PERKIN 2

Cyanine borates revisited. Study of the kinetics of photoinitiated free radical polymerization *via* intermolecular electron transfer process

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Three series of cyanine butyl triphenyl borate salts were prepared and tested as initiators of free radical polymerization photoinitiated *via* the photoinduced electron transfer process. To illustrate the influence of the primary process on the rate of photoinitiated polymerization the fluorescence lifetime of the tested dye containing non-electron donating counterion as well as electron donating borate ion were measured. The fluorescence lifetime measurements were performed using a pico/femtosecond spectrometer allowing a successful analysis of fluorescence decay signals in the range of single picoseconds. As obtained results show, for cyanine dyes bi-exponential decay of fluorescence was observed, while for cyanine with a substituent at the *meso* position, for the majority of dyes, mono-exponential decays were obtained. Based on fluorescence measurements the rate of the electron transfer process between excited dyes and borate anions was calculated and a short discussion on photophysics of cyanine dyes is given. Several important conclusions arrive from the theoretical and experimental data: (i) the experimental data reveal that the relationship between the rate of the electron transfer and the free energy for this reaction display typical "normal Marcus region" kinetic behavior; (ii) the experimental results show that the relationship between the logarithm of the rate of polymerization and the logarithm of the rate constant for the electron transfer is linear in character. This finding permits the conclusion that the rate of photopolymerization is a function of the free energy change of the electron transfer (ΔG_{el}). This type of relationship is observed only for cyanines with no substituent in the *meso* position. These observations allow the conclusion that in the case of *meso*-cyanines the fluorescing state of the dye is not the state that is reduced by the borate. The main conclusion derived from the data presented in the paper is that the Marcus theory of electron transfer can be extended for the description of certain types of photoinitiated polymerization.

Introduction

Schuster and co-workers discovered that 1,4-dicyanonaphthalene solutions containing an alkyl triphenyl borate salt, when irradiated, yield one electron oxidation of the alkyl triphenyl borate leading to carbon–boron bond cleavage and formation of free alkyl radicals.[1] This reaction transferred to the dyeing system led to the preparation of cyanine borates.[2,3] In Gottschalk's hands it was shown that ionic salt pairs formed from cyanine dyes and Schuster's borates could be used as photoinitiators[4] and that they were active in the visible region of the spectrum.

Cyanine borates exist as tight ion pairs even in solvents of medium polarity. Certain salts have even been shown to form ion pairs in which the center-to-center distance between the ions is less than the sum of the individual radii.[5,6] Since the lifetime of the excited singlet state of cyanine dye is quite short, the self-association of the cyanine cation and borate anion is a prerequisite for an efficient photoinduced reaction.

The evidence for the radical formation from the cyanine borates is as follows.

(1) Irradiation of an oxygen-free benzene solution of a cyanine *n*-butyl triphenyl borate at 532 nm gives *n*-octane among other products. Since octane can only form from the coupling of *n*-butyl radicals, one can conclude that irradiation of cyanine *n*-butyl triphenyl borate generates free butyl radicals.

(2) Irradiation of a benzene solution of cyanine benzyl triphenyl borate with an 18 ps light pulse at 532 nm gives the transient spectrum containing the negative absorption (reduced absorption) due to the bleaching of the dye and a new absorption band with a maximum at 430 nm. This maximum was assigned to the cyanine dye radical. For cyanine borates containing leaving groups that absorb in the mid-UV, *e.g.* cyanine 1-methyl-2-naphthyl triphenyl borate, laser photolysis gives rise to a new feature. In this case, the absorption at 385 nm that can be attributed to the presence of naphthylmethyl radical is observed.

Laser flash photolysis of the benzyl triphenyl borate salt shows rapid bleaching of the cyanine absorption and formation of the cyanine dye radical. Similar experiments carried out with vinyl triphenyl borate show that the processes occur with efficiency significantly less than was observed for the benzyl borate. The conclusion is that the radical elimination step impacts the kinetics of the overall electron transfer process. With the tetraphenyl borate salt one finds little formation of cyanine radical and the excited singlet state of the dye is nearly completely returned to the cyanine ion ground state by the end of the pulse.

These data, by analogy, suggest the mechanism of the polymerization initiation process. The irradiation of the ion pair with visible light generates the excited singlet state of the cyanine, which can undergo three possible reactions: fluorescence, photoisomerization or electron transfer to form the cyanine and boranyl radicals. The cyanine–boranyl radical pair may undergo back electron transfer to regenerate the substrate, or undergo cleavage of a carbon–boron bond to form an alkyl radical [R$^\bullet$] and triphenylboron. The [Cy$^\bullet$][R$^\bullet$] radical pair formed in the latter process might undergo electron transfer to form [Cy$^+$] and an alkyl anion [R$^-$]. The radicals formed might

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couple to form an alkylated cyanine [Cy–R] or to diffuse from the initial solvent cage giving free radicals.

In our earlier papers[7,8] we presented a possibile application of the Marcus[9–11] theory for the description of the rate of the photoinduced polymerization *via* an intermolecular electron transfer process. Essentially, one can test a possibile application of the Marcus theory for the prediction of the photoinitiated polymerization rate by: (1) the use of one electron acceptor and a series of electron donors or (2) the use of a series of dyes and only one type of electron donor. The first method usually yields free radicals with different reactivities[12] and this might have an impact on the final rate of the photoinitiated polymerization. The use of the cyanine borates represents the second method and, as one would expect, creates a unique opportunity to change the driving force of the electron transfer process without a change in the type of the yielding free alkyl radicals. Translating this to a practical application of the Marcus equation to the photoinitiation process, one can anticipate that under certain conditions (identical or very similar free radicals formed), the rules regulating the primary processes can be also applied for the secondary processes. The series of cyanine *n*-butyl triphenyl borate, described earlier,[12,13] illustrates this type of behavior.

In this work, it is our intention to extend the study on cyanine borates, especially the relationship between the rate of the primary process, *e.g.* the rate of electron transfer and the rate of photoinitiated polymerization. This might allow verification that the rules regulating the primary processes (electron transfer) can also be applied to the secondary processes (polymerization photoinitiation reaction).

Experimental

Substrates used for preparations of dyes, monomers and solvents were purchased from Fluka, Merck and Aldrich. Cyanine dyes and cyanine borates were prepared in our laboratory. A general method for synthesis of cyanine dyes, alkyl triphenyl borates[14] and cyanine borates[15] is shown in Scheme 1

The purity of synthesized dyes was controlled by thin layer chromatography and their identity was checked by ^{1}H NMR, UV-Vis and IR spectroscopy.

The kinetics of free radical polymerization were studied using a polymerization solution composed of 1 ml of 1-methylpyrrolidin-2-one (MP) and 9 ml of 1,1,1-tris(acryloyloxymethyl)propane (TMPTA). The cyanine borate concentration was 1×10^{-3} M. As a reference sample a polymerizing mixture containing cyanine iodides or ethyl sulfates (dye without an electron donor) were used. The methodology of measurements of the kinetics of free radical polymerization was described earlier.[7,8,12] Irradiation of the polymerization mixture was carried out using the emission of an Omnichrome argon ion laser Model 543-500 MA with the intensity of light of 30 mW per 0.78 cm^2.

