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Generalization of the Kinetic Scheme for a Dye-Photosensitized Free-Radical Polymerization Initiating System via an Intermolecular Electron-Transfer Process. Application of Marcus Theory

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ABSTRACT: We present a theoretical description of the kinetics for dye-initiated photopolymerization via an intermolecular electron-transfer process which considers the properties of the organic redox pair forming initiating radicals. An application of the Marcus theory yields a kinetic scheme, which considers both the thermodynamical and kinetic aspects of the electron-transfer process. The intermolecular electron transfer is the limiting step in the polymerization initiation. The theory is supported by experimental data. Two organic redox pairs forming free radicals have been tested, (1) a series of pyrazolone azomethine dyes (PAD) (electron acceptors) and *N*-phenylglycine (NPG) (electron donor) and (2) the Rose Bengal derivative (RBAX) (C2′ benzyl ester, sodium salt), serving as an electron acceptor and series of tertiary aromatic amine (TAA) electron donors. The following conclusions are reached: (i) The experimental data demonstrate the inverted region or inverted-region-like kinetic behavior; e.g., the rate of polymerization decreases with an increasing thermodynamic driving force ($-\Delta G°$) for electron transfer. This behavior allows the use of the Marcus theory for analyzing or predicting the ability of organic redox systems for light-induced free-radical polymerization. (ii) The dependence of the rate of polymerization on $\Delta G°$ suggests that the dark stability of the monomer-initiating system mixture may be due to the excited-state activation energy (E_{00}). (iii) Considering the reorganization energy factor λ (for the reacting molecules and the monomer), one may suspect that the molecular geometry and structure effect the photoinitiation efficiency.

Panchromatic sensitization of vinyl polymerization requires the presence of suitable dyes as primary absorbers of irradiation. The photophysical energy transfer between the initially populated dye excited state and other molecules, which would yield free-radical initiating species, is generally disfavored energetically. A nonclassical endothermic energy transfer process is required. The intermolecular electron-transfer process represents one such alternative. The traditional[1] kinetic scheme, used for the description of light-induced polymerization processes, is as follows:

$$\mathrm{A} \xrightarrow{h\nu} \mathrm{A}^* \qquad I_{\mathrm{a}} \text{ for singlet state or } \Phi_{\mathrm{T}} I_{\mathrm{a}} \text{ for triplet state} \tag{1}$$

$$\mathrm{A}^* + \mathrm{D} \rightarrow 2\mathrm{R}^\bullet \text{ or } \mathrm{R}^\bullet \tag{2}$$

$$\mathrm{R}^\bullet + \mathrm{M} \xrightarrow{k_p} \mathrm{RM}^\bullet \qquad k_p[\mathrm{R}^\bullet][\mathrm{M}] \tag{3}$$

$$\mathrm{RM}^\bullet + \mathrm{RM}^\bullet \xrightarrow{k_{\mathrm{t}}} \text{inert polymer} \qquad k_{\mathrm{i}}[\mathrm{RM}^\bullet]^2 \tag{4}$$

In the steady state:

$$\frac{\mathrm{d}[\mathrm{R}^\bullet]}{\mathrm{d}t} - \frac{\mathrm{d}[\mathrm{RM}^\bullet]}{\mathrm{d}t} = 0 \tag{5}$$

and

$$\frac{\mathrm{d}[\mathrm{R}^\bullet]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{RM}^\bullet]}{\mathrm{d}t} = k_{\mathrm{t}}[\mathrm{RM}^\bullet]^2 \tag{6}$$

$$[\mathrm{R}^\bullet] = \left(\frac{2I_{\mathrm{a}}}{k_t}\right)^{1/2} \quad \text{or} \quad [\mathrm{R}^\bullet] = \left(\frac{2I_{\mathrm{a}}\Phi_{\mathrm{T}}}{k_{\mathrm{t}}}\right)^{1/2} \tag{7}$$

where I_{a} is the intensity of light. The rate of polymerization is then

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_{\mathrm{p}}\left(\frac{2I_{\mathrm{a}}}{k_{\mathrm{t}}}\right)^{1/2}[\mathrm{M}] \quad \text{or} \quad -\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_{\mathrm{p}}\left(\frac{2I_{\mathrm{a}}\Phi T}{k_{\mathrm{t}}}\right)^{1/2}[\mathrm{M}] \tag{8}$$

The above kinetic scheme does not take into consideration the rate constant for intermolecular electron transfer (eq 2). The thermodynamical limitation, commonly used in the literature, comes only from the Rehm−Weller equation.[2]

$$0 > \Delta G = E_{\mathrm{ox}}(\mathrm{D/D}^{\bullet+}) - E_{\mathrm{red}}(\mathrm{A}^{\bullet-}/\mathrm{A}) - Ze^2/\epsilon a - E_{00} \tag{9}$$

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 excited-state activation energy, and $Ze^2/\epsilon a$ is the Coulombic energy which is considered negligible to the overall magnitude of the ΔG in the present systems.

