

Asymmetric Cyanine Dyes as Fluorescence Probes and Visible-Light Photoinitiators of Free-Radical Polymerization Processes

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ABSTRACT: This article introduces asymmetric cyanine dyes employed as visible-light photoinitiators of vinyl monomer polymerization and as fluorescence probes monitoring the progress of polymerization. A degree of polymer cure from the measurement of the changes in the probe emission intensity and position shifts during the thermally initiated polymerization of monoacrylate was obtained. A distinct increase in the intensity of the probe fluorescence was observed during polymerization when the degree of monomer conversion was gradually increasing. This effect was accompanied by a blue-shift of the probe emission maxima. The second part of this work is focused on the possibility of an application of the tested dyes, in combina-

tion with borate anions, as photoinitiating systems. The kinetics of polymerization of trimethylolpropane triacrylate, with cyanine borates as photoinitiators, was studied by a microcalorimetric method. Asymmetric cyanine borates were found to be effective photoinitiators, and both the initiator and coinitiator concentration as well as the light intensity strongly affected the progress of photopolymerization, leading, for example, to an increase in the polymerization rate. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 207–217, 2006

Key words: dyes/pigments; fluorescence; kinetics (polym.); photopolymerization

INTRODUCTION

Cyanine dyes have been known for a long time and have received considerable attention with respect to their commercial applications.

They are used as sensitizers for color photography,¹ as markers for flow cytometry,² for the study and detection of nucleic acids,³ as phototherapeutic agents,⁴ and so forth.

Asymmetric cyanine dyes usually consist of an electron-donating moiety and a heterocyclic or polyaromatic moiety that can function as an electron-deficient acceptor. Furthermore, the donor and acceptor can be in direct electronic conjugation via a mono- or polymethine π system, and the acceptor moiety itself can be charged or uncharged.⁵

The asymmetric cyanine dyes with electron-donor-acceptor moieties on opposite sides of the styryl bond are particularly attractive for their spectral sensitivity

toward the local host environment and can be used as probing fluorophores.

Fluorescent probes are perhaps the most popular and powerful tools that can be used to understand the physical and chemical processes that occur at the molecular level. It is possible because their fluorescence is sensitive to the mobility and/or (micro)viscosity of the molecular environment in which the probe molecules are located. This sensitivity can be achieved via a number of physical interactions: intramolecular reorientation, such as molecular rotors⁶ and intramolecular excimer formation,⁷ diffusion-controlled interactions, such as intermolecular excimer formation,⁸ and solvent dipole stabilization of the excited state of the probes (charge-transfer probes^{9,10}). The physical origin of the sensitivity to the molecular environment, for a given probe molecule, is not necessarily determined by only one of the aforementioned interactions.¹¹

It is also well known that asymmetric cyanine dyes are able to form salts with various organoborate anions.¹² Such a combination of cyanine cations with borate anions gives photoredox pairs that can be applied as initiators of vinyl monomer photopolymerization operating in the visible-light area.

Photopolymerization is based on the use of photoinitiator systems suitable for absorbing light radiation of the appropriate wavelength and producing primary radical species able to convert a monomer into a poly-

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mer. Such photoinitiators are sought mostly because visible light is cheap and safe and possesses higher penetration ability (in comparison with ultraviolet radiation) in the presence of ultraviolet-absorbing monomers, pigments, and other substances. Among the most studied photoinitiator systems are those in which radicals are formed by a bimolecular process consisting of a chromophore and an electron donor.¹³ For such a case, the polymerization chain reaction starts as a result of photoinduced intermolecular electron transfer (PET), which is a nonclassical, endothermic energy-transfer process.

Marcus^{14,15} provided a simple approach allowing the prediction of the kinetics of the electron-transfer process, using thermodynamic and spectroscopic parameters characterizing both an electron donor and an electron acceptor. On the basis of the thermodynamics of the electron exchange, it is possible quantitatively to predict a relationship between the rate of the free-radical formation and the free energy of activation for the electron-transfer process. Besides the thermodynamics of the electron-transfer process, one should take into account the fact that the photoinitiation ability of the photoredox pair depends on the nature of the reacting partners.¹⁶

In this report, it is demonstrated that asymmetric cyanine dyes can be used as fluorophores for monitoring the progress of methyl methacrylate (MMA) polymerization. The relationship between the change in the emission spectra of probe molecules and the degree of monomer conversion during thermally initiated polymerization is presented. Moreover, the photoinitiation activity of asymmetric cyanine borate salts is presented as well. The tested dyes are components of new electron-transfer photoinitiators that form free radicals in bimolecular processes and are composed of asymmetric cyanine dyes acting as a light absorber (electron acceptor) and a borate functioning as an electron donor.

EXPERIMENTAL

Methylmethacrylate (MMA), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA), tetramethylammonium *n*-butyltriphenylborate (B2), tetrabutylammonium perchlorate, 1-methyl-2-pyrrolidinone (MP), and all spectroscopic-grade solvents were purchased from Aldrich or Fluka (Poznań, Poland).

MMA, before use, was purified with conventional methodology.

Absorption spectra were recorded on a Varian Cary 3E spectrophotometer (Mulgrave, Victoria, Australia). Fluorescence measurements were performed on an Hitachi F-4500 spectrofluorimeter (Tokyo, Japan) with classical measurements for the monitoring of the degree of MMA polymerization. The fluorescence mea-

surements were performed at the ambient temperature.