The reduction potentials of the dyes were measured by cyclic voltammetry. An Electroanalytical MTM (Krakow) Model EA9C-4z was used for the measurements, and an Ag–AgCl electrode served as a reference electrode. The supporting electrolyte was 0.5 M tetrabutylammonium perchlorate.

The absorption spectra were recorded with a Varian Cary 3E Spectrophotometer, and the fluorescence spectra were obtained using a Hitachi F-4500 Spectrofluorimeter. The absorption and emission spectra were recorded using spectroscopic quality ethyl acetate and tetrahydrofuran, respectively, as solvents. The measurements were performed at ambient temperature.

The fluorescence lifetime measurements were performed using a 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.[16,17] The apparatus uses a pico/femtosecond tunable Ti : Sapphire laser generating pulses of about 1 ps for the excitation. 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 a concentration able to provide equivalent absorbances at 460 or 480 nm (0.2–0.4 in the 10 mm cell).

Results and discussion

Chart 1 shows the structure of the cyanine borate salts tested.

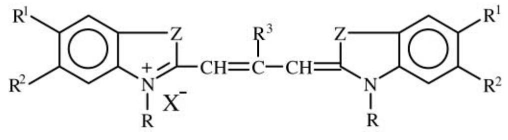


Chart 1

Dithiacarbocyanine and dioxacarbocyanine dyes are characterized by an intense absorption band in the orange spectral region, with the more intense peaks ($\varepsilon_{max} \approx 10^5$ dm^3 mol^{-1} cm^{-1}) located for dithiacarbocyanines in the range between 550–600 nm and the second, less intense, blue-shifted by about 6000 cm^{-1} (Fig. 1). For dioxacarbocyanines the absorption bands are shifted to the blue area of visible light of about 60–70 nm. The position of absorption λ_{max}, essentially does not depend on the type of borate ion (Table 1). The two bands are assigned to the 0,0 and 0,1 vibronic transitions within the first excited state of the dye. The tested series of dyes contain several (Cy4, Cy11, Cy33, Cy59, Cy60, Cy65 and Cy66) *meso*-substituted analogues. The principle difference between dyes substituted and non-substituted in the *meso* position is reflected in the value of the molar absorption coefficient, which is about one order of magnitude lower for *meso*-alkyl substituted derivatives. The introduction of *meso*-alkyl substitution is known to destabilize the all-*trans* isomer of cyanine dye in solution, which is normally the preferred ground state isomer.

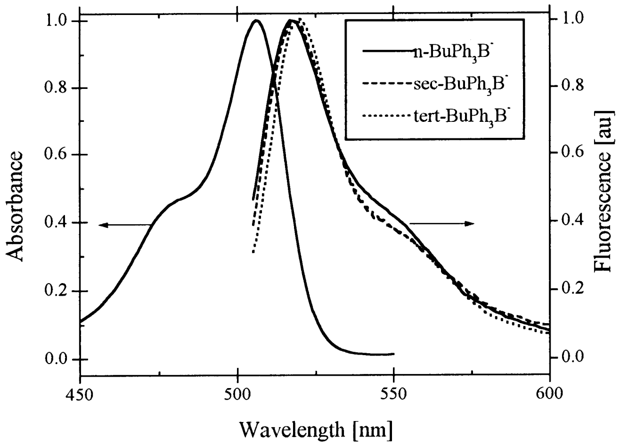
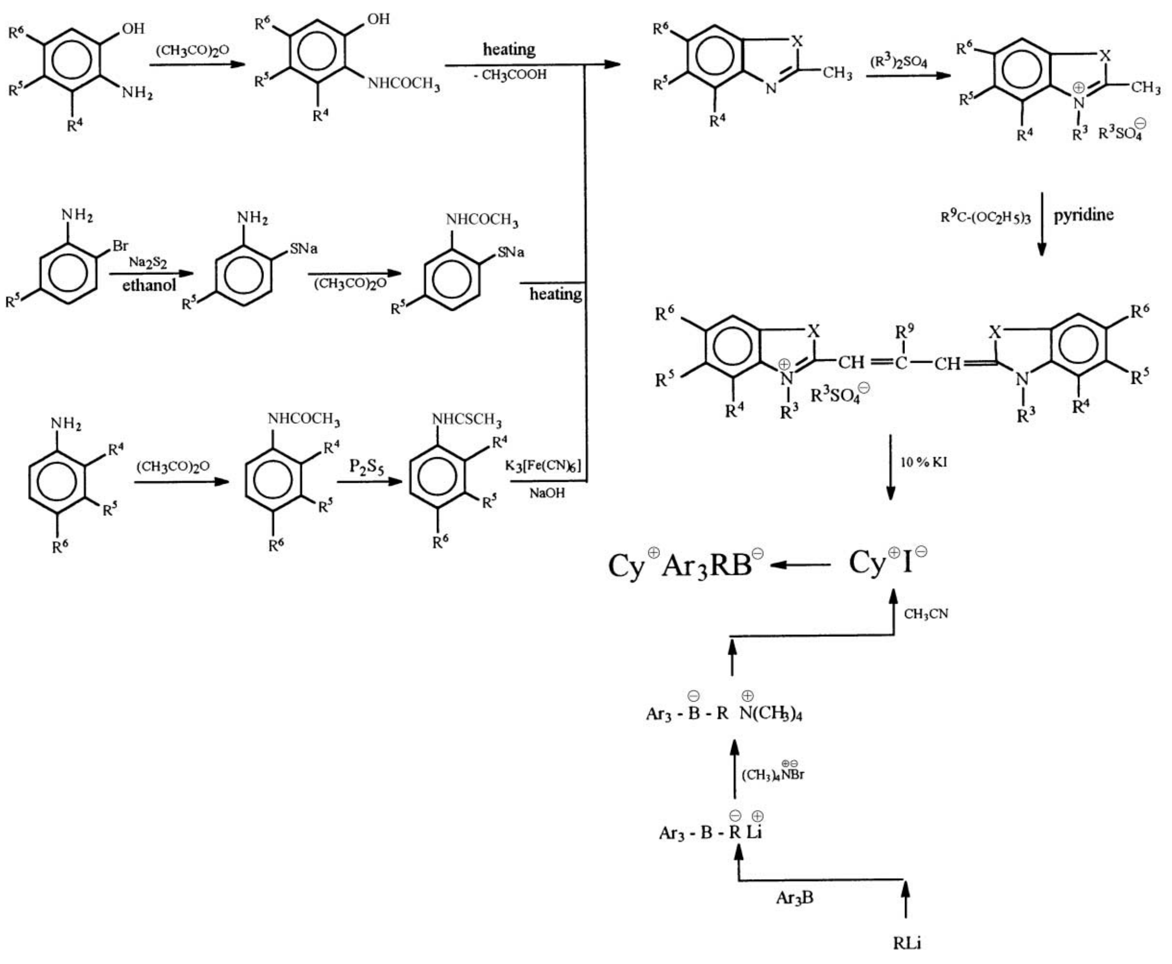


Fig. 1 Electronic absorption and fluorescence spectra of an example of cyanine borate tested (Cy52). Spectra recorded in EtAc.

