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Generalization of the Kinetic Scheme for Photoinduced Polymerization via an Intermolecular Electron Transfer Process. 2. Application of the Marcus Theory

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ABSTRACT: This paper presents a theoretical description of the kinetics of free radical dye initiated photopolymerization via an intermolecular electron transfer process. Analysis considers the properties of organic redox pair forming initiating radicals. An application of the Marcus theory gives the kinetic scheme, which considers both the theromodynamic and kinetic aspects of the electron transfer process. The analysis shows that both the reactivity of free radicals resulting from the photoinduced intermolecular electron transfer (PET) process and the rate of the PET process can limit the rate of the polymerization initiation process. The theory is supported by experimental data. Several organic redox pairs forming free radicals have been tested. As the electron-accepting molecules, xanthene dyes and camphorquinone have been tested. As the electron donors, tertiary aromatic amines (TAAs) and *N*-phenylglycines (NPGs) were used. Several important conclusions are drawn from the theoretical and experimental data: (i) For the process with the rate of PET much lower than the rate of the diffusion-controlled process, the Marcus theory can be used for analyzing or predicting the ability of organic redox systems for light-induced free radical polymerization. (ii) For the process controlled by the diffusion, the reactivity of radicals formed as a result of the PET process limits the rate of the polymerization initiation. It is shown that this relationship can also be presented as a function of thermodynamic driving forces of the photoredox reaction ($-\Delta G°$). (iii) Experimental results show that one can describe the rate of photoinitiated polymerization as a function of thermodynamic driving forces of the photoredox reaction ($-\Delta G°$; described by the Rehm−Weller equation) of the organic donor−acceptor pair. For the photoinduced electron transfer occurring much slower than diffusion-controlled processes, the relationship between the rate of polymerization and $-\Delta G°$ presents a classical Marcus parabolic relationship. For PET controlled by diffusion, the relationship between the rate of polymerization and $-\Delta G°$ is dependent on the reactivity of free radicals resulting from the PET process and gives a linear relationship indicating the "inverted region-like" kinetic behavior.

Introduction

Eberson[1] in his book emphasizes that "a classical study shows the salient features of photochemical electron transfer from the kinetic point of view". The classical studies are based on the determination of the rate constants for a primary process, e.g., fluorescence quenching of the excited states studied by Rehm and Weller[2] and reconsidered by Hug and Marciniak,[3] studies of the rates of the back electron transfer processes described more recently,[4−6] or the study on long-distance electron transfer in radical anions in rigid matrices.[7]

All these above-mentioned studies describe the rate of a photoinduced intermolecular electron transfer (PET) process using the Marcus theory.[8] However, the practical application of the Marcus theory is commonly used for the study of the primary photochemical processes. The description of the kinetics of the photoinitiated polymerization via an intermolecular electron transfer process is one more example applying this theory to practice.[9,10]

Marcus' theory of electron transfer leads to the familiar prediction that the rate of electron transfer first should increase with an increase in the thermodynamic driving force ($-\Delta G^{\#}$) and should ultimately decrease with an increase of the thermodynamic driving force. This is due to driving forces, $\Delta G^{\#}$, on the free energy of activation for an electron transfer process[8,11−13]

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$$\Delta G^{\#} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{\circ}_{\mathrm{el}}}{\lambda}\right)^2 \qquad (1)$$

where $\Delta G^{\#}$ is the total free energy of activation, being the sum of the individual free energies:

$$\Delta G^{\#} = \Delta G^{\#}_{\mathrm{v}} + \Delta G^{\#}_{\mathrm{s}} \qquad (2)$$

where the subscripts refer to the energy involving bond distortions of interacting molecules and solvent changes in the ionic sphere surrounding the reactants (s = solvent); λ is defined as the total reorganization energy. Thus, $\lambda = \lambda_{\mathrm{v}} + \lambda_{\mathrm{s}}$, where λ_{v} is the inner-sphere reorganization energy referring to the energy changes of the molecule geometry during the electron transfer step and λ_{s} is the outer-sphere reorganization energy which is caused by the energy change as the solvent shell surrounding the reactants rearrange. Finally, $\Delta G^{\circ}_{\mathrm{el}}$ is expressed by the Rehm–Weller[14] equation

$$\Delta G^{\circ}_{\mathrm{el}} = E_{\mathrm{ox}}(\mathrm{D/D}^{\bullet+}) - E_{\mathrm{red}}(\mathrm{A}^{\bullet-}/\mathrm{A}) - Ze^2/\epsilon a - E_{00} \qquad (3)$$

where $E_{\mathrm{ox}}(\mathrm{D/D}^{\bullet+})$ is the oxidation potential of the electron donor, $E_{\mathrm{red}}(\mathrm{A}^{\bullet-}/\mathrm{A})$ is the reduction potential of the electron acceptor, E_{00} is the energy of the excited state, and $Ze^2/\epsilon a$ is the Coulombic energy, which is considered negligible with respect to the overall magnitude of the ΔG in the present systems.