The reduction potentials of the tested dyes (SH1–SH21) and the oxidation potentials of B2 were measured by cyclic voltammetry. An EA9C-4z electroanalytical system (MTM, Cracow, Poland) equipped with a small-volume cell was used for the measurements. A 1-mm platinum disc electrode served as a working electrode, a Pt wire constituted the counter electrode, and an Ag–AgCl electrode was used as the reference electrode. The supporting electrolyte was 0.1M tetrabutylammonium perchlorate in dry acetonitrile.¹⁷

The synthesis methodologies of the tested asymmetric cyanine dyes were previously reported.^{18,19} Their spectroscopic properties are under study and will be the subject of a further publication.²⁰

Monitoring the free-radical polymerization of monoacrylate

A deoxygenated MMA solution, containing α,α' -azobisisobutyronitrile (AIBN) as a thermal free-radical polymerization initiator (1%) and a tested probe at a concentration giving an intensity of the absorption at maximum of about 0.2, was placed in Pyrex test tubes. The polymerization was initiated at 50°C. The samples were periodically (20 or 30 min) removed from the water bath and cooled with ice to about 0°C to stop the polymerization and then were warmed to room temperature. The fluorescence of the solutions was measured after the subsequent time of polymerization, and the degrees of polymerization were estimated by a gravimetric method after the precipitation of the polymer in ethanol.^{21,22}

Monitoring of the kinetics of the free-radical polymerization of polyacrylate

This was based on the measurements of the rate of heat evolution during polymerization in a sample 2–3 mm thick.^{16,17,23–25} The 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 irradiation of the polymerization mixture was carried out with the emission of an Omnicrome model 543–500 MA argon-ion laser (Chino, CA), which emitted two visible-light wavelengths at 488 and 514 nm (for dyes SH1–SH11), and the emission (lines of equal intensity at 361 and 351 nm) of an Inova model 90-4 argon-ion laser (for dyes SH12–SH21) (Coherent Inc., Palo Alto, CA). The irradiation intensity was measured with a coherent power meter (543–500 mA) and was 64 mW/cm².

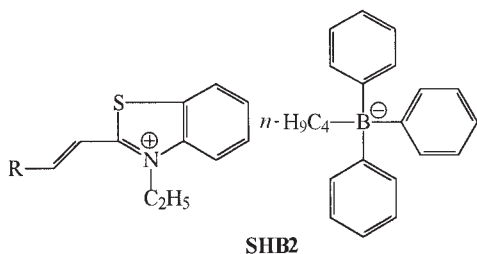
A polymerization solution was composed of 1 mL of MP and 9 mL of TMPTA. The initiator concentration varied in the range from 10⁻³ to 10⁻² M. As a refer-

ence sample, a polymerizing mixture containing a dye without an electron donor was used.

RESULTS AND DISCUSSION

The asymmetric cyanine dyes (SHX) were investigated as both fluorescent probes and visible-light initiators. Their chemical structures are given in Table I. They consist of two different character fragments conjugated by the vinyl group. They were prepared according to the procedure given by Hamer.¹⁸

The exchange of an anion type from iodide on borate was performed with the guidelines given by Schuster et al.¹⁹ This group of the dyes being transferred into an efficient free-radical polymerization initiating system (SHB2). The general structure of the tested asymmetric cyanine borates is shown below:



A high number of asymmetric cyanine salts, possessing substituents different in character in the phenyl ring, were studied to achieve a better understanding of their sensing and initiating properties.

Fluorescence monitoring of the thermally initiated polymerization of MMA

The first objective of this study was to investigate the fluorophore response to viscosity and polarity changes that occurred during the thermally initiated polymerization of MMA. All the probes under study were quite soluble both in the monomers and in the solid polymers. There was no indication that during the course of polymerization molecular aggregates were formed or precipitation of the probes occurred.

Figures 1 and 2 show the fluorescence spectra of the SH1 probe during the thermally initiated polymerization of MMA for different degrees of polymerization. The changes in the fluorescence intensity observed at the fluorescence maximum show its gradual increase below the gel point. A distinct increase in the intensity of the probe fluorescence was observed during MMA polymerization when a liquid polymer solution was transferred into the solid polymer matrix (above the gel point). The fluorescence intensity increase was accompanied by a blue-shift in the emission maxima (see Figs. 1 and 2). Our results are in a good agreement with Sczepan et al.'s²⁶ studies. These authors found

quantitatively similar behavior when the temperature of neat solutions of such types of dyes decreased.

The fluorescence intensity increases because of changes in the viscosity of the probe microenvironment that occur during the polymerization. This behavior can be attributed to the intramolecular charge-transfer excited-state relaxation to lower energy charge-transfer states obtained by rotation about the single and double bonds of the molecule.²⁷ In general, in such a case, the radiative deactivation constant is not affected, but a decrease in the nonradiative deactivation constant is related to an increase in the environment viscosity.²⁸

Figure 3 summarizes the changes in the fluorescence intensity observed for the SH15 probe during thermally initiated polymerization of MMA. Figure 3 shows an S shape of the curve versus the polymerization time. This is a common behavior and is observed in the polymerization that shows a distinct transition from a fluid to a rigid glass. To quantify the results presented in Figure 3, we have assumed that the probe emission intensity increases as the polymerization propagates. In other words, as the monomer consumption increases because of the polymerization, probe molecules are starting to be trapped in the rigid poly(methyl methacrylate) environment, and as a result, the emission intensity increases. Below the time needed for the onset of the gel effect, because the probe molecules are relatively free, they can easily relax to the ground state. This causes a low fluorescence intensity of the probe. However, above the time needed for the onset of the gel effect, because the reaction mixture is highly viscous, the relaxation processes become less effective, and the emission intensity can rise to a high values. In general, the specific behavior of the probes in the transition area of a fluid monomer to a rigid polymer can be explained by the dramatic increase in the viscosity, and this, in turn, rapidly reduces the efficiency of nonradiative deactivation of the emitting state.