The fluorescence emission in THF exhibits a maximum, red-shifted by less than 1000 cm^{-1}. The value of the Stokes shift slightly depends on the type of borate ion and is highest for the *n*-butyl triphenyl borate ion. The fluorescence emission spectra are roughly a mirror image of the absorption spectra.

The electrochemical reduction of cyanine cation (Fig. 2A) in acetonitrile solution is reversible. However, the oxidation of borate anion is irreversible (Fig. 2B). This is caused by the very short lifetime of alkyl triphenyl borate radical. The oxidation of alkyl triphenyl borate is dissociative and this in turn causes the electrochemical process to be irreversible. The oxidation potential can be established using an indirect, kinetic method



Scheme 1

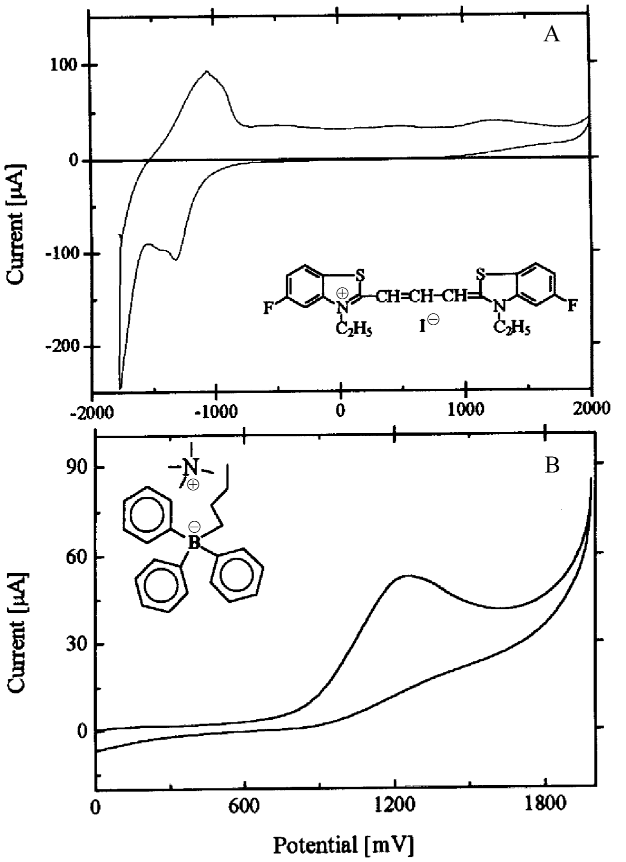


Fig. 2 Cyclic voltammograms of selected compounds. Type of molecule tested shown in insets.

described by Murphy and Schuster.[18] Results measured electrochemically and kinetically differ by about 0.3 V. The obtained electrochemical values (or values obtained kinetically) may have thermodynamic meaning and allow the calculation of the free energy of activation (ΔG_{el}) for the photoinduced electron transfer process (PET).

It is well known from the basic Rehm–Weller [19,20] requirement that the free energy of activation for the PET (ΔG_{el}) process should have a negative value (eqn. (1)),

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

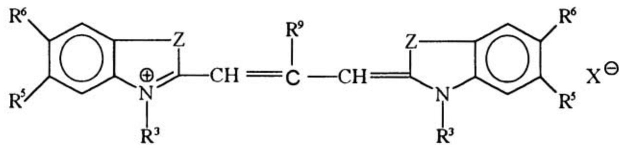
where E_{ox} ($D/D^{\bullet+}$) is the oxidation potential of the electron donor, $E_{red}(A^{\bullet-}/A)$ is the reduction potential of the electron acceptor, E_{00} is the energy of the excited state and $Ze^2/\varepsilon a$ is the Coulombic energy gained by bringing the radical ions formed to an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

The measured electrochemical and spectroscopic, as well as calculated (using the Rehm–Weller equation) thermodynamical properties of cyanine borate salts tested are listed in Table 1. For the calculation of ΔG_{el} the energy of the 0,0 transition for the singlet excited state was taken into account.

The thermodynamical properties for cyanine borates were calculated for three different borate anions. Their measured oxidation potentials are compiled in Table 2.

Figs. 3 and 4 present the kinetic curves observed during an argon-ion laser initiated polymerization of a solution composed of 1 ml of 1-methylpyrrolidin-2-one (MP), 9 ml of 1,1,1-tris(acryloyloxymethyl)propane (TMPTA) and initiating cyanine borate with a concentration of 1×10^{-3} M. It is apparent from the inspection of the initial rates of polymerization that the efficiency of tested cyanine borates when they are used

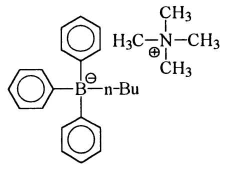
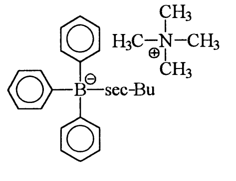
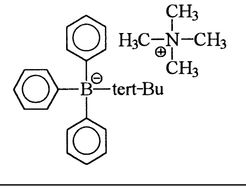
Table 1 Characteristics of cyanine borates tested