In our earlier paper,[10] we have shown that the Marcus equation can be applied for the description of the kinetics for a dye-photoinitiated polymerization via an intermolecular electron transfer process. It was shown that the initial rate of free radical polymerization of viscous polyolacrylates presents the Marcus "inverted-region-like" kinetic behaviors. In this paper, it is our intention to extend the kinetic consideration to a wider range of viscosity and polarity and to illustrate the "inverted-region-like" kinetic behaviors by a series of experiments performed using different techniques to measure the rate of polymerization with the use of various electron acceptors and donors.

Experimental Section

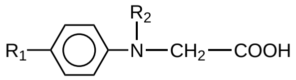
Substrates used for preparation of dyes and the electron donors were purchased from Fluka, Merck, or Aldrich. 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and 1-methyl-2-pyrrolidinone (MP) were purchased from Aldrich.

Dye initiators were prepared as follows. (1) RBAX: the Rose Bengal derivative was prepared from Rose Bengal according to the procedure described by Neckers et al.[15] Its reduction potentials were assumed to be equal to the reduction potential of the Rose Bengal C2′ benzyl ester sodium salt[16] ($E_{\mathrm{red}}(\mathrm{A}^{\bullet-}/\mathrm{A}) = -0.80$ V and its triplet $E_{00} = 1.7$ eV).[17,18] (2) TIHF: tetraiodohydrofluorescein (2,4,5,7-tetraiodo-6-hydroxyfluorone) was synthesized according to the method of Shi and Neckers.[19] Its reduction potential and triplet state energy according to Rodgers and Neckers[20] are $E_{\mathrm{red}}(\mathrm{A}^{\bullet-}/\mathrm{A}) = -0.99$ V (V(SCE)) and $E_{00}^{(\mathrm{T})} = 1.83$ eV (42.3 kcal/mol). For photopolymerization experiments, TIHF was acetylated by a procedure similar to that used for RBAX.[15]

Camphorquinone (CQ) was purchased from Aldrich. Its reduction potential is $E_{\mathrm{red}}(\mathrm{A}^{\bullet-}/\mathrm{A} = -1.249$ V and $E_{00}^{(\mathrm{T})} = 51.0$ kcal/mol.

Electron donors were prepared as follows: (1) The tertiary aromatic amines used (TAAs) are described in an earlier paper.[10] (2) *N*-Phenylglycine derivatives (NPGs) were prepared based on procedures described in organic chemistry journals[21−24] and are listed in Table 1. The oxidation potentials for the electron donors were measured by cyclic voltammetry. An Electroanalytical Cypress System Model CS-1090 was used for measurements, and a AgCl electrode served as a reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP).

Table 1. Structures, Oxidation Potentials, and Method of Synthesis of Tested Electron Donors with General Formula



no.	N substituent R_2	*p* substituent R_1	E_{ox} (mV)	method of synthesis
1	H	H	426	purchased from Aldrich or synthesis[21]
2	H	NC	707	ref 22
3	H	NO_2	781	ref 23
4	H	$CH_3C(O)$	635	ref 23
5	H	PhC(O)	661	ref 23
6	H	EtOC(O)	639	ref 23
7	H	Cl	479	ref 23
8	H	CH_3	437	ref 23
9	H	*t*-Bu	436	ref 23
10	H	PhO	479	ref 23
11	H	MeO	343	ref 23
12	Me	H		ref 23
13	$C(O)CH_3$	H		ref 23
14	Ph	H		ref 24

The kinetics of free radical polymerization were studied using a polymerization solution composed of 1 mL of MP and 9 mL of TMPTA. Dye concentration was 5×10^{-4} M, and the electron donor concentration was 0.1 M.

The kinetics of polymerization were measured using two different techniques. The first, real-time IR spectroscopy (RTIR),[25−27] allowed the rate of monomer double-bond disappearance to be monitored in real time. By following the disappearance of the IR absorption of the acrylic double bond, one can quantitatively evaluate the rate of polymerization. The IR spectrometer (Secord-IR 71, Carl-Zeiss Jena) was set in the transmission mode and the detection wavelength fixed at a value where the monomer double bond exhibits a discrete and intense absorption, e.g., at 810 cm^{-1} for acrylic monomers ($CH{=}CH_2$ twisting). The signal was transformed with an analog/digital data acquisition board interfaced to a computer. A thin film (transmittance at 810 cm^{-1} in the range of 90%) coated onto a polyethylene sheet, placed between NaCl salt disks, was irradiated with an Omnichrome Model 543-500 MA argon ion laser with a light intensity of 200 mW/0.785 cm^2. Measurements for each electron donor were repeated at least three times.

The second method is based on measurement of the heat evolution during polymerization in a sample 2−3 mm thick. Measurements were performed in a homemade microcalorimeter. A semiconducting diode immersed in a 2 mm thick layer (0.25 mL) of a cured sample was used as a temperature sensor. The amplified signal was transformed with an analog/digital data acquisition board interfaced to a computer. Irradiation of the polymerization mixture was carried out using the emission of an Omnichrome Model 543-500 MA argon ion laser with a light intensity of 30 mW/0.785 cm^2. An average value of the rate of polymerization was established based on measurements repeated at least three times.