Changes in probe emission intensities, measured at wavelengths specific for each of them, were also assumed as values characterizing the probe response to an increase in the degree of polymerization. The illustrative experimental results are shown in Figure 4. The relationship between the changes in the probe emission and changes in the degree of monomer conversion into the polymer was linear for low degrees of polymerization (see the inset in Fig. 4). At higher degrees of monomer conversion, a sudden increase in the fluorescence intensity occurred, which was attributed to the effect connected with conversion of the polymer solution into the rigid polymer matrix (Fig. 4). In principle, the probe intensity emission can be used to characterize the kinetics of polymerization, but only when a linear relationship between the increase in the fluorescence intensity and the amount of

TABLE I
Spectroscopic, Electrochemical, and Thermodynamic Properties of the Asymmetric Cyanine Borates Tested

No.	SHX structure	SHX $E_{\text{red}}(\text{V})^a$	SHB2 λ_{max}^A (nm) ^b	SHB2 $\lambda_{\text{max}}^{\text{F1}}$ (nm) ^b	SHB2 E_{∞}^S (eV)	SHB2 ΔG_{el} (eV) ^c	R_p ($\pm 10\%$) ^d	SHB2 $1 + \ln R_p$ (au)
SH1		-0.97	519	596	2.21	-0.09	0.0024 ^e	1.46 ^e
SH2		-1.01	527	601	2.17	-0.005	0.0022 ^e	1.39 ^e
SH3		-0.92	532	608	2.18	-0.10	0.0021 ^e	1.32 ^e
SH4		-0.90	529	618	2.13	-0.07	0.0020 ^e	1.28 ^e
SH5		-0.95	531	601	2.17	-0.07	0.0022 ^e	1.40 ^e
SH7		-1.07	525	602	2.21	0.02	0.0017 ^e	1.13 ^e
SH8		-1.08	520	607	2.16	0.09	0.0015 ^e	1.00 ^e
SH9		-0.92	538	616	2.14	-0.07	0.0019 ^e	1.22 ^e
SH10		-0.98	537	610	2.16	-0.02	0.0021 ^e	1.34 ^e
SH11		-0.84	558	620	2.11	0.10	0.0015 ^e	1.02 ^e
SH12		-0.99	376	479	2.85	-0.70	0.0025 ^f	1.00 ^f
SH13		-1.02	385	494	2.98	-0.80	0.0032 ^f	1.22 ^f

TABLE I Continued

No.	SHX structure	SHX $E_{\text{red}}(\text{V})^{\text{a}}$	SHB2 $\lambda_{\text{max}}^{\text{A}}$ (nm) ^b	SHB2 $\lambda_{\text{max}}^{\text{F1}}$ (nm) ^b	SHB2 E_{∞}^{S} (eV)	SHB2 ΔG_{el} (eV) ^c	R_p ($\pm 10\%$) ^d	SHB2 $1 + \ln R_p$ (au) ^f
SH14		-1.00	400	526	2.78	-0.62	0.0030 ^f	1.18 ^f
SH15		-1.11	408	516	2.74	-0.47	0.0027 ^f	1.07 ^f
SH16		-0.90	411	518	2.69	-0.64	0.0028 ^f	1.11 ^f
SH18		-0.93	361	477	2.96	-0.87	0.0044 ^f	1.55 ^f
SH19		-1.07	375	483	3.00	-0.77	0.0030 ^f	1.17 ^f
SH21		-0.97	381	481	2.89	-0.76	0.0036 ^f	1.34 ^f

^a Measured in acetonitrile.

^b Measured in ethyl acetate.

^c Calculated with the Rehm-Weller equation; $E_{\text{ox}}(\text{D}/\text{D}^+) = 1.160$ eV.

^d The relative rate of polymerization (assumed as the slope of the linear part of the kinetic curve).

^e Measured for a photoinitiator concentration of 10^{-3} M.

^f Measured for a photoinitiator concentration of 10^{-2} M.

the obtained polymer is observed. For the tested probes, this property was observed for the degree of monomer conversion below the gel point.

Kinetic study of multifunctional acrylate polymerization

Several photoredox pairs consisting of an asymmetric cyanine dye (acting as an electron acceptor) and *n*-butyltriphenylborate anion (acting as an electron donor) were tested as photoinitiating systems for the polymerization of the multiacrylate monomer. The kinetic curves obtained for the photoinitiated polymerization of a TMPTA-MP (9 : 1) mixture recorded for selected cyanine borate salts (SHB2), under irradiation with a visible light, are shown in Figure 5 for illustration. The relative rates of photoinitiated polymerization measured for all the tested photoredox pairs are collected in Table I.

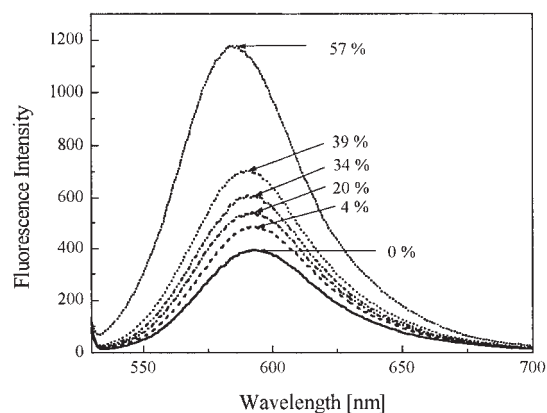


Figure 1 Changes in the fluorescence spectra of SH1 during the thermally initiated polymerization of MMA recorded for conversions below the transition point of the liquid sample into a rigid polymer matrix.