The process of free-radical formation involves many steps including an electron transfer between an excited acceptor (A) and an electron donor (D). The common case of the electron-transfer process is a bimolecular reaction between A and D. The simplest kinetic scheme

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is the collide-and-react model.[3]

$$\mathrm{A}^* + \mathrm{D} \underset{k_{-\mathrm{d}}}{\overset{k_\mathrm{d}}{\rightleftharpoons}} [\mathrm{AD}]^* \xrightarrow{k_\mathrm{el}} \mathrm{A}^{\bullet-} + \mathrm{D}^{\bullet+} \qquad (10)$$

The steady-state approximation applied to (AD)* gives an expression for k_obs ($\mathrm{A}^* \xrightarrow{k_\mathrm{obs}} \mathrm{A}^{\bullet-} + \mathrm{D}^{\bullet+}$), the experimentally accessible rate.

$$k_\mathrm{obs} = \frac{k_\mathrm{d}}{1 + \dfrac{k_\mathrm{d}k_\mathrm{d}}{k_\mathrm{el}k_\mathrm{d}}} = \frac{k_\mathrm{d}}{1 + \dfrac{k_\mathrm{d}}{K_\mathrm{d}k_\mathrm{el}}} \qquad (11)$$

where K_d is the equilibrium constant for the formation of the precursor complex (AD)*. For an optional concentration of an electron donor, the second step of the kinetic scheme is

$$\mathrm{A}^* + \mathrm{D} \xrightarrow{k_\mathrm{obs}} \mathrm{A}^{\bullet-} + \mathrm{D}^{\bullet+} \qquad k_\mathrm{obs}I_\mathrm{a}[\mathrm{D}] \quad \text{or} \quad k_\mathrm{obs}I_\mathrm{a}\Phi_\mathrm{T}[\mathrm{D}] \qquad (12)$$

For $[\mathrm{D}] \gg I_\mathrm{a}$, k_obs becomes practically a first-order rate constant and the rate of process can be expressed in a simpler form as $k_\mathrm{obs}'I_\mathrm{a}$ for singlet excited-state process of $k_\mathrm{obs}'I_\mathrm{a}\Phi T$ for the process via a triplet excited state. In the steady-state approximation

$$[\mathrm{R}^\bullet] = \left(\frac{k_\mathrm{obs}'2I_\mathrm{a}}{k_\mathrm{t}}\right)^{1/2} \quad \text{or} \quad [\mathrm{R}^\bullet] = \left(\frac{k_\mathrm{obs}'2I_\mathrm{a}\Phi_\mathrm{T}}{k_\mathrm{t}}\right)^{1/2} \qquad (13)$$

and in the rate of polymerization

$$R_\mathrm{p} = -\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{M}]\left(\frac{2I_\mathrm{a}k_\mathrm{obs}'}{k_\mathrm{t}}\right)^{1/2} \quad \text{or}$$

$$R_\mathrm{p} = -\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{M}]\left(\frac{2I_\mathrm{a}\Phi_\mathrm{T}k_\mathrm{obs}'}{k_\mathrm{t}}\right)^{1/2} \qquad (14)$$

The limiting step, k_el, of the electron-transfer process can be expressed as:

$$k_\mathrm{el} = \chi Z \exp(-\Delta G^\ddagger/RT) \qquad (15)$$

where Z is a universal frequency factor, ca. 6×10^{12} s^{-1} at 25 °C, χ is the transmission coefficient, k_el is the rate constant, and $\Delta G^\ddagger$ is the free energy of activation given by the Marcus[4] equation for neutral reactants as:

$$\Delta G^\ddagger = \frac{\lambda}{4}\left(1 + \frac{\Delta G^\circ}{\lambda}\right)^2 \qquad (16)$$

where λ is a reorganization energy necessary to reach the transition state both of excited molecules and of solvent molecules, and ΔG^0 is expressed by the Rehm–Weller equation (9).