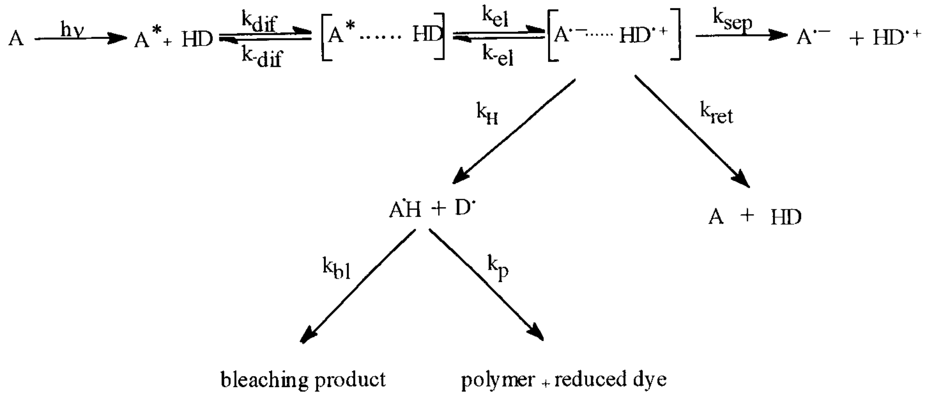
The light intensity was measured by a Coherent Model Fieldmaster power meter.

All calculations were made using Microsoft Excel 4 software. Grafts and calculations of fittings and calculations of statistic fitting parameters were performed using SideWrite Plus 2 software.

Results and Discussion

The process of free radical initiated polymerization via the intermolecular transfer process involves many steps including an electron transfer between an excited acceptor (A) and an electron donor (D) (aromatic amines) followed by a proton transfer from the electron donor

Scheme 1



radical cation to the dye radical anion,[28] which yields a neutral radical-initiating polymerization and the reduced radical of the dye. The radicals are formed from an electron donor and a dye. The cross-coupling between radical pairs of donor and acceptor terminates photoreaction.[29] The cross-coupling between radicals competes with free radical initiation of polymerization. Additionally, one should mention that if the reaction does take place within the solvent cage, the products that are formed may revert back to starting reactants or leave the solvent cage by ion dissociation.

Scheme 1 summarizes possible processes which may occur during the free radical photoinitiated polymerization via the photoinduced intermolecular electron transfer process (PET) in the presence of aromatic amines. In Scheme 1, k_{dif} is the rate constant representing the rate of diffusive encounters between reactants, which can dissociate apart with rate constant k_{-dif}, k_{el} is the first-order rate constant of electron transfer with the reverse step denoted by the rate constant k_{-el}, k_H is the rate constant of proton transfer between ion radicals, the cross-coupling step is designated by the rate constant k_{bl}, the polymerization step is denoted by k_p, and k_{ret} denotes the rates constants for the process of polymerization and electron return. The steady-state approximation applied to the donor neutral free radical [D•] gives the following expression:

$$\frac{d[D^\bullet]}{dt} = k_H[HD^{\bullet+}\cdots A^{\bullet-}] - k_{bl}[D^\bullet\cdots A^\bullet H] - k_t[D^\bullet M]^2 = 0 \quad (4)$$

where k_t is the constant rate of the macroradical termination process and [D•M] is the concentration of polymeric macroradical formed from an initiating radical D• and monomer. For [HD•+] in the steady-state approximation

$$\frac{d[HD^{\bullet+}]}{dt} = k_{obs} - k_{ret}[HD^{\bullet+}\cdots A^{\bullet-}] - k_H[HD^{\bullet+}\cdots A^{\bullet-}] = 0 \quad (5)$$

Thus we obtain

$$k_{obs} - k_{ret}[HD^{\bullet+}\cdots A^{\bullet-}] - k_t[D^\bullet M]^2 - k_{bl}[D^\bullet\cdots A^\bullet H] = 0 \quad (6)$$

where k_{obs} denotes the rate constant of the simplified photochemical process

$$A^* + DH \xrightarrow{k_{obs}} A^{\bullet-} + HD^{\bullet+}$$

According to Zakrzewski and Neckers,[28] the photochemical reduction of Rose Bengal ($\lambda_{irr} > 500$ nm) in the presence of tertiary amine does not yield the free radical coupling reaction (Rose Bengal bleaches; however, the bleaching product of this process is the dihydro dye (e.g., the electron transfer is followed by a proton transfer and then the radical anion formed abstracts hydrogen either from the electron donor or from the solvent). Therefore, for Rose Bengal derivatives in the presence of amines, $k_{bl}[D^\bullet][A^\bullet H] = 0$ and then

$$k_{obs} - k_{ret}[HD^{\bullet+}\cdots A^{\bullet-}] - k_t[D^\bullet M]^2 = 0 \quad (7)$$

However, according to Phillips and Read[30] in the photoreduction of an eosin analog by tribenzylamine, 52% yield of the dihydro derivative and 39% yield of the cross-coupling product were obtained. More recently, Neckers et al. observed that Rose Bengal derivatives in the presence of triphenyl *n*-butyl borate as well as 5,7-diiodo-3-butoxy-6-fluorone[31] in the presence of both triphenyl *n*-butyl borate and aromatic tertiary amine yield bleaching products that are the result of radical cross-coupling. Similar behavior is observed for pyrazolone azomethine dyes.[32] In the steady-state approximation [D•] = [D•M], one obtains for the rate of polymerization

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left[\frac{k_{obs} - k_{ret}[HD^{\bullet+}\cdots A^{\bullet-}] - k_{bl}[D^\bullet\cdots A^\bullet H]}{k_t}\right]^{1/2} \quad (8)$$

for the process with free radicals coupling as a competition channel for free radical initiated polymerization and

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left[\frac{k_{obs} - k_{ret}[HD^{\bullet+}\cdots A^{\bullet-}]}{k_t}\right]^{1/2} \quad (9)$$

for the process in the absence of the radical cross-coupling reaction.