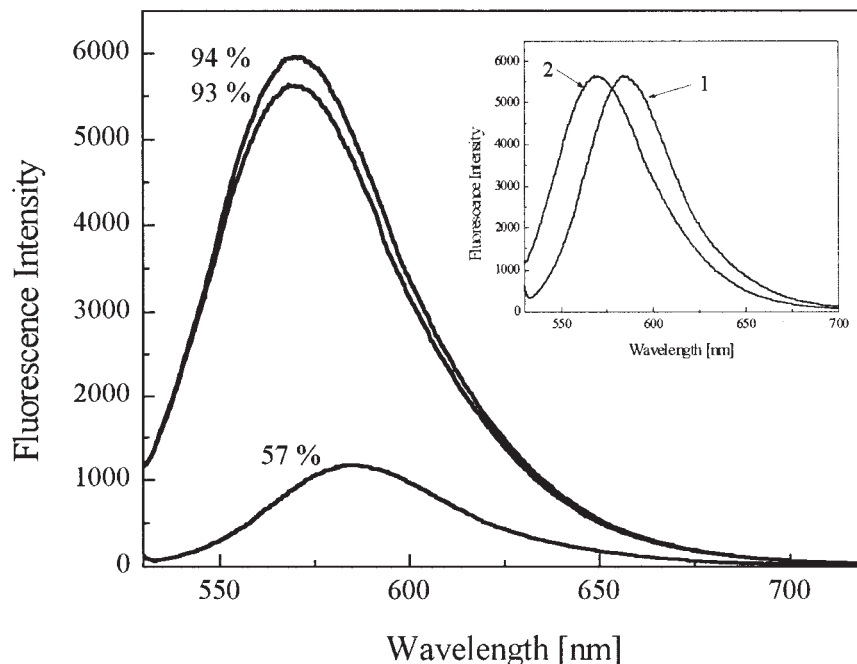


Figure 2 Changes in the fluorescence spectra of SH1 during the thermally initiated polymerization of MMA recorded above the point of transition of the liquid sample into a rigid polymer matrix. The inset shows normalized emission curves illustrating a blue-shift observed during the thermally initiated polymerization recorded at a high degree of monomer conversion; the degrees of polymerization were (1) 57 and (2) 94%.

It is apparent from an inspection of the initial rates of polymerization that the efficiency of the tested photoinitiators depended strongly on their structure. The highest rates of photoinitiated polymerization for the group of dyes possessing an electron-donating group in the phenyl ring were observed for SH1, SH2, SH5, and SH10. For most of these dyes (SH1, SH2, and SH5), the rotation about the bond linking the dialkylamino group and phenyl ring is possible; for dye SH10, it is largely restricted in motion because of a

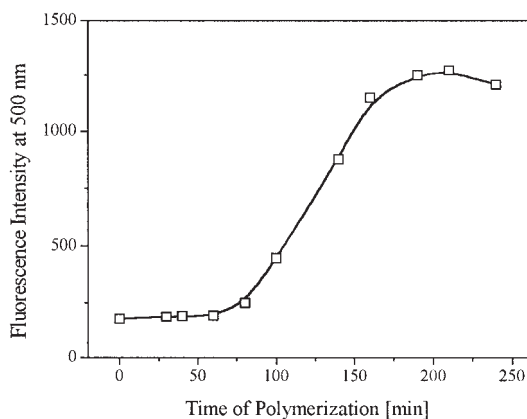


Figure 3 Changes in the fluorescence intensity (measured at $\lambda = 500$ nm) for the SH15 probe during the thermally initiated polymerization of MMA in the presence of AIBN (1%).

semibridged aniline bond. For the initiators possessing other than dialkylamino substituents in the para position, the best performance was observed for SH13, SH18, and SH21 photoredox pairs. Generally, the initiators with electron-donating groups different than dialkylamino groups and with electron-withdrawing groups had a somewhat higher rate of heat evolution (the slope of the linear part of the kinetic curve) in comparison with the photoredox pair with the dyes possessing dialkylamino electron-donating substituents. This conclusion was drawn from the results obtained for the experiments in which the entire light emitted by the argon-ion laser was absorbed by the dye. This in turn was controlled by the concentration of the photoinitiators (see the data in Table I).

Influence of the light intensity

Generally, the polymerization rate can be expressed by eq. (1):

$$R_p = -\frac{d[M]}{dt} = k_p \left(\frac{\phi_d I_a}{2k_t} \right)^{0.5} [M] \quad (1)$$

where k_p is the rate constant of the propagation step, k_t is the rate constant of the termination step, and ϕ_d is the quantum yield of free radical formation.

In this expression, the polymerization rate (R_p) depends on the square root of the absorbed light inten-

