Cyanine Borates Revisited. Application of the Marcus Equation for the Description of the Kinetics of Photoinitiated Free Radical Polymerization. IV.

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Introduction. The work of Schuster and co-workers[1] on the photochemistry of cyanine borates led to the preparation of the first color-tunable, operating in the visible region, and commercial photoinitiators.[2] The mechanism of the initiation step of cyanine dye−tetraorganoborates involves alkyl radical formation as a result of photoinduced electron transfer from borate anion to the singlet excited state of cyanine dye, followed by the rapid cleavage of the alkyl boron bond of the boranyl radical (see Scheme 2). This reaction is useful for the initiation of photopolymerization of vinyl monomers.

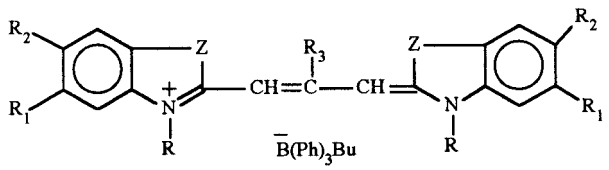
The cyanine and borate exist as an ion pair even in medium polarity solvents,[3,1b] and some of them even form penetrated ion pairs for which the center-to-center distance between the ions is less than the sum of the individual ionic radii.[4] Since the lifetime of the excited singlet state is too short to allow an efficient diffusive encounter at an achievable concentration of the borate, self-association of the cyanine cation and borate anion is a prerequisite for photoinduced reaction. This is not crucial for other dye−borates systems with processes occurring via the triplet excited state.[5]

In our earlier papers,[6] we have studied the possibility of the application of the Marcus theory for the description of the rate of photoinduced polymerization via an intermolecular electron-transfer process. Various electron donors and electron acceptors have been tested in order to verity the possibility of the application of the Marcus equation. However, the variations of the driving force of the electron transfer were introduced by using a series of electron donors, which yield free radicals with different reactivities (substituent effect). The use of cyanine borates creates a unique opportunity to change the driving force of the electron-transfer process without a change in the type of the yielding free radical.

It so happens that besides the knowledge that the cyanine borate initiator is tunable by the number of conjugated alkene units and a good knowledge of photochemistry and photophysics of the first step of the process, little is known about the real polymerization initiation ability. Therefore, it is our intention to revisit the cyanine borates and describe the measurements of their practical photoinitiation capability and inspect whether their photoinitiation ability presents a correlation predicted by the Marcus theory.

Experimental Section. Substrates used for preparations of dyes, monomers, and solvents were purchased from Fluka, Merck, or Aldrich. A general route for synthesis of cyanine dyes prepared during this work is

Chart 1



shown in Scheme 1, where R is a general notation for a substituent. In the course of this work, it was necessary to exchange the counterion generated in the synthesis of the cyanine dye for the borate anion. Synthesis of the cyanine borates were prepared using procedure described by Schuster et al.[1b] The cyanine borate generally precipitates from a solution of cyanine dye and 1 equiv of the tetramethylammonium borate in acetonitrile. Precipitation occurs when the mixture becomes more concentrated.

The kinetics of free radical polymerization were measured based on measurement of the rate of heat evolution during polymerization.[6] Photopolymerization was initiated using an Omnichrome argon-ion laser, Model 543-500 MA. The average power of irradiation was 30 mW/0.785 cm^2. All irradiation procedures were made on the one type of formulation which consists of the mixture of 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and 1 mL of 1-methyl-2-pyrrolidinone (MP) at the cyanine borate concentration of 1×10^{-3} M. A semiconducting diode immersed in the 2 mm thick layer (0.25 mL) of a cured sample was used as a temperature sensor. The amplified signal was transformed with a data acquisition board to a computer.

The reduction potentials of the cyanine dyes were measured by cyclic voltammetry. An electroanalytical Cypress System Model CS-1090, equipped with small-volume cell, was used for measurements. A platinum 1 mm disk electrode was used as the working electrode, a Pt wire constituted the counter electrode, and a Ag−AgCl electrode served as the reference electrode. The supporting electrolyte was 0.5 M tetrabutylammonium perchlorate in dry acetonitrile. Absorption spectra were recorded with a Varian Cary 3E spectrophotometer, and 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. Fluorescence measurements were performed at ambient temperature.