It is not yet clear whether the rate of radical ion pair separation (k_{sep}) plays an important role as a path for free radical formation. However, one can suspect that the rate of radical ion pair separation for aromatic amines has a rather small effect on the final rate of polymerization. Jacques[33] et al. have shown that the quantum yield of radical ion pair separation for aromatic amines is about 1%, and therefore it is negligible in our consideration.

Equations 8 and 9 can be simplified with the reasonable assumption that $k_{ret}[A^{\bullet-}\cdots HD^{\bullet+}] \ll k_q[D] = k_{obs}$.[34]

Thus we obtain for the rate of polymerization

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left[\frac{k_{obs} - k_{bl}[D^{\bullet}\cdots A^{\bullet}H]}{k_t}\right]^{1/2} \tag{10}$$

for the process with free radicals cross-coupling and

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left(\frac{k_{obs}}{k_t}\right)^{1/2} \tag{11}$$

for the process not yielding products of the free radicals cross-coupling.

Dealing with slow electron transfer (ET) step, one should take into account the fact that back ET in the successor complex might compete with its reactions, described by one composite unimolecular rate constant k_3 ($k_3 = k_{ret} + k_H + k_{sep}$). The steady-state treatment of the concentrations of the precursor and successor complexes leads to the conclusion that k_{obs} should be related to the microscopic rate constants of Scheme 1 as in eq 12:

$$k_{obs} = \frac{k_{dif}}{1 + (k_{-dif}/k_{el})[1 + k_{-el}/k_3]} \tag{12}$$

and in the inverted form as

$$\frac{1}{k_{obs}} = \frac{1}{k_{dif}} + \frac{1}{K_d k_{el}} + \frac{1}{K_d k_{el}}\left(1 + \frac{k_{-el}}{k_3}\right) \tag{13}$$

There are several possibilities for simplifying eq 13:

(i) When k_{-el} becomes larger than k_3, the first terms of eq 13 become negligible. Thus we obtain

$$\frac{1}{k_{obs}} = \frac{1}{K_d K_{el} k_3}; \qquad k_{obs} = K_d K_{el} k_3 \tag{14}$$

where K_{el} is the equilibrium constant of the ET process. The relationship ln $k_{obs}/\Delta G°$ enters a linear region with a slope equal to $-1/RT$.

(ii) When $k_3 \gg k_{-el}$, k_{obs} becomes

$$\frac{1}{k_{obs}} = \frac{1}{k_{dif}} + \frac{1}{K_d k_{el}}; \qquad k_{obs} = \frac{k_{dif}}{1 + k_{dif}/(K_d k_{el})} \tag{15}$$

(iii) If $k_{el} \ll k_{-dif}$, the rate of processes described by k_3 becomes

$$\mathrm{k_{obs} = K_d k_{el}} \tag{16}$$

(iv) In the solid state or in very viscous media (diffusionless electron transfer), the following holds:

$$k_{obs} \cong K k_{el} \cong k_{el} \tag{17}$$

Entering eqs 14–17 into eq 11 gives the final equations describing the rate of initial polymerization for a wide range of photophysical, photochemical, and physicochemical conditions which may occur during photoinitiated polymerization via the intermolecular electron transfer process.

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left[\frac{K_d K_{el} k_3 - k_{bl}[D^{\bullet}\cdots A^{\bullet}H]}{k_t}\right]^{1/2} \tag{18a}$$

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left[\frac{\dfrac{k_{dif}}{1 + k_{dif}/(K_d k_{el})} - k_{bl}[D^{\bullet}\cdots A^{\bullet}H]}{k_t}\right]^{1/2} \tag{18b}$$

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left[\frac{K_d K_{el} - k_{bl}[D^{\bullet}\cdots A^{\bullet}H]}{k_t}\right]^{1/2} \tag{18c}$$

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left[\frac{k_{el} - k_{bl}[D^{\bullet}\cdots A^{\bullet}H]}{k_t}\right]^{1/2} \tag{18d}$$

All of the above presented equations contain a rate constant describing the rate of the electron transfer from the donor to the acceptor molecules.