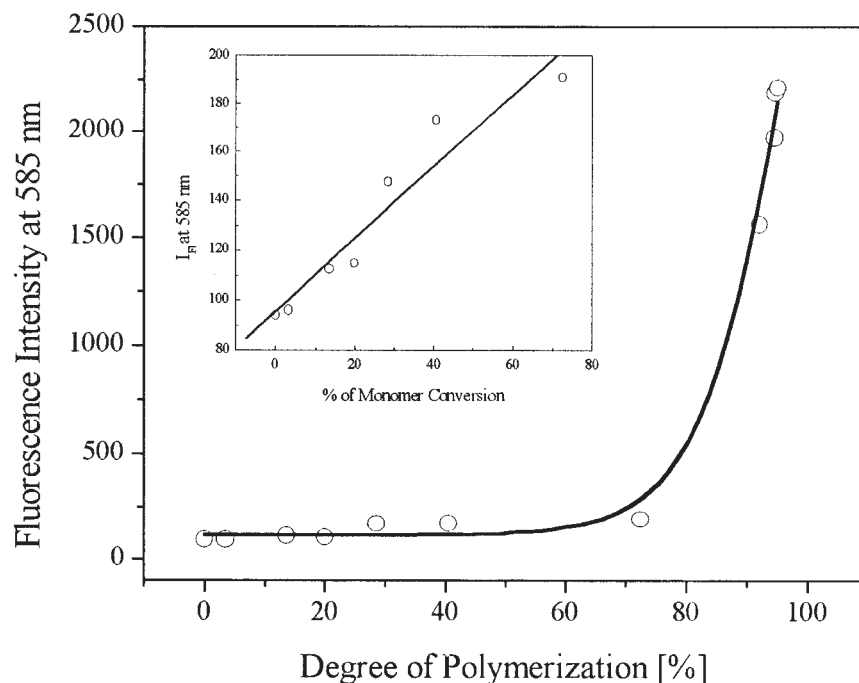


Figure 4 Relationship between the probe emission intensity (probe SH10, recorded at $\lambda = 585$ nm) versus the degree of monomer conversion into the polymer during the polymerization of MMA at 50°C . The inset shows linear relationships between the fluorescence intensity and degree of polymerization recorded at $\lambda = 585$ nm for SH10 probes, illustrating their sensitivity (I_{FI} = fluorescence intensity).

sity (I_a) and is directly proportional to the monomer concentration ($[M]$).

Figure 6 shows the effect of the light intensity on the rate of polymerization photoinitiated by asymmetric cyanine borate photoredox pairs. An increase in the light intensity leads to an increase in the polymerization rate. The observed trend is in good accordance with eq. (1). The slopes of the linear part of the curve

observed for the initial time of polymerization (assumed to be the polymerization rates) are, as shown in Figure 7, proportional to the square root of I_0 . This observation shows that the light intensity has no effect on the quantum yield of free-radical formation.¹³ Moreover, this suggests that the photoinitiated polymerization of the system proceeds by a conventional mechanism in which bimolecular termination occurs by a reaction between two macroradicals. This allows

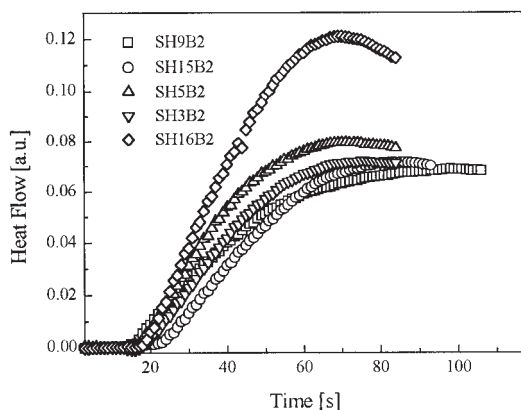


Figure 5 Family of kinetic curves recorded during the measurements of the flow of heat during the photoinitiated polymerization of a TMPTA/MP (9/1) mixture initiated by asymmetric cyanine borates. The dye concentration was 1×10^{-3} M, and I_a was 64 mW/cm^2 . The applied dyes possessed various chromophores and identical borate.

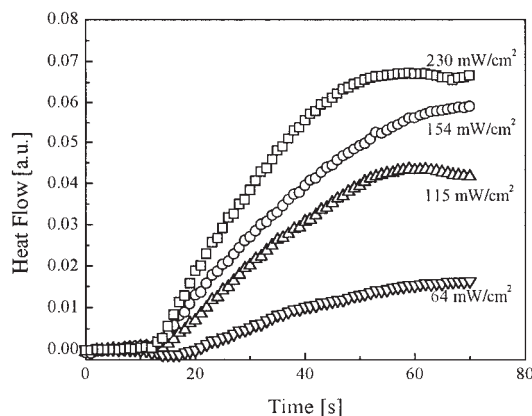


Figure 6 Family of kinetic curves recorded during the measurements of the flow of heat for the photoinitiated polymerization of a TMPTA/MP (9/1) mixture initiated by SH1B2, illustrating the effect of the light intensity on the polymerization rate.

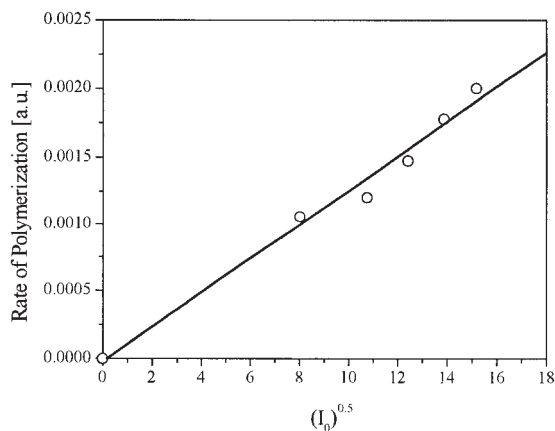


Figure 7 Rate of polymerization versus the light intensity for the asymmetric cyanine–borate system (SH1B2). The photoinitiator concentration was 1×10^{-3} M.

us to conclude that the free radicals formed from the cyanine ion after the PET process do not act as terminators of polymer chains.