For the present systems k_obs becomes practically identical to k_el (if $k_\mathrm{el} \le 0.1k_\mathrm{d}$, k_obs becomes practically identical to k_el; from studies on Rose Bengal bleaching,[5] it is known that k_el is ca. 10^8 mol s^{-1}), and we can use the simplest version of the Marcus equation for k_obs.

$$k_\mathrm{el} = k_\mathrm{obs}' = 10^{11} \exp\left[-\left[\frac{\dfrac{\lambda}{4}\left(1 + \dfrac{\Delta G^\circ}{\lambda}\right)^2}{RT}\right]\right] \qquad (17)$$

Introducing k_obs' to the equation describing the rate of polymerization (eq 15), one obtains the equation for the rate of polymerization:

$$R_\mathrm{p} = -\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} =$$

$$k_\mathrm{p}[\mathrm{M}]\left[\frac{2I_\mathrm{a}}{k_\mathrm{t}}10^{11} \exp\left[-\left\{\frac{\left[\dfrac{\lambda}{4}\left(1 + \dfrac{\Delta G^\circ}{\lambda}\right)^2\right]}{RT}\right\}\right]\right]^{1/2} \qquad (18)$$

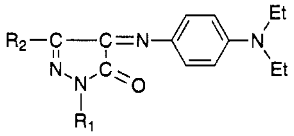
For the reaction in the triplet excited state, $2I_\mathrm{a}$ is replaced by $2I_\mathrm{a}\Phi T$. Considering that for the initial time of polymerization $[\mathrm{M}] \approx$ const, $[\mathrm{D}] =$ const, $k_\mathrm{p} =$ const, and $2I_\mathrm{a}/k_\mathrm{t}(2I_\mathrm{a}\Phi_\mathrm{T}/k_\mathrm{t}) =$ const, one obtains for monomolecular termination:

$$\ln R_\mathrm{p} = A - \frac{\lambda\left(1 + \dfrac{\Delta G^\circ}{\lambda}\right)^2}{4RT} \qquad (19)$$

where A is a constant. The value of A is dependent on k_p, I_a, k_t, [M], and [D]. (For a monomacroradical, bimolecular termination $\ln R_\mathrm{p} = A' - \lambda(1 + \Delta G^\circ/\lambda)^2/4RT$).

Equation 19 shows that if an intermolecular transfer process between the excited dye and an electron donor is a limiting step for photoinitiated polymerization, one should observe a parabolic relationship between the logarithm of the rate of polymerization and the thermodynamical parameter ΔG°. ΔG° is a measurable quantity and is accessible by experimental determination.

The Marcus theory approach for photoinduced polymerization has been tested using two different dye (acceptor)–electron donor pairs. The first pair is a series of pyrazolone azomethine dyes (PAD) as the electron-accepting molecule and *N*-phenylglycine (NPG) as the electron-donating molecule.[6] The second system contains only one dye, e.g., Rose Bengal,[7] and a series of tertiary aromatic amines (TAA). Table 1 presents spectroscopic and electrochemical characteristics of the pyrazolone azomethine dyes which were tested.



pyrazolone azomethine dyes, general structures (PAD)

The Rose Bengal derivative (RBAX) was prepared from Rose Bengal which was first decarboxylated[8] and then acetylated. Its reduction potential was assumed to be equal to the reduction potential of Rose Bengal, C2′ benzyl ester, sodium salt,[9] e.g., $E_\mathrm{red}(\mathrm{A}^{\bullet-}/\mathrm{A}) = -0.80$ V and its triplet $E_{00} = 1.7$ eV.[10]

As coinitiators (electron-donating molecules) the tertiary aromatic amines, presented in Table 2, have been used.

The rates of polymerization were tested using a dye–electron donor system as a photoinitiator and polyolacrylates as monomer. In order to eliminate diffusion-controlled termination (according to Anseth and Bowman,[11] the diffusion-controlled termination starts to dominate the rate of polymerization above 5% of conversion for multiacrylates and 40–50% for linear polymerization), the initial rates of polymerization were taken into account (see Figure 1).