Finally, one should express the rate of radical ion pair formation as a function of light intensity, e.g., to describe the step of radical ion pair formation starting from the acceptor molecule in its ground state

$$A \xrightarrow{h\nu} A^* + D \xrightarrow{k_{obs}} A^{\bullet-} + D^{\bullet+} \qquad k'_{obs} I_a[D] \tag{19}$$

For $[D] \gg I_a$, k_{obs} becomes practically a first-order rate constant and the rate of the process can be expressed in a simpler form as $k_{obs}I_a$. Considering this, the final expressions for the rate of photoinitiated polymerization can be formulated as follows:

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left[\frac{I_a K_d K_{el} k_3 - k_{bl}[D^{\bullet}\cdots A^{\bullet}H]}{k_t}\right] \tag{20a}$$

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left[\frac{\dfrac{I_a k_{dif}}{1 + k_{dif}/(K_d k_{el})} - k_{bl}[D^{\bullet}\cdots A^{\bullet}H]}{k_t}\right]^{1/2} \tag{20b}$$

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left[\frac{I_a K_d K_{el} - k_{bl}[D^{\bullet}\cdots A^{\bullet}H]}{k_t}\right]^{1/2} \tag{20c}$$

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left[\frac{I_a k_{el} - k_{bl}[D^{\bullet}\cdots A^{\bullet}H]}{k_t}\right]^{1/2} \tag{20d}$$

The final equations describing the rate of polymerization become more complex after introducing into eqs 20a–d the term describing the rate of the photoinduced intermolecular electron transfer. In the simplest form, k_{el} can be expressed as

$$k_{el} = \chi Z \exp(-\Delta G^{\#}/RT) \tag{21}$$

where Z is a universal frequency factor, ca. 6×10^{12} s^{-1} at 25 °C, χ is the transmission coefficient, and $\Delta G^{\#}$ is described by the Marcus equation (1).

Experimental verification of the above presented kinetic considerations requires a wide range of experiments. Therefore only some of the properties of equations 20a–d were tested using well-known, as described by Neckers, xanthene dyes as electron acceptors.[19,20,31,34,35]

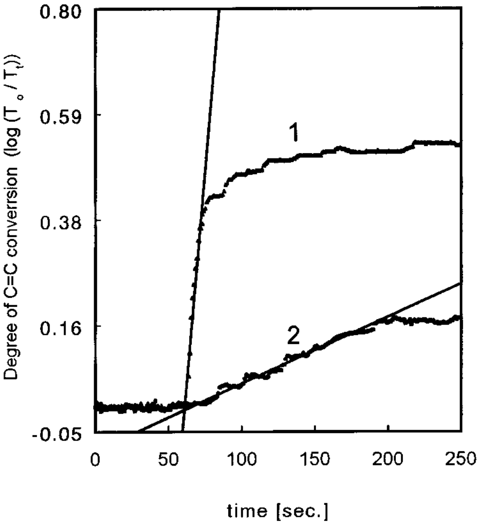


Figure 1. Polymerization of TMPTA−MP mixture initiated by (1) RBAX-*p*-CN-*N*-phenylglycine and (2) RBAX-*p*-OCH$_3$-*N*-phenylglycine. Experimental curves of monomer double-bond conversion as a function of irradiation time. The double-bond conversion was monitored at 810 cm^{-1} using RTIR spectroscopy, where T_0 is the transmitance of the monomer sample before polymerization and T_t is the transmitance of the monomer sample after time *t* of polymerization. The fitting parameters of the linear part of the kinetic curves are as follows: (1) slope = 0.034, R^2 = 0.98; (2) slope = 0.0013, R^2 = 0.98.

Variations of the driving force of the electron transfer process were introduced by using a series of tertiary aromatic amines (TAAs) or by using a series of *N*-phenylglycines (NPGs). The rate of polymerization was measured using two different techniques. The first technique is real-time IR spectroscopy. The characteristic curves of the rates of the laser-initiated polymerization monitored by RTIR are presented in Figure 1. The second method is based on is measurement of heat evolution during polymerization. Examples of the kinetic curves of photopolymerization recorded by this method are presented in Figure 2. In order to eliminate diffusion-controlled termination,[36,37] initial rates of polymerization were taken into account for further consideration. Figure 3 presents the Marcus plot for the polymerization rate (arbitrary units (au)) of TMPTA using RBAX−TAA initiating pairs. The rates of polymerization were measured using the RTIR method.

The Marcus plot for the RBAX−TAA initiating system was verified by using the second method for the rate of polymerization measurement, i.e., the thermal method. Results are shown in Figure 4. Similar kinetic behavior is observed for RBAX−NPG initiating pairs (Figure 5).

The experimental results presented in Figures 3−5 show that the intermolecular electron transfer process might be the limiting step in the photoinitiated polymerization. Data show that the rates of polymerization slow down when the thermodynamic driving force (−Δ*G*°) is increasing, namely demonstrates "inverted-region-like" kinetic behavior. The experimental results shown in Figures 3−5 can be fitted to the shape of a parabola or can be presented as a linear relationship (see Figure 7).

Neckers and Scaiano[34] established that the rates of Rose bengal derivative triplet quenching by aromatic amines oscillate between 10^9−10^{10} M^{-1} s^{-1}, i.e., are close to the rate constant calculated for the diffusion-controlled reaction ($k_d \approx 1.2 \times 10^{10}$ M^{-1} s^{-1}). The above-mentioned observation allows us to conclude that for RBAX−TAA and RBAX−NPG initiating pairs, the rate of intermolecular electron transfer is not the limiting step for the entire process. Classical Rehm−Weller observation for the fluorescence quenching deals with experimental anomalies such as the apparent nonexistence of the inverted region, which is demonstrated by a plateau region. Assuming that the intermolecular electron transfer for the tested system is diffusion-controlled, i.e., is Δ*G*° independent, as an explanation of the existence of "inverted-region-like" behavior, one can assume the variation of the reactivity of free radicals formed as a result of processes presented in Scheme 1. Variation of the free radical reactivity can be explained as a substituent effect on the rate of the polymerization chain initiation. Mateo et al.[38] have shown that the relative reactivity of radicals derived from dimethylanilines increases as the Hammett parameter (σ_p) increases. The relationship between −Δ*G*° and the Hammett constant (σ_p) for the tested electron donors is presented in Figure 6. The results clearly