Influence of the initiator concentration

The kinetic curves recorded for photoinitiated polymerizations at different initiator concentrations are presented in Figure 8. Data in Figure 8 show that the time needed to reach the curve maximum decreases when the initiator (SH1B2) concentration increases. The observed property is caused by two specific behaviors different in character. The first is related to the rate of heat evolution for the initial time of polymerization (the slope of the linear part of the kinetic curve), and the second is related to the time needed for the start of polymerization (the induction time). Under similar experimental conditions, at a low concentration of the initiator, the induction time is about 30 s,

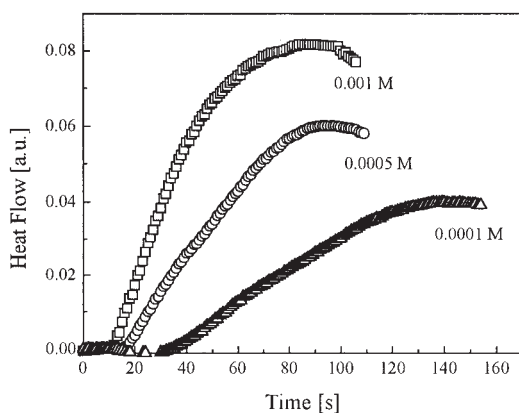


Figure 8 Family of kinetic curves recorded during the measurements of the flow of heat for the photoinitiated polymerization of a TMPTA/MP (9/1) mixture initiated by SH1B2 at different concentrations. I_a was 64 mW/cm^2 .

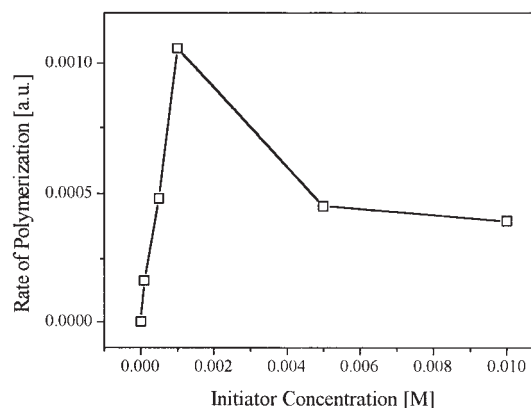


Figure 9 Rate of polymerization versus the photoinitiator (SH1B2) concentration.

whereas for a concentration of about 1 magnitude higher, the induction time decreases to 15 s (e.g., decreases ca. two times). Simultaneously, the slope of the linear part of the kinetic curves increases when the concentration of the initiator is increasing.

Figures 9 and 10 present the relationship between the initial rate of polymerization (the slope of the linear part of the kinetic curve) and the concentration of the photoinitiators (SH1B2 and SH14B2). As the photoinitiator concentration increases, the initial rate of polymerization increases and reaches a maximum followed by a continuous, mild decrease. For the tested photoinitiators with the alkylamino groups, the highest rates of polymerization for a 3-mm-thick sample (Fig. 9) were achieved at an initiator concentration of about 1×10^{-3} M. For the initiators possessing another substituent in the phenyl ring, the optimal initiator concentration was about 1×10^{-2} M (Fig. 10). The observed differences can be explained by the elec-

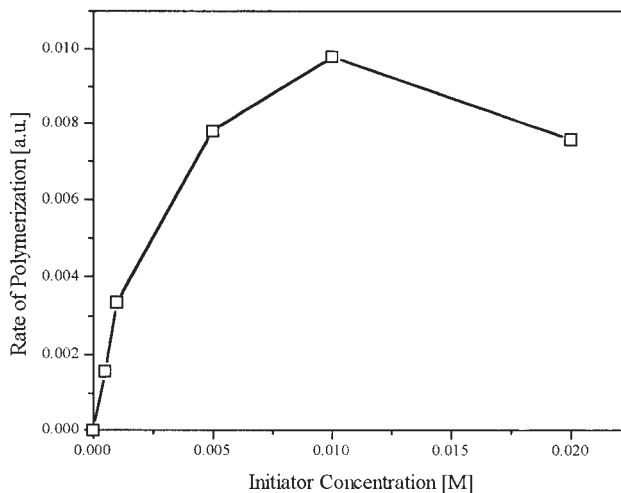


Figure 10 Rate of polymerization versus the photoinitiator (SH14B2) concentration.

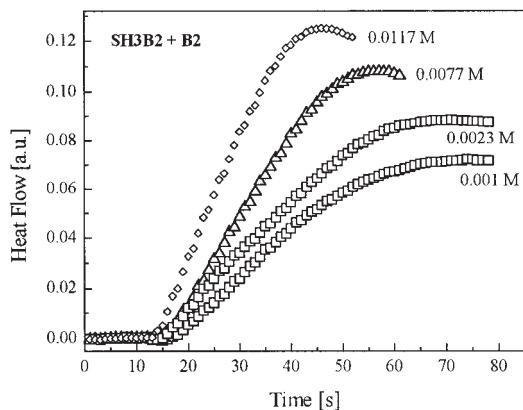


Figure 11 Family of kinetic curves recorded during the measurements of the flow of heat for the photoinitiated polymerization of a TMPTA/MP (9/1) mixture initiated by SH3B2 for various concentrations of the electron donor (B2).

tronic absorption spectroscopy properties of the studied dyes. The absorption maximum for dyes SH1–SH11 is located at about 500 nm, whereas for series SH12–SH21, the maximum of absorption appears at about 390 nm. Therefore, for SH12–SH21 dyes at a concentration of $1 \times 10^{-3} M$, only a small part of light emitted by an argon-ion laser is absorbed. The reduction of the photoinitiated polymerization rate at a high initiator concentration, for the applied technique of polymerization rate measurement, can easily be understood if we take the decrease in the penetration depth of the laser beam as a result of the so-called internal filter effect.²⁹

Influence of the coinitiator concentration

The kinetic curves, recorded for the polymerization initiated by photoredox pairs with different initiator/coinitiator concentration ratios under irradiation with visible light, are shown in Figure 11. The data in Figure 11 apparently show that the rate of photoinitiated polymerization by a dye–coinitiator pair strongly depends on the concentration of the coinitiator (Fig. 10). The insertion of an additional amount of the coinitiator (B2) to the dye leads to an enhancement of the polymerization rates for all the systems studied.

