49 \cdot 10^{9}$	—	$5.94 \cdot 10^{9}$	—	—	—	$8.95 \cdot 10^{8}$
Cy28	—	$1.22 \cdot 10^{9}$	—	—	—	$1.54 \cdot 10^{9}$	—	—

*) In almost all cases, the rate constants of electron transfer process were calculated for two fluorescence lifetimes of cyanine dyes; it is the reason of two values of k_{el} for the same dye.

change of this reaction. The relationships between the rate constant of the electron transfer process and free energy change of this process, for the tested salts, are shown in Figs. 11 and 12.

The data presented in these figures are consistent with the theory of the photoinduced electron transfer process. The observed relationships allow to conclude that the excited state, which is quenched by the borate anion, is the fluorescing state of cyanine dye. The Marcus relationship is not observed for the cyanine dyes with an alkyl group in *meso* position.

The influence of the rate constant of electron transfer process in cyanine-borate ion pair on the rate of photoinitiated free radical polymerization

One of the main purposes of the presented research was also to extend the study on the photochemistry of the cyanine borate salts by studying the relationship

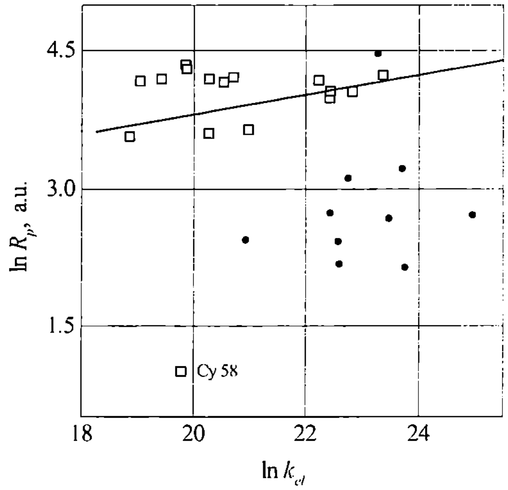


Fig. 13. The dependence of the rate of photopolymerization (R_p) on the rate constant of electron transfer (k_{el}) for cyanine n-butyltriphenylborates (B2); ☐ — cyanines, ● — meso-cyanines

between the rate of the primary process, *i.e.* the rate of the electron transfer process, and the rate of the photoinitiated polymerization. The kinetic analysis of the photoinitiated polymerization leads to the conclusion that if there is a direct relationship between the rate of the electron transfer process and the rate of photoinitiated free radical polymerization one should observe a linear relationship between logarithm of the rate constant of the electron transfer process and the logarithm of the polymerization rate. It is illustrated in Figs. 13 and 14.

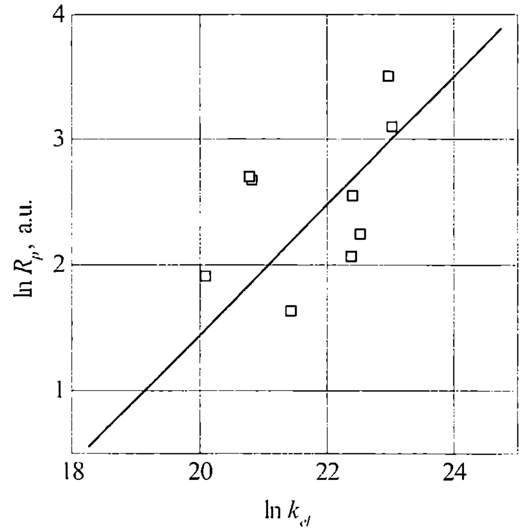


Fig. 14. The dependence of the rate of photopolymerization (R_p) on the rate constant of electron transfer (k_{el}) for cyanine sec-butyltriphenylborates (B3)

On the basis of the data presented in these figures one can conclude that for the cyanines without *meso* substitution there are two possibilities: the first showing no relationship between the rate of the electron transfer (Fig. 14) and second indicating a linear relationship between these values (Fig. 13). This second possibility is not observed for cyanine dyes substituted in the *meso* position. The conclusions presented above are consistent with the relationship presented in Figs. 11 and 12 for the dyes without the substituent in *meso* position. Therefore, one can ascertain that the practical application of Marcus theory to the prediction of the kinetics of the photoinitiated free radical polymerization is possible only for a selected group of cyanine dyes.

CONCLUSIONS

— Butyltriphenylborate anions as co-initiators with cyanine dyes can be used in the visible-light-induced polymerization of acrylates.

— The rate of the electron-transfer process is dependent on the structure of the alkyl group bound to the boron atom of the borate.

— The practical application of Marcus theory to the prediction of the rate of photoinitiated polymerization is possible only for selected initiating photoredox pairs.

ACKNOWLEDGMENT

This research was sponsored by the State Committee for Scientific Research (KBN), grant No 4 TO9A 051 22 and BW 3/99.

LITERATURE

1. Marcus R. A.: *Annu. Rev. Chem.* 1964, **15**, 155.
2. Pączkowski J., Kucybała Z.: *Macromolecules* 1995, **28**, 269.
3. Pączkowski J., Pietrzak M., Kucybała Z.: *Macromolecules* 1996, **29**, 5057.
4. Kabatc J., Pączkowski J.: *Polimery* 2003, **48**, nr 5.
5. Pączkowski J., Kucybała Z.: *Macromolecules* 1995, **28**, 269.
6. Kabatc J., Kucybała Z., Pietrzak M., Ścigalski F., Pączkowski J.: *Polymer* 1999, **40**, 735.
7. Karolczak J., Komar D., Kubicki J., Szymański M., Wroazowa T., Maciejewski A.: *Bull. Pol. Acad. Sci., Chem.* 1999, **47**, 361.
8. Dobek K., Karolczak J., Komar D., Kubicki J., Szymański M., Wroazowa T., Maciejewski A., Ziołek M. A.: *Opt. Appl.* 1998, **28**, 201.
9. Chatterjee S., Davis P. D., Gottschalk P., Kurz M. E., Sauerwein B., Yang X., Schuster G. B.: *J. Am. Chem. Soc.* 1990, **112**, 6329.
10. Chatterjee S., Gottschalk P., Davis P. D., Schuster G. B.: *J. Am. Chem. Soc.* 1988, **110**, 2326.
11. Tatikolov A. S., Dzhulibekov Kh. S., Shvedova L. A., Kuzmin V. A., Ischenko A. A.: *J. Phys. Chem.* 1995, **99**, 6525.
12. Murphy S., Yang X., Schuster G. B.: *J. Org. Chem.* 1995, **60**, 2411.
13. Yang X., Zaitsev A., Sauerwein B., Murphy S., Schuster G. B.: *J. Am. Chem. Soc.* 1992, **114**, 793.
14. Owen D. J., Schuster G. B.: *J. Am. Chem. Soc.* 1996, **118**, 259.
15. Pączkowski J., Kabatc J., Jędrzejewska B.: *J. Polym. Sci., A* 2000, **38**, 2365.
16. Pączkowski J., Kabatc J., Pietrzak M.: *J. Chem. Soc., Perkin Trans. 2.* 2002, 287.
17. Murphy S. T., Zou Ch., Miers J. B., Ballew R. M., Dlott D. D., Schuster G. B.: *J. Phys. Chem.* 1993, **97**, 13152.
18. Murphy S. M., Sauerwein B., Drickamer M. G., Schuster G. B.: *J. Phys. Chem.* 1994, **98**, 13476.

Received 22 VI 2002.