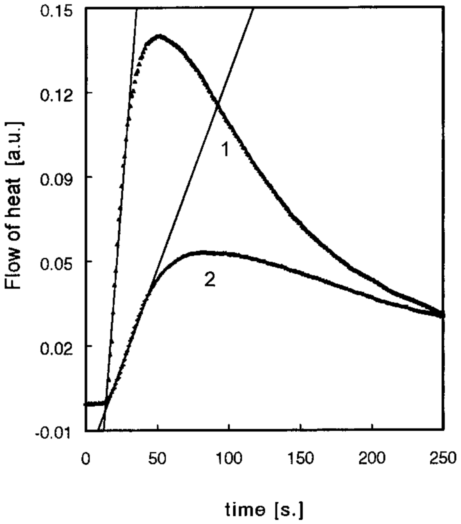


Figure 2. Rate of heat evolution (au) during the laser-initiated polymerization of a 9:1 TMPTA−MP mixture photosensitize by camphorquinone−*N*-phenylglycine derivatives: (1) *p*-CN-*N*-phenylglycine; (2) *p*-OCH$_3$-*N*-phenylglycine. The fitting parameters of the linear part of the kinetic curves are as follows: (1) slope = 0.006974, R^2 = 0.99; (2) slope = 0.001474, R^2 = 0.997. Under the experimental conditions (intensity of laser beam = 30 mW/0.785 cm^{-2}), a slope of 0.001 s^{-1} corresponds to a rate of polymerization of 0.998 μmol/s.

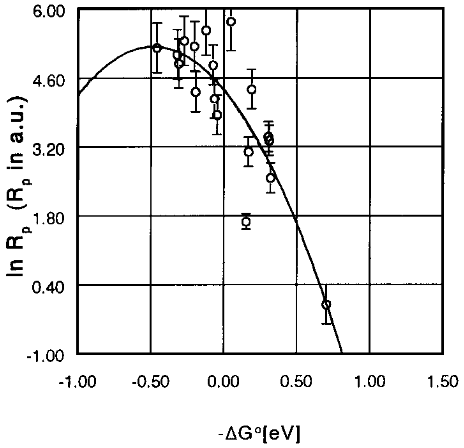


Figure 3. Marcus plot of rates of polymerization (au) of 9:1 TMPTA−MP mixture for RBAX−TAA initiating systems. Rates of polymerization were monitored using RTIR method. The parabolic fitting curve gives R^2 = 0.86. The linear fitting gives R^2 = 0.82.

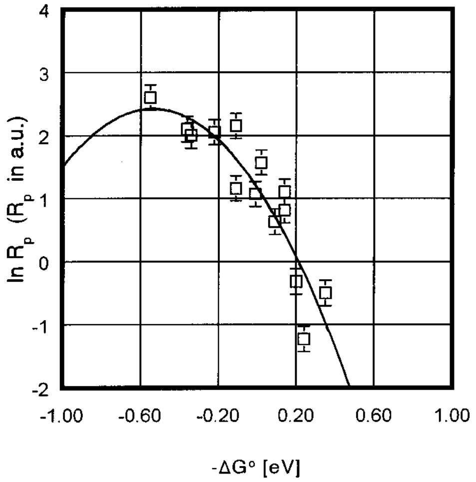


Figure 4. Marcus plot of rates of polymerization (au) of 9:1 TMPTA−MP mixture for RBAX−TAA initiating systems. Rates of polymerization were monitored using the measurements of heat evolution. The parabolic fitting curve gives R^2 = 0.91.

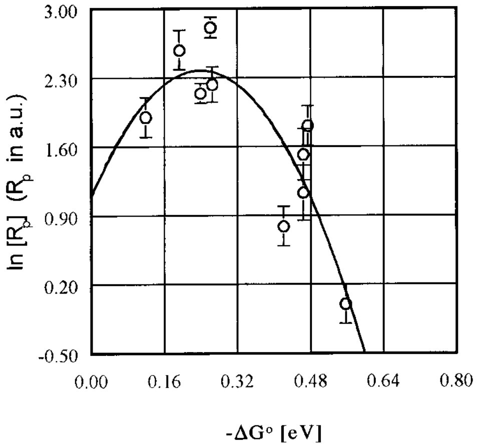


Figure 5. Marcus plot of rates of polymerization (au) of 9:1 TMPTA−MP mixture for RBAX−NPG (*N*-phenylglycine derivatives) initiating systems. Rates of polymerization were monitored using the measurements of heat evolution. The parabolic fitting curve gives R^2 = 0.87.