According to Chatterjee et al.'s³⁰ studies on symmetrical cyanine borate initiators, in nonpolar or medium-polarity solvents, one can treat asymmetric cyanine cation and borate anion as an ion pair. However, the study of the influence of the borate concentration on the rate of photoinitiated polymerization indicates, for an identical monomer–dye formulation, a distinct increase in the rate of polymerization as the concentration of borate anion increases. Figure 12 illustrates this relationship.

On the basis of this experiment, it appears that at the concentration of borate anion equal to the concentra-

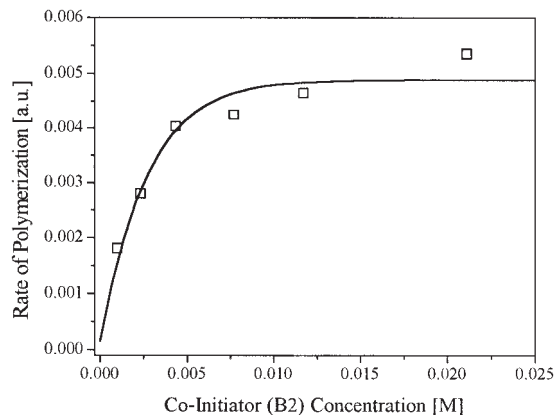


Figure 12 Dependence of the rate of photoinitiated polymerization on the concentration of the electron donor (B2). The initial dye (SH3B2)–borate concentration was $1 \times 10^{-3} M$.

tion of asymmetric cyanine cation, only a part of the photoredox pairs exists as the ion pair. Because the electron transfer for cyanine dyes occurs in their singlet state, the existence of cyanine cation and borate anion as an ion pair is the basic prerequisite for the effective electron transfer. From the dependence shown in Figure 13, it is clear that the additional amount of borate anion shifts the equilibrium between the free ions and ion pair to the higher concentration of the ion pair. This is the reason that the addition of the coinitiator causes an increase in the photoinitiation efficiency, which is enhanced by a more efficient electron-transfer reaction.

Influence of the thermodynamic parameter

A discussion of cyanine borate photochemistry should also include an estimation of the thermodynamic driv-

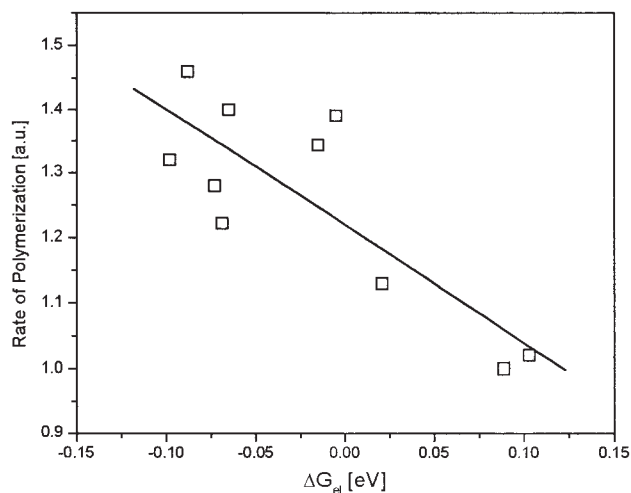


Figure 13 Relationship between the rate of polymerization (TMPTA/MP) and ΔG_{el} for asymmetric cyanine–borate photoredox pairs (for dyes SH1–SH11, initiator concentration = $1 \times 10^{-3} M$). The irradiation of the polymerization mixture was carried out with the visible emission of an argon laser with an irradiation intensity of 64 mW/cm^2 .

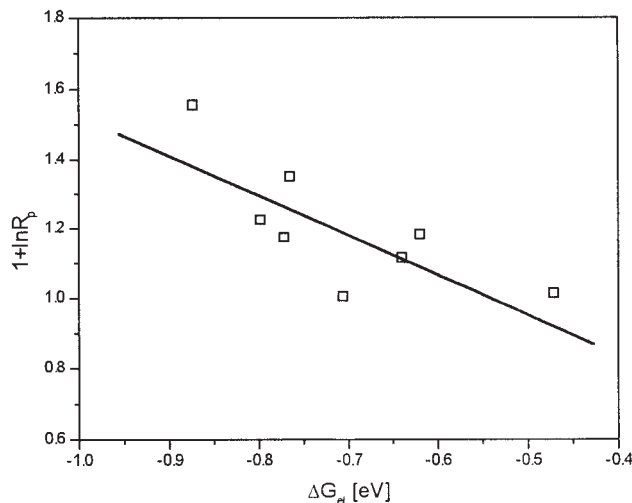


Figure 14 Relationship between the rate of polymerization (TMPTA/MP) and ΔG_{el} for asymmetric cyanine–borate photoredox pairs (for dyes SH12–SH21, initiator concentration = 1×10^{-2} M). The irradiation of the polymerization mixture was carried out with the visible emission of an argon laser with an irradiation intensity of 64 mW/cm^2 .

ing force of the PET process. It is well known that the main prerequisite for PET reactions is described by the Rehm–Weller equation,³¹ which states that the free energy of activation for the PET process (ΔG_{el}) should have a negative value:

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

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

The measured values of the aforementioned variables and the calculated values of the free energy change (ΔG_{el}) for the PET process are also summarized in Table I. The data indicate that for the series of asymmetric cyanine borates possessing *n*-butyltriphenylborate counterion, the free energy of activation for an electron-transfer reaction between cyanine cation and borate anion is characterized by a negative ΔG_{el} value (with the exception of dyes SH7, SH8, and SH11); that is, they fulfill the basic requirements for the effective PET process. The practical application of the theory of electron transfer^{14,15} in the polymerization photoinitiation process can be limited to certain conditions (identical free radical formed), assuming that the rules regulating the primary processes might also be applied for the secondary reactions. The results of such a treatment are presented in Figures 13 and 14. Because the initiator concentration was 1 order of magnitude higher for dyes SH12–SH21 in comparison with series SH1–SH11, the relationship between the rate of polymerization and the thermodynamic driving force of the PET process has to be presented separately for both groups of photoredox pairs.