Figure 2 presents the Marcus plot for polymerization rates (arbitrary units) of PTA (pentaerythrytol triacry-

Table 1. Characteristics of Tested Pyrazolone Azomethine Dyes

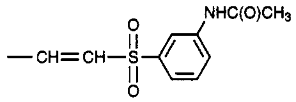
no.	R_1	R_2	λ_{max} (nm) I Abs.	II Abs.	ϵ_{λ_I}	$\epsilon_{\lambda_I}/\epsilon_{\lambda_{II}}$	R_p (au)	$E_{1/2}^{red}$ (V)
I	Ph	$-CH_3$	520	441	35 000	0.40	1.60	−0.70
II	Ph	$-NH_2$	503	424	39 000	0.241	1.00	−0.62
III	Ph	−NHPh	515	427	44 000	0.177	1.15	−0.53
IV	Ph	−NHC(O)Ph	527	436	46 000	0.156	2.35	−0.79
V	$2,4,6PhCl_3$	$-CH_3$	533	437	38 000	0.25	4.85	−1.07
VII	$2,4,6\text{-}PhCl_3$	−NHPh	520	420	48 500	0.130	3.85	−0.77
VI	$2,4,6\text{-}PhCl_3$	−NHC(O)Ph	534	434	50 500	0.121	4.20	−0.85
IX	$2,4,6PhCl_3$	−NHC(O)NHPh	537	426	55 000	0.109	3.10	−0.76
X		$-CH_3$	543	438	39 500	0.197	2.5	−0.65
XI	*p*-IPh	$-CH_3$	517	429	36 000	0.422	2.35	−0.63
XII	$2,4,6PhBr_3$	$-CH_3$	522		28 000		2.45	−0.72
XIII	Ph	$-C(O)OC_2H_5$	553	460	39 000		4.50	−0.88

Table 2. Electron-Donating Molecules Used as Coinitiators for RBAX−TAA Initiating Pairs and Their Oxidation Potentials

electron-donating compd	E_{ox}	electron-donating compd	E_{ox} (V)
N,N-dimethylaniline	0.71	*N,N*,3,5-tetramethylaniline	0.731
Jololidine	0.59	butyl 4-(*N*-piperidino)benzoate	0.854
ethyl 4-(dimethylamino)benzoate	1.103	butyl 4-(*N*-morpholino)benzoate	1.173
1-phenylpiperidine	1.095	4-nitro-*N,N*-dimethylaniline	1.353
4-(dimethylamino)benzophenone	0.975	*N*-methylindoline	0.61
N-phenylmorpholine	0.947	4-(*N,N*-dimethyl)toluidine	0.58
4-bromo-*N,N*-dimethylaniline	0.965	4-(dimethylamino)benzonitrile	1.222
N,N,N′,N′-tetramet6hyl-*p*-phenylenediamine, monoperchlorate	1.21	1-methyl-4-(4-nitrophenyl)piperazine	0.590
N,N,N′,N′-tetramethyl-*p*-phenylenediamine	0.196	diethyl 4-(*N,N*-dimethylamino)benzalmalonate	0.975
trans-4-(dimethylamino)cinnamonitrile	0.747	ethyl 4-(*N,N*-dimethylamino)cinnamate	0.84

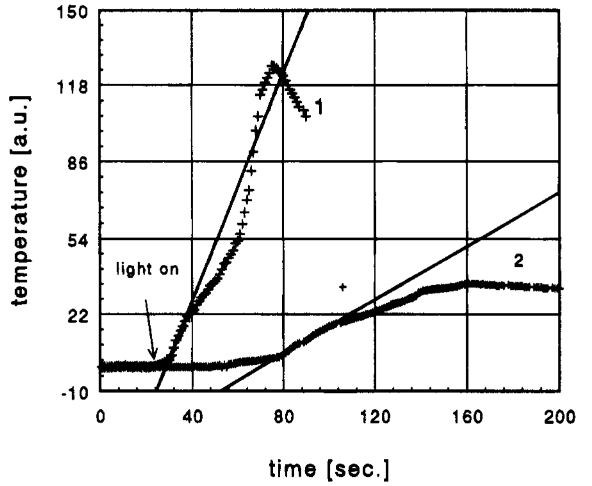


Figure 1. Rate of heat evolution during the laser-initiated polymerization of TMPTA–MP (9:1) mixture photosensitized by (1) a 4-(dimethylamino)benzophenone (0.1 M)–RBAX system and (2) a *N,N*,3,5-tetramethylaniline (0.1 M)–RBAX system.