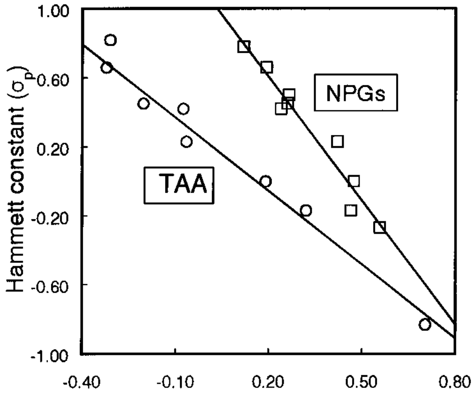


Figure 6. Relationship between the Hammett constant and the photoredox properties of the photoinitiating systems (RBAX−TAAs and RBAX−NPGs) described by the Rehm−Weller equation. The linear fitting gives for experimental points (A) R^2 = 0.97 and (B) R^2 = 0.99.

show a linear relationship. Assuming

$$R_p = \rho\sigma_p \tag{22}$$

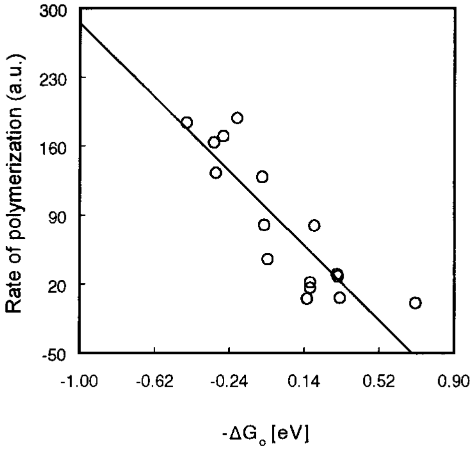


Figure 7. Relationship between the rate of polymerization of 9:1 TMPTA−MP mixture and the free energy of activation for photoredox reaction for RBAX−TAA initiating systems. The linear fitting gives for experimental points R^2 = 0.87.

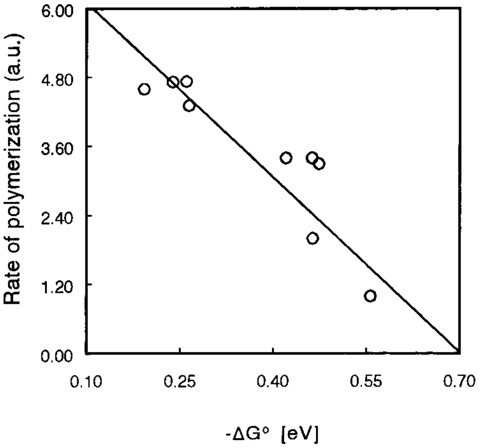


Figure 8. Relationship between the rate of polymerization and the free energy of activation for photoredox reaction for camphorquinone−NPG initiating systems. The linear fitting gives for experimental points R^2 = 0.95.

and

$$-\Delta G^\circ = \rho'\sigma_p \tag{23}$$

combination of eqs 22 and 23 gives

$$\mathrm{Rp} = \frac{\rho}{\rho'}(-\Delta G^\circ) \tag{24}$$

Figure 7 presents the relationship between the rate of polymerization observed and the free energy of activation for the redox reaction of the tested organic redox pairs. It is known that the substituent effect on the rate of reaction is a composite function of polar ($\rho\sigma$), resonance (R), and steric (E_s) effects. For the tested electron donors (flexible, rigid dialkylamino groups), the steric effect can not be neglected and might cause changes in the reaction rate. That is why the results shown in Figure 7 present a general linear relationship with data slightly dispersed. This behavior can be additionally supported by results obtained for camphorquinone−*N*-phenylglycines[39] tested as an initiating system for 3D and dental application (see Figure 8). Romani[40] et al. report that the quenching of the camphorquinone phosphorescence by spirooxazine dye, treated according to the Stern−Volmer equation, yielded $k_q = 2.2 \times 10^9$ M^{-1} s^{-1}, which corresponds to an almost diffusion-controlled process. Under this condition, the

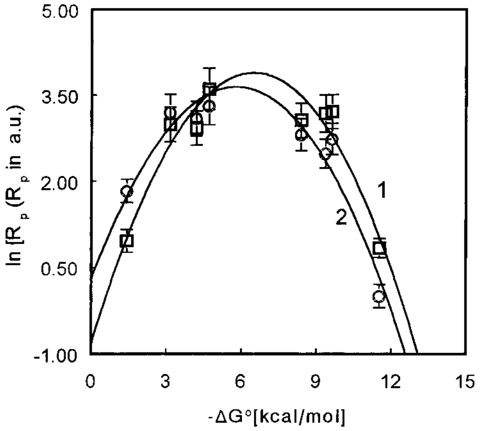


Figure 9. Marcus plots of the rates of polymerization (au) of (1) 10:4 TMPTA−MP and (2) 14:1:6 TMPTA−MP−THF for TIHF−NPG initiating systems. Rates of polymerization were monitored using the measurements of heat evolution. The curves fitted to the Marcus equation give for (1) $\lambda = -6.49$ kcal/mol, $R^2 = 0.91$ and (2) $\lambda = -5.78$ kcal/mol, $R^2 = 0.92$.