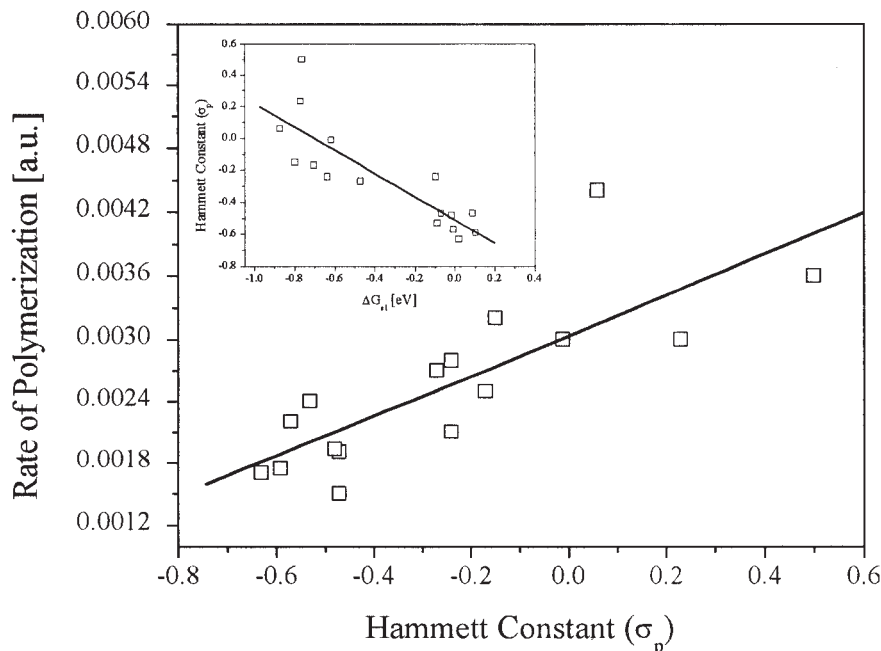


Figure 15 Relationship between the rate of polymerization (initiator concentration = 1×10^{-3} M for SH1–SH11 and 1×10^{-2} M for SH12–SH21) and the Hammett constant. The inset shows the relationship between the Hammett constant and, as described by the Rehm–Weller equation, the photoredox properties of the tested photoinitiating systems.

Figure 13 shows the relationship between the rate of polymerization and the thermodynamic driving force (ΔG_{el}) of the PET process obtained for the dyes with absorption maximum in the range of 500 nm, whereas Figure 14 shows the relationship for the dyes possessing the absorption maximum at about 390 nm. According to an inspection of the data presented in Figure 13, the rate of free-radical polymerization initiated by the groups of dyes SH1–SH11 increases as the driving force of the electron-transfer reaction increases. This behavior is predicted by the classical theory of the electron-transfer process.^{14,15} For the group of the SH12–SH21 dyes, when the initiator concentration is $1 \times 10^{-2} M$, the observed trend is similar to that shown by the SH1–SH11 dyes.

A word of caution is required for the presentation of the dependence between the rate of polymerization and the Hammett constant. The tested photoredox pairs show a linear correlation between ΔG_{el} and the Hammett constant (see Fig. 15). The photoinitiation ability of the entire group of dyes under study, at concentration from 10^{-3} to $10^{-2} M$, shows a linear relationship between the rate of polymerization and the Hammett constant. This is demonstrated in Figure 15.

Figure 15 shows that the initiators with other than alkylamino groups in the phenyl ring initiate free-radical polymerization with a rate lower than that of the photoredox pairs with electron-donating groups (see also the data in Table I). The photoinitiating ability increases as the electron-donating character of the substituents in the phenyl ring increases, even though the cyanine radical does not directly initiate the polymerization. The cyanine radical probably influences the processes that can occur after the PET process (e.g., the radical coupling reaction yielding an alkylated cyanine) or might undergo back-electron transfer to recover the cyanine cation and borate anion pair.²³

CONCLUSIONS

The studied asymmetric cyanine salts can be applied both as spectroscopic probes monitoring the degree of cure in their environment and as visible-light photoinitiators of free-radical polymerization.

The fluorescence intensity of the tested probes, though low in the liquid monomer, increases considerably when the monomer goes into a rigid polymer matrix. This effect is accompanied by a blue-shift in the emission maxima. This property makes asymmetric cyanine dyes promising fluorophores for the monitoring of the free-radical polymerization process.

The asymmetric cyanine dyes combined with borate salts can be used as visible-light photoinitiators. The initiation ability of the studied photoinitiating systems

increases when both the initiator and the coinitiator concentration as well the light intensity increase. The relationship between the rate of polymerization and ΔG_{el} displays normal Marcus kinetic behavior for both groups of dyes (e.g., for the dyes possessing alkylamino groups or other types of substituents in the phenyl ring).

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