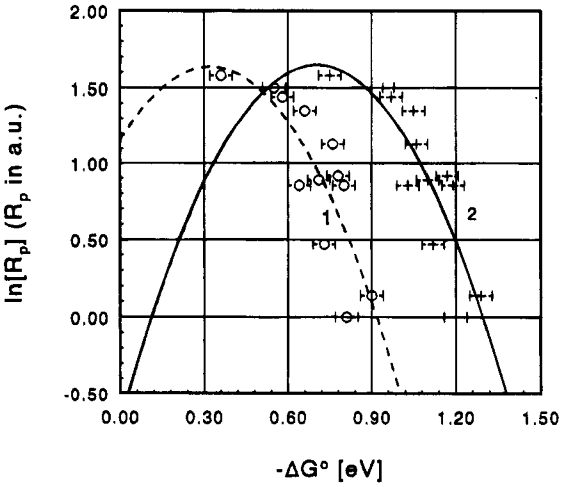


Figure 2. Marcus plot of the rates of polymerization of TMPTA (au) for a PADs–nPG initiating system (the reorganization factor λ is not taken into consideration). The value of triplet E_{00} = 43 kcal/mol, (1.87 eV) from: Herstroeter, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 3090. Since PADs do not fluoresce, for calculation of E_{00} for a possible process via the singlet excited state, the positions of absorption λ_{max} are assumed to be the E_{00}'s. For *N*-phenylglycine, measured by cyclic voltammetry E_{ox} = 0.43 V.

late) using PAD–NPG initiating redox pairs, as a function of $\Delta G°$.

A similar plot for RBAX–TAA initiating pairs is shown in Figure 3.

The experimental results presented in Figures 2 and 3 can be fitted to the shape of a parabola. The results show that the limiting step in the photoinitiated polymerization by the intermolecular electron-transfer mechanism is the process related to the intermolecular electron transfer (under conditions eliminating the diffusion effect of an electron donor, e.g., high concentration of an electron donor).

Figures 2 and 3 show two different kinds of behaviors. For the polymerization initiated by the PADs–NPG system, one sees a maximum of the curve at a positive $-\Delta G°$, and the observed process demonstrates inverted region kinetic behavior. Since the mechanism of electron-transfer photosensitization for PADs is not clarified yet, the maximum for the curve can be expected at about $-\Delta G°$ = 0.35 eV for a process via triplet state or about $-\Delta G°$ = 0.75 eV for singlet state sensitization. On the other hand, for the polymerization initiated by RBAX–TAAs, the maximum occurs at a negative $-\Delta G°$. This is impossible considering the classical Marcus theory.

Photoinitiated polymerization was performed in weakly polar monomer. The radical-ion pairs are short-lived, and if separation did not occur, chemical reaction would

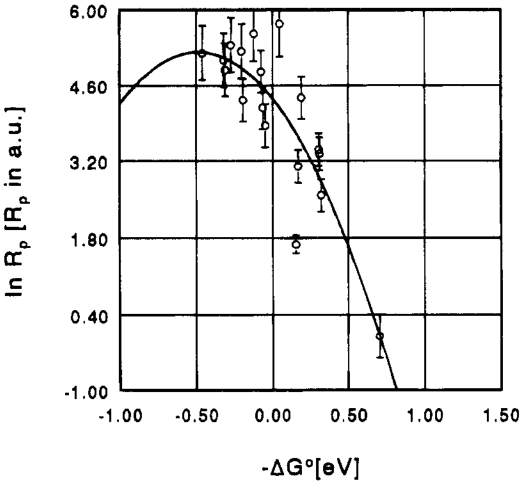


Figure 3. Marcus plot of the rates of polymerization of TMPTA (au) for a RBAX–TAAs initiating system (the reorganization factor λ is not taken into consideration).

have to be very rapid in order to compete with recombination. Therefore, the quantum yields for product formation in many photoinduced electron-transfer reactions (among others, polymerization) are equivalent to the efficiency with which separated radical ions are formed. For sensitized electron transfer between neutral acceptors and donors, the quantum yield for formation of separated ions Φ_{sep} is determined by the competition between return electron transfer, k_{-et}, and separation of the radical-ion pairs, k_{sep},

$$\Phi_{sep} = \frac{k_{sep}}{k_{-et} + k_{sep}} \tag{20}$$

Analysis of the data presented in recent papers[12–14] indicates that k_{-et} increases from $-\Delta G^\circ < 0$ up to the maximum whose position depends on the type of solvent. Therefore, if Φ_{sep} determines the rate of polymerization, one should observe the maximum of the polymerization rate at the minimum of k_{-et}, e.g., for the low (even negative) values of $-\Delta G^\circ$. For these reasons the relationship $\ln R_p = f(-\Delta G^\circ)$ presents the Marcus "*inverted-region-like*" kinetic behaviors.