Results and Discussion. Table 1 summarizes the basic spectroscopic, electrochemical, and thermodynamical properties of cyanine dyes (Chart 1) tested.

Figure 1 presents the kinetic curves observed during the argon ion laser initiated polymerization of a solution composed of 1 mL of 1-methyl-2-pyrrolidinone (MP), 9 mL of 2-ethyl-2-(hydroxymehyl)-1,3-propanediol triacrylate (TMPTA), and dyes with a concentration of 10^{-3} M. It is apparent from the inspection of the initial rates that the photoinitiation ability of a dye depends on its structure. It is also apparent that cyanine borates initiate free radical polymerization with the rate much lower than RBAX[7]−*N*-phenylglycine initiating photoredox pair.

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Scheme 1

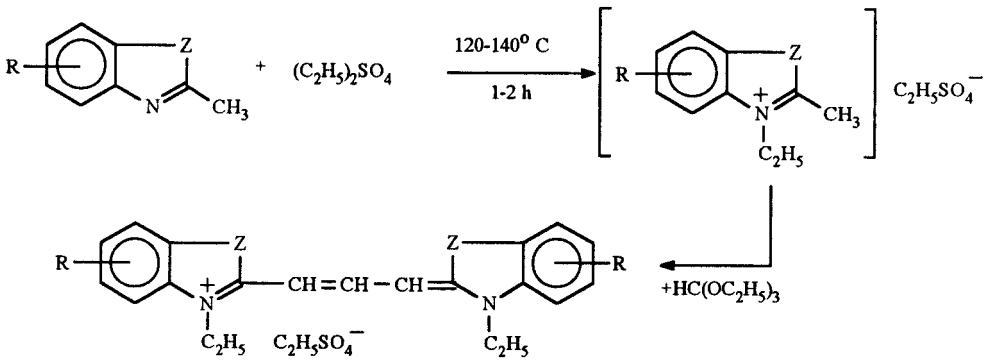


Table 1. Characteristics of the Cyanine Borates Tested

dye	Z	R_1	R_2	R_3	R	λ^{A}_{max} [d] (nm)	λ^{Fl}_{max} [e] (nm)	E_{red} (V)	$\Delta G°_1$ [a] (eV)	$\Delta G°_2$ [b] (eV)	$\Delta G°_3$ [c] (eV)
P-22	O	Cl	H	H	C_2H_5	484	509	−1.16	−0.736	−0.226	−0.232
P-23	O	CH_3	H	H	C_2H_5	488	511	−1.31	−0.576	−0.066	−0.072
P-21	O	H	H	H	C_6H_{13}	486	504	−1.27	−0.561	−0.051	−0.057
P-29	O	C_6H_5	H	C_2H_5	C_2H_5	502	528	−1.13	−0.55	−0.040	−0.046
P-19	O	H	H	H	C_2H_5	482	507	−1.30	−0.544	−0.034	−0.040
P-20	O	H	H	H	C_3H_7	484	508	−1.24	−0.542	−0.032	−0.038
P-18	O	H	H	H	CH_3	482	505	−1.28	−0.526	−0.016	−0.022
P-25	O	C_6H_5	H	H	C_2H_5	494	529	−1.12	−0.502	0.008	0.014
P-28	O	C_6H_5	H	C_2H_5	C_2H_5	502	527	−1.29	−0.454	0.056	0.050
P-27	O	CH_3O	H	C_2H_5	C_2H_5	504	528	−1.37	−0.377	0.133	0.127
P-24	O	CH_3O	H	H	C_2H_5	498	520	−1.31	−0.540	−0.030	−0.036
P-8	S	F	H	H	C_2H_5	562	593	−0.94	−0.491	0.019	0.013
P-6	S	H	H	H	C_3H_7	558	582	−1.04	−0.460	0.050	0.046
P-9	S	CH_3	H	H	C_2H_5	564	594	−0.99	−0.449	0.061	0.056
P-4	S	H	CH_3	CH_3	C_2H_5	542	579	−1.44	−0.440	0.070	0.064
P-10	S	H	H	H	C_2H_5	572	597	−1.10	−0.376	0.134	0.126
P-11	S	CH_3O	H	C_2H_5	CH_2CH_2OH	564	600	−1.026	−0.366	0.144	0.138
P-33	S	H	C_2H_5	H	C_2H_5	572	600	−1.014	−0.408	0.102	0.094
P-36	S	NO_2	H	H	C_2H_5	556	585	−1.086	−0.405	0.105	0.099

[a] $\Delta G°_1$: calculated using data obtained from cyclic voltametry measurements in Me CN solution. [b] $\Delta G°_2$: calculated using oxidation potentials determined kinetically by the method of Rehm−Weller. [c] $\Delta G°_3$: calculated using $\Delta G°_2$ corrected by the change in solvent from acetonitrile to polymerizing mixture. [d] Measured in ethyl acetate. [e] Measured in THF.