Dye	Z	R^5	R^6	R^9	R^3	λ_{max}abs / nm methanol	E_{red}/ V CyX	ΔG°_1/ eV CyB2[a]	ΔG°_1/ eV CyB3[a]	ΔG°_1/ eV CyB4[a]
Cy3	S	H	H	H	C_2H_5	556	−1.241	0.169	0.046	0.002
Cy4	S	H	H	CH_3	C_2H_5	542	−1.268	0.167	0.059	0.014
Cy6	S	H	H	H	C_3H_7	558	−1.274	0.145	0.085	0.039
Cy8[b]	S	F	H	H	C_2H_5	562	−1.235	0.137	0.061	0.012
Cy9[b]	S	CH_3	H	H	C_2H_5	564	−1.229	0.121	0.063	0.008
Cy10[b]	S	H	CH_3O	H	C_2H_5	572	−1.224	0.156	0.093	0.043
Cy11	S	CH_3O	H	C_2H_5	CH_2CH_2OH	564	−1.229	0.017	0.012	0.069
Cy18	O	H	H	H	CH_3	482	−1.312	−0.116	−0.183	−0.243
Cy19	O	H	H	H	C_2H_5	482	−1.196	−0.212	−0.304	−0.352
Cy20	O	H	H	H	C_3H_7	484	−1.389	0.029	−0.078	−0.074
Cy21	O	H	H	H	C_6H_{13}	486	−1.284	−0.115	−0.209	−0.250
Cy22[b]	O	Cl	H	H	C_2H_5	488	−1.35	−0.054	−0.120	−0.168
Cy23[b]	O	CH_3	H	H	C_2H_5	488	−1.279	−0.134	−0.143	−0.240
Cy24[b]	O	CH_3O	H	H	C_2H_5	498	−1.389	0.029	−0.078	−0.074
Cy25[b]	O	C_6H_5	H	H	C_2H_5	494	−1.21	−0.178	0.218	−0.270
Cy27	O	CH_3O	H	C_2H_5	C_2H_5	504	−1.300	−0.038	−0.1	−0.162
Cy28	O	C_6H_5	H	C_2H_5	C_2H_5	502	−1.378	0.050	−0.033	−0.081
Cy33[b]	S	H	C_2H_5	H	C_2H_5	580	−0.817	−0.250	−0.310	−0.360
Cy36[b]	S	NO_2	H	H	C_2H_5	556	−1.081	−0.082	−0.117	−0.161
Cy41[b]	O	H	H	CH_3	C_2H_5	494[c]	−1.334	−0.065	−0.118	−0.161
Cy45[b]	O	H	H	C_2H_5	C_2H_5	496[c]	−1.295	−0.120	−0.147	−0.189
Cy47[b]	S	CH_3	H	C_2H_5	C_2H_5	567[c]	−1.16	0.024	0.011	−0.050
Cy48[b]	O	Cl	H	CH_3	C_2H_5	500[c]	−1.075	−0.320	−0.384	−0.432
Cy52[b]	O	C_6H_5	H	CH_3	C_2H_5	506[c]	−1.251	−0.095	−0.143	−0.206
Cy54[b]	S	H	H	CH_3	C_3H_7	564[c]	−1.307	0.159	0.121	0.083
Cy56[b]	S	F	H	CH_3	C_2H_5	561[c]	−1.211	0.067	0.034	−0.028
Cy58[b]	S	OH	H	H	C_2H_5	580[c]	−1.147	0.100	0.054	−0.006
Cy59[b]	S	OH	H	CH_3	C_2H_5	575[c]	−1.334	0.256	0.254	0.175
Cy60[b]	S	OH	H	C_2H_5	C_2H_5	564[c]	−1.356	−0.049	−0.109	−0.140

[a] Calculated for the data obtained from cyclic voltametry measurements in an MeCN solution. $X^- = (Ph)_3B$-*n*-C_4H_9 (B2); $(Ph)_3B$-*sec*-C_4H_9 (B3); $(Ph)_3B$-*tert*-C_4H_9 (B4). [b] Dyes prepared in our laboratory. [c] Measured in ethyl acetate solution.

Table 2 Oxidation potentials of borates tested

Abbr.	Borate	E_{ox}/V
B2		0.70
B3		0.696
B4		0.78

as photoinitiators depends strongly on the structure (Table 3). In general, cyanine borates are not particularly efficient photoinitiators. For example the RBAX–*N*-phenylglycine (RBAX = an acetylated derivative of decarboxylated Rose Bengal) photoredox pair is much more efficient.[21] However, the fact that the cyanine borates give substantial wavelength flexibility means that they have become quite useful.

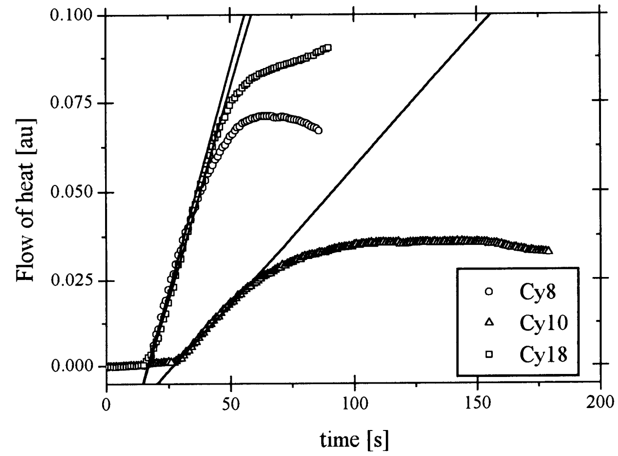
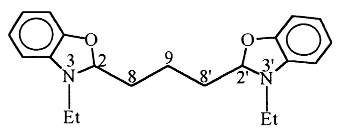
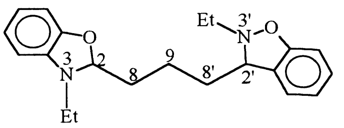
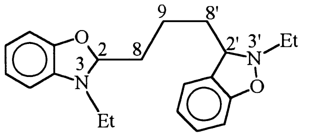
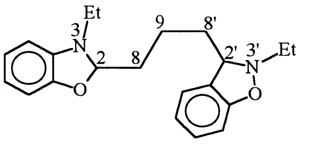
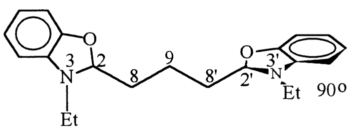


Fig. 3 Rate of heat evolution during argon-ion laser photoinitiated polymerization of mixture composed of 1-methylpyrrolidin-2-one (MP, 1 ml) and 9 ml of 1,1,1-tris(acryloyloxymethyl)propane (TMPTA) initiated by a selected cyanines (marked in inset); *tert*-butyl triphenyl borate with a concentration of 10^{-3} M.

We have shown earlier[7,8,12,22] that the rate of the photoinitiated polymerization can be described by eqn. (2) (M =

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left[\frac{I_a k_{el}}{k_t}\right]^{1/2} \tag{2}$$

Table 3 The enthalpy of molecule formation and electron density calculated for geometric and conformational isomers of simplest dioxacarbocyanine dye

Dye structure	$\Delta_f H$/kJ mol^{-1}	Electron density 2	2′	3	3′	8	8′	9
	869.0	0.287	0.285	−0.173	−0.181	−0.330	−0.335	0.112
	860.6	0.283	0.285	−0.173	−0.181	−0.337	−0.334	0.130
	911.3	0.306	0.249	−0.131	−0.195	−0.309	−0.356	0.105
	895.0	0.289	0.288	−0.177	−0.179	−0.337	−0.335	0.138
	921.3	0.283	0.350	−0.196	−0.123	−0.377	−0.414	0.107

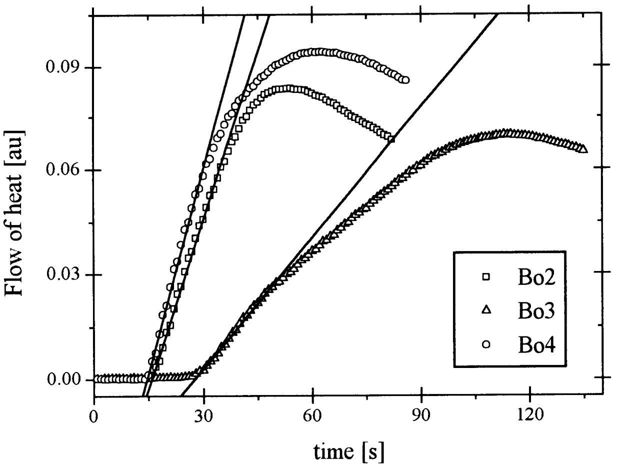


Fig. 4 The effect of the borate type (marked in inset) on the rate of heat evolution during argon ion laser photoinitiated polymerization of 1-methylpyrrolidin-2-one (MP, 1 ml) and 9 ml of 1,1,1-tris-(acryloyloxymethyl)propane (TMPTA) mixture initiated by Cy9 with concentration of 10^{-3} M.

monomer, k_t = rate constant of termination process, I_a = light intensity).