Considering these, one can conclude that, for initiation via an intermolecular electron-transfer process, the rate of polymerization can be described by the generalized equation (19). To our knowledge there are no published reports describing the general kinetic scheme for dye-initiated polymerization via an intermolecular electron-transfer process which considers both kinetic and thermodynamical aspects of the process.

Marcus' theory of electron transfer leads to the familiar prediction that the rate of electron transfer should ultimately decrease with an increase in the thermodynamic driving force ($-\Delta G^\circ$). This prediction of "inverted" rate behavior remained controversial and unsupported for a number of years. Presented in Figures 2 and 3 are results of the experimental demonstrations of the inverted region (or inverted-region-like) kinetic behaviors. Recent studies have confirmed Marcus prediction for a range of organic,[13] organometallic,[14] and interfacial[15] redox processes. However, to the best of our knowledge, this phenomenon has never been demonstrated for the light-induced polymeriation.

Several important conclusions follow from eq 19.

(i) Marcus theory can help to predict the free-radical polymeriation photoinitiation ability of organic redox systems.

(ii) By direct dependence between the rate of polymerization and ΔG°, one can understand the dark instability of the monomer-initiating system mixture. (Dark reactions between the activator and the dye often take place. A moderately basic electron donor can deprotonate or protonate the dye, changing its spectroscopic properties and causing polymerization.[16] Consequently, often dye-sensitized systems do not meet storage stability requirements.) The dark stability of the composition, according to eq 9 and 19, may be due to the E_{00} value. Dyes absorbing at longer wavelengths give less stable mixtures in the dark.

(iii) The regoranization energy factor is comprised of energy changes that are necessary to reach the transition state by bond lengthening, compression, and/or torsion of reacting molecules λ_i and reorganization of solvent molecules λ_s.

$$\lambda_s = \frac{e^2}{2}\left(\frac{1}{r_a} + \frac{1}{r_d} - \frac{2}{r_{12}}\right)\left(\frac{1}{n^2} - \frac{1}{\epsilon}\right) \tag{21}$$

Here, 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 the solvent. Considering the reorganization energy factor λ (often used as an adjustable parameter), it is easy to understand the role of the molecular geometry and structure as well as the type of solvent on photoinitiation efficiency. The reorganization energy factor contribution may reach tens kilocalories per mole. The λ effect on the photoinitiation efficiency of organic redox pairs explains the unusual difference between the efficiency of the photoinitiation observed for Rose Bengal derivatives[7] and that of fluorone derivatives studied by Neckers.[17]

Experimental Section

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

All PAD dyes were characterized earlier.[6] Their reduction potentials were measured using a mercury dropping electrode (MDE) in dry acetonitrile (Aldrich) using as the supporting electrolyte 0.1 M tetrabutylammonium perchlorate (TBAP) and SCE as a reference electrode.

The oxidation potentials for the electron donors were measured using a cyclic voltammetry. For measurements an Electroanalytical Cypress System Model CS-1090 has been used. The measurements were made using dry acetonitrile (Aldrich); an Ag–AgCl electrode served as a reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP). The measured potentials for oxidation were compared to the values obtained by Seo and Nelson.[18]

The kinetics of polymerization were studied using a polymerization solution composed of 1 mL of MP and 9 mL of triacrylate. Dye concentration was 5×10^{-4} M, and the electron donor concentration was 0.1 M. Measurements were performed using a thick layer technique which permitted measurement of the rate of heat evolution in a sample 2–3 mm thick. A semiconducting diode (1 mm diameter) was used as a detector.

Irradiation of the polymerization mixture for PAD–NPG mixtures was carried out using the entire visible emission from a xenon lamp (Philips CSX 150 W/1 with intensity of light $I = 5.17 \times 10^{-8}$ einsteins cm^{-2} s^{-1}. The visible light intensity was measured using Reinecke's salt as an actinometer. For polymerization initiated by RBAX–TAA systems, as a light source an Omnichrome argon ion laser Model 543-500 MA was used with intensity of light $I = 63.7$ mW cm^{-2} measured by a Coherent power meter Model Fieldmaster.

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