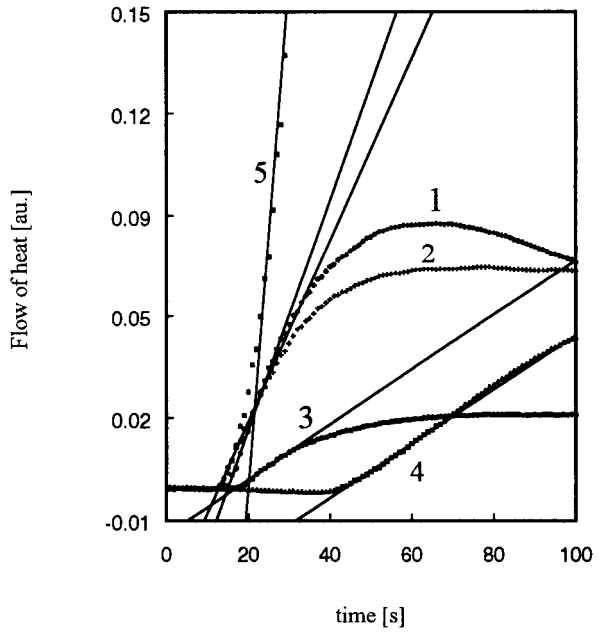


Figure 1. Rate of heat evolution during argon ion laser photoinitiated polymerization ($I_a = 30$ mW/0.78 cm^2), for a dye concentration of 1×10^{-3} M. Initiators: (1) P-36, (2) P-32, (3) P-24, (4) P-10, and (5) RBAX.[6a]

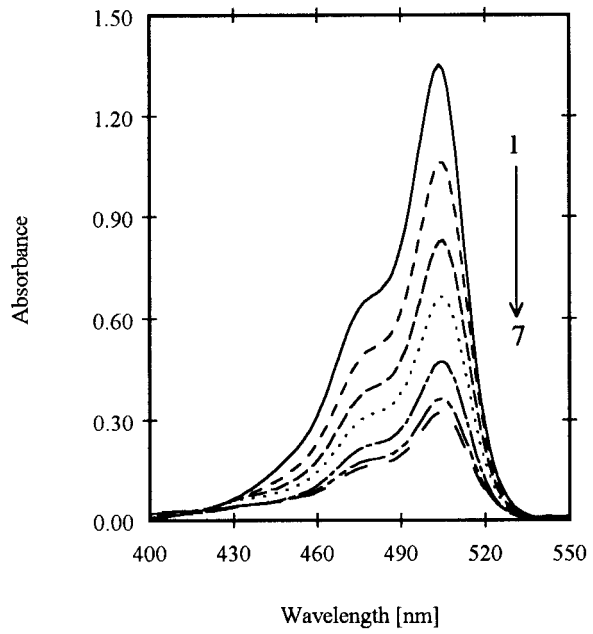
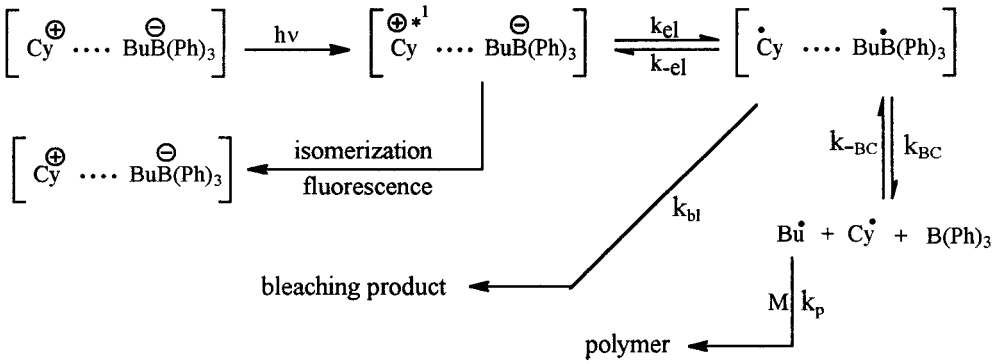