The rate constant of the electron transfer process can be expressed by eqn. (3),

$$k_{el} = \chi Z\exp(-\Delta G^{\ddagger}/RT) \tag{3}$$

where Z is an universal frequency factor (6×10^{12} s^{-1}) at 25 °C, χ is the transmission coefficient, and $\Delta G^{\ddagger}$ is the total free energy of activation described by the Marcus equation [eqn. (4)]

$$\Delta G^{\#} = \frac{\lambda}{4}\left(1+\frac{\Delta G_{el}}{\lambda}\right)^2 \tag{4}$$

where λ is defined as the total reorganization energy, and ΔG_{el} is expressed by the Rehm–Weller[19,20] equation [eqn. (1)].

After taking into account the Marcus relationship, as a final equation describing the rate of the photoinitiated polymerization for viscous or solid monomer one obtains eqn. (5), or in logarithmic form, eqn. (6),

$$R_p = -\frac{d[M]}{dt} = k_p[M]\sqrt{\frac{I_a\chi Z\exp[-(\lambda+\Delta G_{el})^2/4\lambda RT]}{k_t}} \tag{5}$$

$$\ln R_p = A - (\lambda + \Delta G_{el})^2/4\lambda PT \tag{6}$$

where A combines all constant data for the initial time of polymerization. It is apparent from the analysis of eqn. (6), that for the photoinduced polymerization occurring *via* the electron transfer process, the relationship between the rate of polymerization and ΔG_{el} should present a classical, Marcus parabolic relationship. Eqns. (5) and (6) predict that the rate of polymerization might be in part controlled by the rate of photoinduced electron transfer. As a consequence, the Marcus equation can be applied for the description of the rate of the polymerization photoinitiated *via* the photoinduced intermolecular electron transfer. Experimental verification of eqns. (5) and (6) for the tested ion pairs is possible by measuring the rate of the primary process of the polymerization initiation process, *e.g.* the rate of the electron transfer between the borate and cyanine ions.

As noted earlier, Schuster and co-workers[2,3] established that the single electron transfer from the alkyl triphenyl borate to the excited cyanine dye occurs rapidly. These authors established also that only the unassociated cyanine cations fluoresce and there is no (or very little) fluorescence from the cyanine–borate ion pair, and finally they concluded that the fluorescing state of the cyanine is not the state that is reduced by the borate.[2] In order to clarify the relationship between the rate of the polymerization and the photophysical properties of the

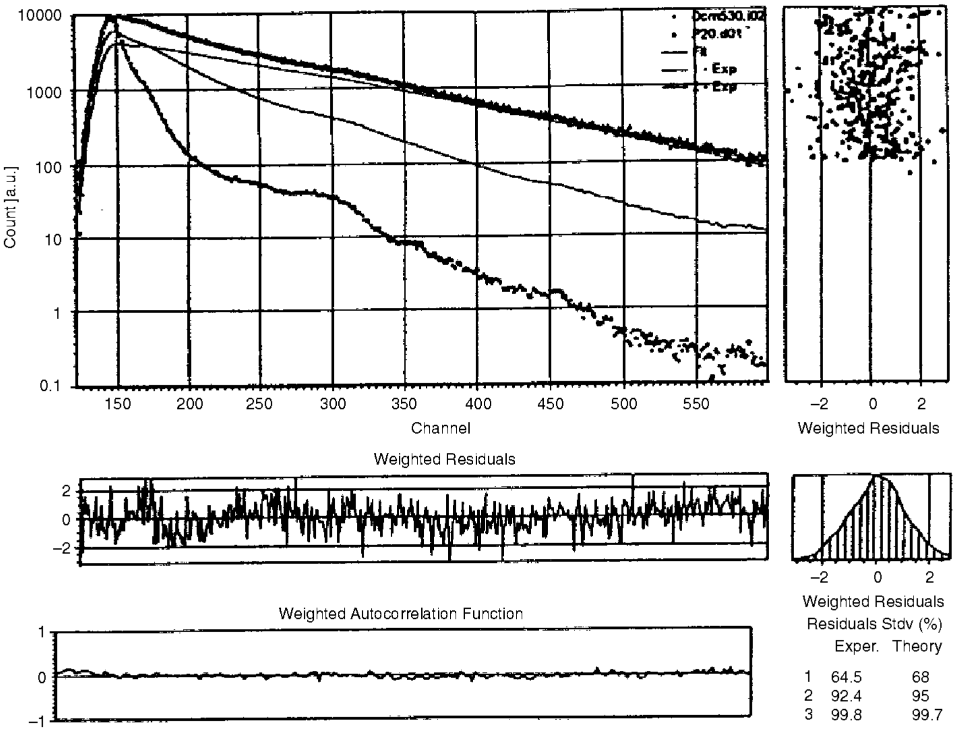


Fig. 5 Graphical report for the picosecond fluorescence lifetime measurement recorded for Cy9$^+$EtSO$_4^-$.

cyanine dyes tested, fluorescence lifetime measurements were performed, allowing the decay of the lifetime to be established with the resolution of a single picosecond. It is necessary to emphasize that in order to verify the generalization mentioned earlier the preparation and testing of a large number of dyes were needed. The fluorescence lifetime were measured for the dyes with iodine, ethyl sulfate and parallel with borate ions as the counterion. Surprisingly, mostly these measurements reveal two-expotential fits with the experimental residual very close to the theoretical one. A typical example of this behavior is given in Fig. 5, which presents a graphical report for the picosecond lifetime measurement recorded for Cy9$^+$EtSO$_4^-$. For a few dyes a three-expotential model was necessary in order to obtain the acceptable fits. There is also, mostly for *meso*-cyanines, evidence of single-expotential decay previously reported for thiacarbocyanine (Cy54$^+$I$^-$).[23,24] Similar properties were observed for indocarbocyanine dyes.[25,26]

The alkyl substitution in the *meso* position of the polymethine chain dramatically decreases the fluorescence lifetime (Fig. 6), which is attributed to faster torsional relaxation to the ground state of the excited dye.[27] The effect of the ethylene sulfate ion exchange on borate ion is illustrated in Fig. 7. It is clear from inspection of the data shown in Fig. 7 that the borate ion strongly decreases the cyanine ion fluorescence lifetime.

It is not our intention to discuss the relaxation dynamics of the dyes tested in this paper. However, for better understanding of the relationship between the rate of the electron transfer and the rate of polymerization, a basic explanation of specific photophysical properties of the tested cyanine dyes is needed. The quantum chemical calculations indicate that the dye ground states are exceptionally symmetrical. This specific behavior is illustrated by the data summarized for the simplest dioxacarbocyanine dye in Table 3.