Table 2. Physicochemical Characteristic of Polymerized Mixtures

monomer solution	refractive index n	viscosity (cP)	dielectric constant (ϵ)
A	1.4740	16.798	13.102
B	1.4600	6.385	7.337

rate of polymerization is more likely described by eq 24 than by an equation involving the Marcus relationship.

More interesting is the behavior of a new group of xanthene dyes used for photoinitiation of free radical polymerization.[19] Laser flash photolysis studies performed for novel xanthene dyes[20,31] have shown that the rates of triplet state quenching of iodohydrofluoresceines by aromatic amines are on the order of 2.4×10^7 M^{-1} s^{-1} for tetraiodohydrofluorescein[20] (TIHF) (2,4,5,7-tetraiodo-3-hydroxy-6-fluorone) and 1.21×10^8 M^{-1} s^{-1} for 5,7-diiodo-3-butoxy-6-fluorone (DIBF).[31] Both rates of electron transfer are below the rate of diffusion-controlled reaction. Results for the rates of polymerization measurements for the TIHF−NPG system are presented in Figure 9. Here, important differences can be appreciated in the shape of the curves describing the relationship $R_p = f(-\Delta G°)$. The results clearly show that the change of the acceptor type (change in the rate of triplet quenching) causes significant changes in the kinetics of photoinitiated polymerization. The fitting obtained for the TIHF−NPG initiating system gives the shape of a full parabola, while for the RBAX−NPG system, one observes only a part of this curve. This deviation cannot be explained by the reactivity of the free radicals resulting from ET. Studying the electron photoreduction of DIBF, Neckers[31] has concluded that back electron transfer is a minor process in the DIBF−tertiary aromatic amine (*N*,*N*-dimethyl-2,6-diisopropylaniline) system. For the tested organic photoredox pairs, $k_{el} \ll k_{-dif}$, and the rate of polymerization is defined as

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left(\frac{I_a K_a}{k_t}\right)^{1/2} \times \left[\chi Z \exp\left[-\frac{\frac{\lambda}{4}\left(1 + \frac{\Delta G°}{\lambda}\right)^2}{RT}\right] - k_{bl}[D^\bullet \cdots A^\bullet H]\right]^{1/2} \quad (25)$$

The rate of free radical decay (k_{decay}) for radicals formed from the novel xanthene dye is on the order of 10^4 s^{-1}; i.e., the free radical coupling process is slow and the $k_{bl}[D^\bullet \cdots A^\bullet H]$ term in eq 25 can be neglected. Therefore, the final equation for the rate of polymerization can be given as

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left(\frac{I_a K_a}{k_t}\right)^{1/2} \times \left[\chi Z \exp\left[-\frac{\frac{\lambda}{4}\left(1 + \frac{\Delta G°}{\lambda}\right)^2}{RT}\right]\right]^{1/2} \quad (26)$$

Equation 26 can be also expressed in logarithmic form

$$\ln R_p = A - \frac{\frac{\lambda}{4}\left(1 + \frac{\Delta G°}{\lambda}\right)^2}{RT} \quad (27)$$

where A combines all constant data for the initial time of polymerization (k_p, k_t, [M], [HD], I_a = const). Equation 27 describes a parabola, which is consistent with the data presented in Figure 9. One more interesting feature of the light-induced polymerization via intermolecular electron transfer is illustrated in Figure 9. The Marcus equation contains the reorganization energy factor which comprises the energy changes that are necessary to reach a transition state by bond lengthening, compression, and/or torsion of reacting molecules λ_i and reorganization of the solvent molecules λ_s

$$\lambda_s = \frac{e^2}{2}\left(\frac{1}{r_a} + \frac{1}{r_d} - \frac{2}{r_{12}}\right)\left(\frac{1}{n^2} - \frac{1}{\epsilon}\right) \quad (28)$$

where r_a and r_d are the radii of the electron acceptor and donor, respectively, r_{12} is the distance between the electron donor and acceptor, n is the refractive index, and ϵ is the dielectric constant of solvent.

For the data presented in Figure 9, the λ_i factor remains the same for both curves. However, the λ_s varies since ϵ and n (refractive index) of the polymerizing mixture vary (Table 2).

Since electron transfer in photoinduced polymerization by TIHF−NPG redox pairs is not diffusion-controlled, the viscosity of the reacting medium does not affect the reaction rate. From the data in Table 2, one can calculate that the ratio of $\lambda_A/\lambda_B = 1.153$; i.e., λ_B is lower than λ_A. Simulation of the family of Marcus curves indicates that for selected photoredox reactions, the maximum of the parabola shifts to higher energies of $-\Delta G°$ when λ_s increases or shifts to the lower values of $-\Delta G°$ when λ_s decreases. This is clearly reflected in Figure 9 and strongly supports the proposed mechanism of photoinitiated polymerization via the intermolecular electron transfer process.

Verification of the inverted effect in polymerization may come from the direct measurements of the triplet state quenching of electron acceptors (TIHF or RBAX) by electron donors. Recently, Farrán and Deshayes[41] have shown that the variation in the energy transfer rate constant for triplet state occurring well below the diffusion-limited value can be explained by a Marcus dependence on the thermodynamic driving force that places the exothermic energy transfer in the inverted region. This indicates the necessity of direct measurements of the triplet state quenching of electron acceptors by a series of electron donors used for photoinitiation of polymerization via a PET process.

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