Figure 2. Changes of the electronic absorption spectra of P-28 during argon-ion laser irradiation ($I_a = 20$ mW) in EtAc solution ($V = 4.0$ mL, $c = 1 \times 10^{-5}$ M). Time of irradiation: (1) 0 s, (2) 20 s, (3) 40 s, (4) 60 s, (5) 80 s, (6) 150 s, and (7) 180 s.

Irradiation of cyanine borates causes, as shown in Figure 2, a bleaching process.

These findings clearly indicate that the coupling of the alkyl radical with the cyanine radical[8] competes

Scheme 2



with the free radical cage-escape process (see Scheme 2).

The analysis of the bleaching process shows that the maximum quantum yields of these processes oscillate between 0.001 and 0.02; e.g., it is at least 1 order of magnitude lower than the quantum yield of *n*-butyl radical formation ($\phi = 0.73$).[1b] This observation permits one to conclude that the bleaching process is slow and can be neglected. In our earlier papers we have shown that in the solid state or in very viscous media the rate of polymerization initiated via a photoinduced intermolecular electron transfer can be formulated as follows:[6b,9]

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left(\frac{I_a K_d}{k_t}\right)^{1/2}\{\chi Z \exp[-\lambda/4RT(1 + \Delta G°/\lambda)^2]\}^{1/2} \quad (1)$$

In logarithmic form, it is

$$\ln R_p = A - \lambda/4RT(1 + \Delta G°/\lambda)^2 \quad (2)$$

where *A* combines all constant data for the initial time of polymerization. The symbols in eqs 1 and 2 have their conventional meanings and $\Delta G°$ is the free energy for a photoinduced electron-transfer process described by the equation

$$\Delta G° = E_{ox} - E_{red} - {}^1E_{00} - (W_p - W_r) \quad (3)$$

E_{ox} and E_{red} are the oxidation and reduction potentials of the electron donor and acceptor, ${}^1E_{oo}$ is the energy of the excited state, W_r is the energy needed for bringing the reactants from infinity to the encounter distance, and W_p is a term associated with separating the products from the encounter to infinity. After Schuster,[1b] we set $W_p \approx 0$.

The reduction potentials of $[Cy]^+$ and oxidation potentials of the borates were measured in acetonitrile solution. The photopolymerization experiments were carried out in MP-TMPTA solution ($\epsilon \approx 13.0$). Thus, calculation of $\Delta G°$ requires consideration of the effect of the solvent change on the electrochemical potentials as well as the effect of Coulombic stabilization of the cyanine borate ion pair. Assuming after Schuster,[1b] $W_r \approx 0.96$ in benzene solution and applying eq 4, where r_{A^+}

$$W_r = e^2/2\left[\frac{1}{r_{A^-}} + \frac{1}{r_{D^-}}\right][1/\epsilon_s] \quad (4)$$

and r_{D^-} are the radii of the spherical cation and anion, respectively and ϵ_s is the dielectric constant of solvent,

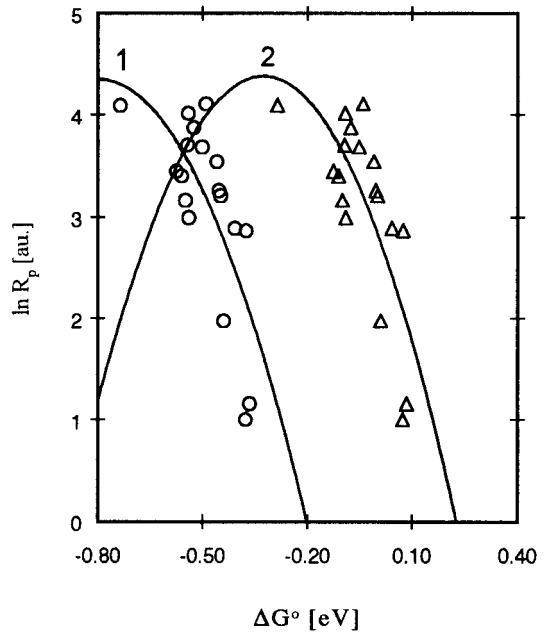


Figure 3. Dependence of the rate of photoinitiated polymerization on the free energy for photoinduced electron transfer process from borate to the excited state of cyanine dye. The circles are the values calculated from the peak potentials of the cyclic voltammograms; the triangles represent values calculated from the kinetically determined potentials.[1b] Solid lines represent the best fit of the Marcus equation (full parabola).