The results obtained by the AM1 calculations show that for the all-*trans* conformer the bonds formed between C^8 or C$^{8'}$ and C^9 are non-differentiated. Similar properties indicate bonds C^2–C^8 and C$^{2'}$–C$^{8'}$. This finding allows the conclusion that the mono-*cis* form of the dye can be formed by twisting of either the C^8–C^9 or C$^{8'}$–C^9 bonds. Twisting around C^2–C^8 and C$^{2'}$–C$^{8'}$ bonds, according to Görner *et al.*[24] also gives *cis*-isomer, however, energetically these conformers differ from that obtained by

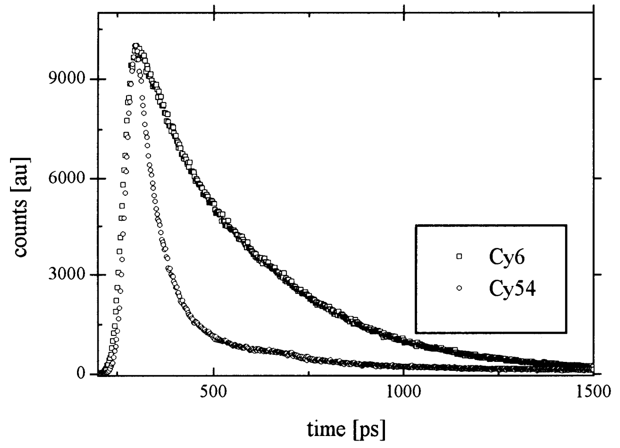


Fig. 6 The influence of the substitution in *meso* position on the fluorescence lifetime of cyanine borates tested. Fluorescence measurements performed for dyes in ethyl acetate solution.

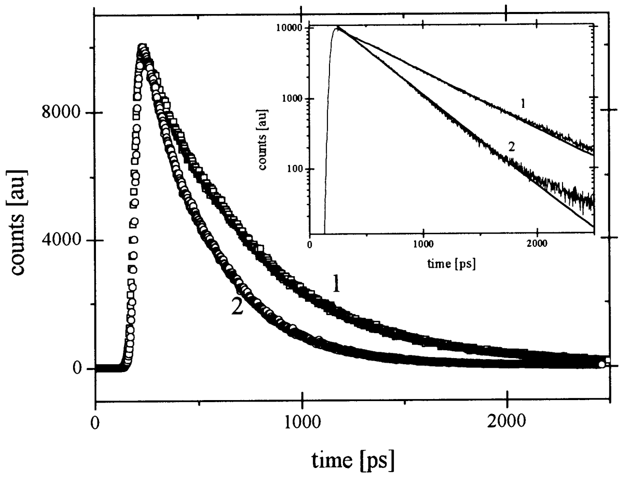


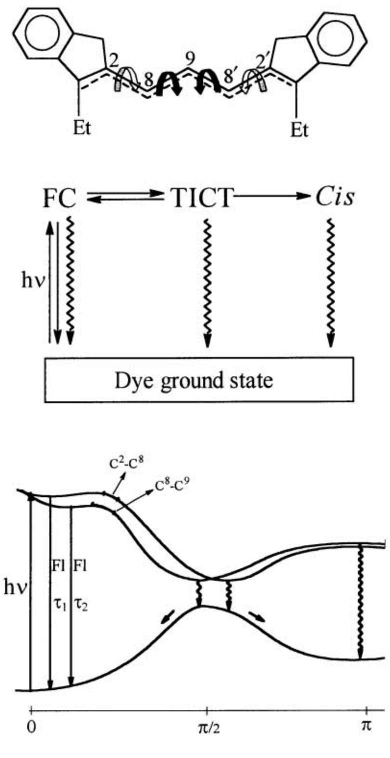
Fig. 7 Influence of the borate ion on the fluorescence intensity decay recorded for cyanine Cy9. Fluorescence measurements performed for dyes in ethyl acetate solution.

Table 4 Measured relative rates of polymerization[a] and rates constants for the electron transfer process in cyanine borates tested

Dye	$1 + \ln R_p$ (au) CyB2	k_{ET}/s^{-1} CyB2	k_{ET}/s^{-1} CyB2	$1 + \ln R_p$ (au) CyB3	k_{ET}/s^{-1} CyB3	k_{ET}/s^{-1} CyB3	$1 + \ln R_p$ (au) CyB4	k_{ET}/s^{-1} CyB4	k_{ET}/s^{-1} CyB4
Cy3	5.27	9.84×10^8	1.48×10^9	4.46	5.27×10^8	1.07×10^9	4.57	2.23×10^8	9.97×10^8
Cy4	3.75	1.55×10^{10}		4.47			3.10	1.34×10^{10}	
Cy6	5.22	8.28×10^8	4.45×10^8	5.40			2.88		
Cy8[b]	5.61	4.21×10^8	4.39×10^8	5.37			3.16	1.41×10^8	3.33×10^8
Cy9[b]	5.36	4.26×10^8	1.03×10^9	5.03			4.93		
Cy10[b]	4.67	6.31×10^8		5.36			2.80		
Cy11	3.21	2.06×10^{10}	3.67×10^9	2.15			1	1.05×10^{11}	4.7×10^9
Cy18	5.12	8.14×10^9	7.36×10^8	5.65	9.94×10^9	9.89×10^8	5.76	4.31×10^9	1.07×10^9
Cy19	5.05	5.45×10^9	1.41×10^9	6.01			5.67	4.34×10^9	1.45×10^9
Cy20	5.12	5.49×10^9	1.09×10^9	1.30			2.48		
Cy21	5.25	2.74×10^8		5.51			2.20		
Cy22[b]	5.43		1.86×10^8	4.62	5.18×10^9		6.29		
Cy23[b]	4.71	1.28×10^9	1.86×10^8	5.22	1.09×10^9	37686765	6.00		
Cy24[b]	3.72	6.38×10^8	2.21×10^8	5.25	1.05×10^9	3.94×10^8	5.07		
Cy25[b]	5.24	4.48×10^9	2.55×10^8	4.19	2.02×10^9	2.83×10^8	4.86	3.7×10^9	1.91×10^8
Cy27	3.50	6.31×10^9		—			—		
Cy28	3.51		1.22×10^9	3.75			5.47		1.54×10^9
Cy33[b]	4.63		1.55×10^8	2.53			2.92		
Cy36[b]	5.30	1.4×10^{10}	2.93×10^9	1.38			2.39	1.44×10^9	2.84×10^9
Cy41[b]	4.18	7.59×10^9		1.29			2.57		
Cy45[b]	5.53	1.27×10^{10}		6.06	9.38×10^9		2.60		
Cy47[b]	3.25	6.5×10^9		3.55	6.33×10^8		2.79	6.09×10^9	
Cy48[b]	1.888	9.22×10^9	4.56×10^9	—			—		
Cy52[b]	3.80		5.49×10^9	4.14		5.94×10^9	1.98		
Cy54[b]	3.78	6.8×10^{10}		2.65			2.43	1.59×10^{11}	
Cy56[b]	4.29	1.97×10^{10}		1.71			2.41	1.6×10^{10}	
Cy58[b]	2.07	3.9×10^8	2.05×10^9	1.30			1.865	6.85×10^9	3.63×10^9
Cy59[b]	1	6.57×10^{10}		—			—		
Cy60[b]	—	4.77×10^{10}		—			—		

[a] Collected results are the averaged values obtained from three independent measurements. Average error is in range of 5–10%. au = arbitrary units.
[b] Dyes prepared in our laboratory.

the rotation of C^8–C^9 or $C^{8'}$–C^9 bonds. The results obtained by AM1 calculations gave a rough guideline regarding the energies of possible ground state conformers (see Table 3). Very recently Robb and Olivucci and co-workers[28] described CASSCF quantum chemical calculations for cyanine dye models of different chain lengths. On the basis of these calculations they concluded that pentamethine cyanine dye may undergo *trans–cis* photoisomerization about C^2–C^8 ($C^{2'}$–$C^{8'}$) and C^8–C^9 ($C^{8'}$–$C^{9'}$) bonds. Based on our, and Robb and Olivucci's, calculations for the explanation of the fluorescence bi-exponential decay of the tested dyes we propose the following kinetic model (see Scheme 2). After excitation, the relaxed Franck–Condon state **FC** is reached. **FC** can emit or can form a twisted structure (TICT) with a different twisted angle (about 100°) for the rotation about C^2–C^8 ($C^{2'}$–$C^{8'}$) and C^8–C^9 ($C^{8'}$–$C^{9'}$) bonds. This configuration corresponds to the minimum on the potential surface of the lowest excited singlet state. The excited state potential energy minimum is reflected in the ground state potential surface, which leads to the occurrence of a conical intersection of potential energy surfaces. Such an intersection provides a universal decay route for the excited conjugated polyatomic molecules. Since the activation energy for the twist about the C^2–C^8 ($C^{2'}$–$C^{8'}$) bond and C^8–C^9 ($C^{8'}$–$C^{9'}$) bond differs, one can expect that the time needed for the formation of the TICT state is different for molecules with a rotation about C^2–C^8 ($C^{2'}$–$C^{8'}$) bond in comparison to the time related to rotation about the C^8–C^9 ($C^{8'}$–$C^{9'}$) bond. A subsequent twist leads to the formation of the non-emitting *cis* form of the dye. Twisting about a C–C bond results in the formation of two decoupled π fragments with an odd and even number of carbon atoms, respectively. At a conical intersection the positive charge is completely localized on the fragment with an odd number of carbon atoms and negative charge is located on the fragment with an even number of carbon atoms. This leads to the formation of a polar molecule. Any emission from this type of excited molecule should exhibit a large Stokes shift. It was mentioned earlier that the fluorescence spectra of cyanines tested show a classical image of the absorption spectra with Stokes shifts ranging from 350 to 650 cm^{-1}. This observation permits the conclusion that the TICT state is the non-emitting state.



Scheme 2

The spectroscopic properties of the *cis* form of cyanine dyes should also be clarified here. In the literature, there is a controversy related with the interpretation of the transient absorption spectra of cyanine dyes. Indocarbocyanine dyes display characteristic transient absorption (apparent absorption maximum at 580 nm) that decays in a nanosecond time scale and according to Sauerwein and Schuster[25] can be attributed to mono-*cis* excited isomer. On the other hand, Serpone and Sahyun[27] for dithiacarbocyanine dyes assigned this transient to the triplet excited state of the dye. However, it is necessary to emphasize that the heavy atom effect creates a transient with an apparent absorption maximum recorded at 620 nm[25] and that the triplet energy transfer sensitization of dithiacarbocyanine also gives an absorption band with a maximum at 630 nm.[25,29] These observations allow us to anticipate that the non-emitting state exhibiting a transient absorption band in the range 480–580 nm can be assigned to the absorption related with the presence of the excited mono-*cis* isomer.

The occurrence of electron transfer between cyanine and borate ions leads to quenching and simultaneous shortening of the fluorescence lifetime of cyanine chromophore. Under the assumption that electron transfer is the only additional quenching route available in the ion pair (lifetime τ_{CyB}) compared to the parent dye (lifetime τ_{CyX}) the rate of the electron transfer for ion pair can be obtained from eqn. (7).

$$k_{el} = \frac{1}{\tau_{CyB}} - \frac{1}{\tau_{CyX}} \qquad (7)$$

The calculated rate constants are collected in Table 4. The main question arising during the quenching experiments is whether the fluorescing state of the cyanine is the state that is quenched and reduced by the borate. It is well known that the rate of the electron transfer is related to the free energy of the reaction through the classical Marcus equation.[9–11] For analysis of the above-mentioned relationship, the fluorescence decay times with higher population have been taken for consideration.

The data presented in Figs. 8A and 8B behave as predicted by the theory of the electron transfer and allows the conclusion that the state which is quenched is the fluorescing state. It is necessary to emphasize that the relationship predicted by the Marcus equation is fulfilled only for cyanines without substitution in the *meso* position. This observation permits the conclusion that *meso*-substituted cyanines are not quenched in their fluorescing state. It should be noted that the points characterizing dyes are dispersed and more likely indicate the trend of the relationship than the superior fit to the Marcus theory. We believe that the high scattering of the experimental points are related to properties of cyanine borates. Schuster and coworkers[30] documented that the maximum lifetime for $[n\text{-BuB(Ph)}_3]^\bullet$ is about 250 fs. It means the oxidation of $[n\text{-BuB(Ph)}_3]^-$ is dissociative or nearly so and therefore the Marcus theory may not predict rates of its electron transfer reaction. It should be noted that the Marcus theory is based upon the assumption that the oxidized and reduced forms of substrates have long enough lifetimes to establish a new equilibrium. If the electron transfer is dissociative, this new equilibrium cannot be reached and the application of the Marcus theory may not be quite appropriate. Concerning the previously discussed specific feature of cyanine borates, one can predict that even a slight change in the radical–ion pair electrochemical properties or size, may cause distinct deviation of the rate constant for the electron transfer from the value predicted by the Marcus theory.