by comparison of ϵ for benzene and polymerizing mixture, one can calculate W_r for the MP−TMPTA monomeric system. Setting after Schuster[1b] $W_p \approx 0$ and considering the change in the solvent from acetonitrile to MP−TMPTA mixture on the value of the electrochemical potentials of the cyanine and borates, one can estimate $\Delta G°$ of the singlet excited cyanine borate ion pairs listed in Table 1. On the basis of the data summarized in Table 1, it appears that the change of the solvent from MeCN to the polymerizing mixture slightly shifts to a negative value the curve describing the rate of polymerization as a function of free energy. The relationship between the rate of polymerization and the free energy of electron-transfer process is shown in Figure 3.

It is clear, from the inspection of the data presented in Figure 3, that the rate of polymerization initiated by series cyanine borates increases as the driving force of electron transfer increases. This behavior is predicted by the classical theory of photoinduced electron transfer.[10]

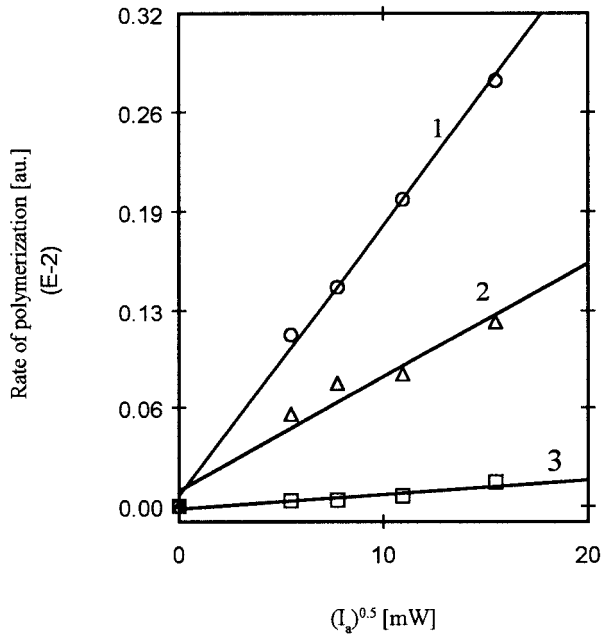


Figure 4. Rate of polymerization versus light intensity for P-10. Concentration of photoinitiator: (1) 1×10^{-3} M, (2) 1×10^{-4} M, and (3) 5×10^{-5} M.

Photopolymerization of the system, as is shown in Figure 4, proceeds by the conventional mechanism in which bimolecular termination occurs by reaction between two macroradicals. This suggests that free radicals formed from cyanine ion after a photoinduced electron-transfer process do not act as terminators of polymer chains.

Conclusions. Cyanine borate salts (thiocarbocyanines and carbocyanines) initiate free radical polymerization. The rate of photopolymerization depends on $\Delta G°$ of electron transfer. This latter value was estimated for a series of cyanine borate salts, and the relationship between the rate of polymerization and the free energy of activation gives the maximum value predicted from Marcus theory. The classical studies on photoinduced electron transfer are based on the determination of the rate constants for primary processes. Since similar relationships for both the rate of electron transfer (for other type of cyanine dyes) and for the rate of polymerization versus $\Delta G°$ are observed, one can conclude that for certain types of secondary processes the Marcus theory of electron transfer can be extended. Thiocarbocyanine and carbocyanines borates photoinitiate polymerization in the visible region. However, they initiate polymerization with the rate significantly lower than classical triplet, xanthene dyes. This is probably due to the very short lifetime of the singlet excited state of dye ion which acts as an electron acceptor. Thiocarbocyanine and carbocyanine borates are stable at ambient temperature in the formulations prepared for photopolymerization experiments.

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