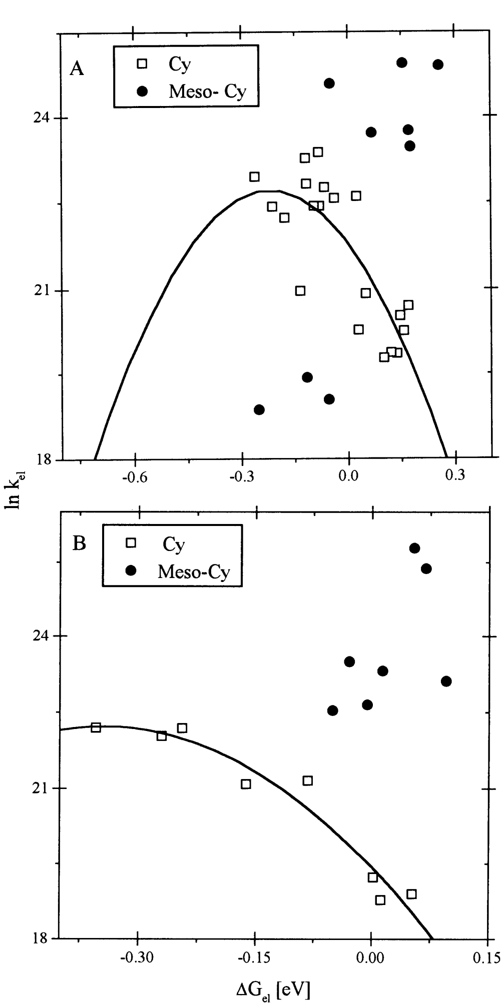


Fig. 8 The dependence of the rate for electron transfer on free energy for transfer of an electron from: (A) *n*-butyl triphenyl borate ion, (B) *tert*-butyl triphenyl borate ion to the cyanine dyes tested.

In the Introduction, it was mentioned that it is our intention to extend the study on the cyanine borates to the relationship between the rate of the primary process, *e.g.* the rate of the electron transfer, and the rate of the photoinitiated polymerization. Our earlier reports have shown that the rate of polymerization might be a function of the thermodynamic driving force of the electron transfer process (ΔG_{el}).[12,13,22] Since the rate of the electron transfer process is much faster than the rate of polymerization, this conclusion may be quite surprising. However, it is obvious that for a consecutive reaction mechanism an increase in the reaction rate for the primary step should automatically increase the rate of the reaction that follows. The photoinitiated polymerization reaction represents such a type of process. Since the one-electron oxidation of an alkyl triphenyl borate generates, in principle, a similar type of an alkyl radical, this type of photoinitiating donor–acceptor system is the best for the testing the relationship between the rate of the primary process (electron transfer) and the rate of the photoinitited polymerization. Therefore, if there is a relationship between the rate of the electron transfer process and the rate of the photoinitaited polymerization, one should observe the linear relationship between the rate of the electron transfer process and the rate of the photoinitited polymerization. These types of relationships are shown in Figs 9A, 9B and 9C.

On the basis of the data presented in Fig. 9 one can conclude that for cyanines without *meso* substitution there are two possibilies: (i) no relationship between the rate of polymerization and rate of electron transfer (slope for ln R_p *vs.* ln k_{el} close to zero; 0.022 s) and (ii) a linear relationship between the logarithm of the polymerization rate and logarithm of the rate of the primary process of the electron transfer reaction. This is not observed for *meso*-substituted cyanines. Additionally, the linear relationship with a negative slope, observed in Fig. 9C, supports, as mentioned earlier, the idea that *meso*-substituted cyanines are not quenched in their fluorescing state. These conclusions correlate with the relationships presented in Fig. 8, which show the Marcus relationships for the cyanine fluorescence quenching process, where only for cyanines without

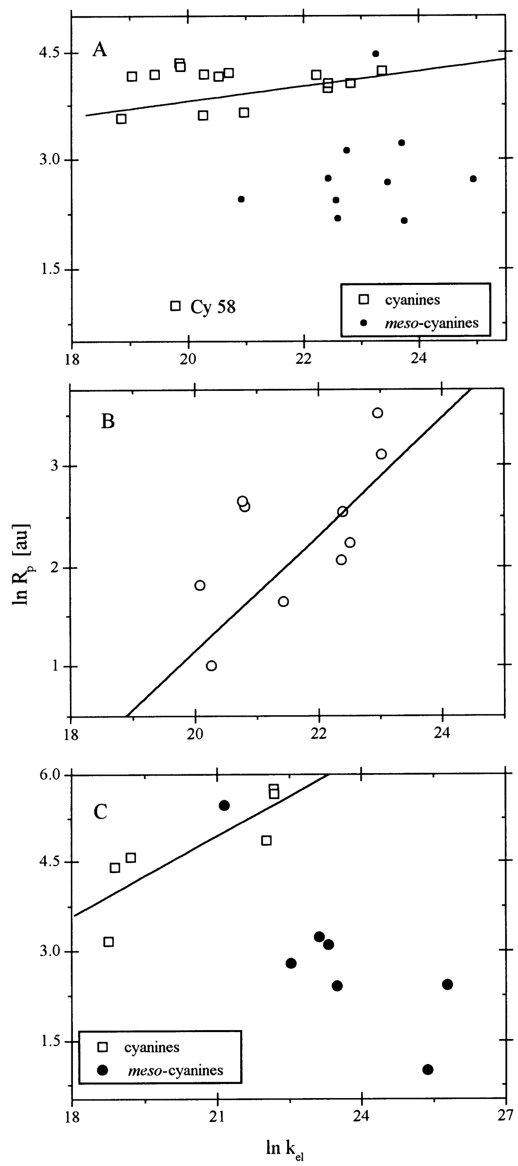


Fig. 9 The dependence of the rate of photopolymerization on the rate constant for electron transfer for: (A) cyanine *n*-butyl triphenyl borates, (B) cyanine *sec*-butyl triphenyl borates and (C) cyanine *tert*-butyl triphenyl borates.

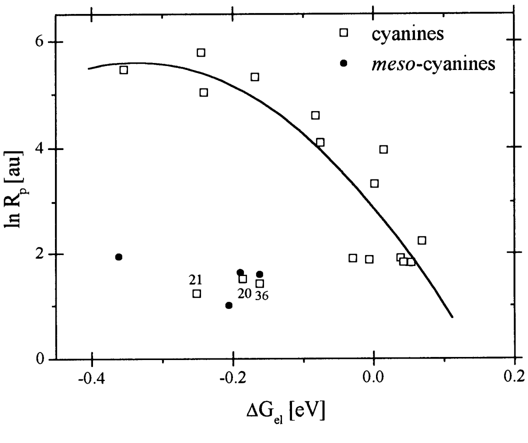


Fig. 10 The Marcus plot of rates of the photopolymerization (au) of TMPTA–MP (9 : 1) mixture for cyanine *tert*-butyl triphenyl borate photoinitiating systems.

meso substitution is this type of feature observed. Transferring this to the practical application of Marcus theory into photoinitiated polymerization, one can conclude that for selected photoredox pairs it is possible to apply the Marcus relationship for the prediction of the rate of the photoinitiated polymerization. A good illustration of this suggestion is the plot presented in Fig. 10, which shows the dependence of the polymerization rate as a function of free energy change for the electron transfer between borate anion and cyanine cation. The observed curve presents a classical parabolic shape, as predicted by Marcus. The range of free energies for the electron transfer reactions shown in Fig. 10 is narrow, however it is possible to establish the reorganization energy for the system.

The analysis of the data shown in Fig. 10, according to eqn. (6) shows that λ is *ca.* −0.3 eV (*ca.* 29 kJ mol^{-1}). This value is similar to the value reported by Schuster and co-workers[3] and supports the postulate of an electron transfer reaction generating free radicals that are able to initiate free radical polymerization.

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