Nr 5 (319—400) MAJ 2003 Tom XLVIII

POLIMERY

MIESIĘCZNIK POŚWIĘCONY CHEMII, TECHNOLOGII i PRZETWÓRSTWU POLIMERÓW

JANINA KABATC, JERZY PĄCZKOWSKI
University of Technology and Agriculture
Faculty of Chemical Technology and Engineering
ul. Seminaryjna 3, 85-326 Bydgoszcz, Poland
e-mail: paczek@atr.bydgoszcz.pl

What affects the rate of free radical polymerization of a multifunctional acrylate photoinitiated by cyanine borate salts?

Part I. KINETIC STUDIES

Summary — Cyanine dyes, widely used in color photography, can also be used as initiators of radical polymerization, initiated with visible light. The aim of this work was to check the possibility of application of borate salts of these dyes as photoinitiators of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate — TMPTA and to determine the effect of photoinitiator structure on the polymerization rate. 32 symmetric cyanine dyes — derivatives of benzothiazole and benzoxazole have been synthesized. Their structures were differentiated by changing of heteroatom (S or O), substituent in the phenyl ring as well as the type of substituents in polymethine chain. Spectroscopic investigations of dyes used as well as their borate salts showed the intensive absorption band localized for thiocarbocyanine dyes in the range 550—600 nm while for carbocyanine dyes — in the range 480—510 nm. Replacement of halogen atom or ethylsulfate anion in the cyanine dye molecule to the following anions: *n*-, *sec*- or *tert*-butyltriphenylborate and tetra-*n*-butylborate gave the borate salts of cyanine dyes. 150 various borate salts of cyanine dyes have been used as photoinitiators of TMPTA photopolymerization. It has been stated that the ability of initiation of TMPTA [as 10 vol.% solution in 1-methyl-2-pyrrolidinone (MP)] polymerization depends on the type of heteroatom in the dye molecule, the type of substituent in the phenyl ring, the type of substituent in *mezo* position in polymethine chain and on borate anion structure. It has been also found that monomer conversion and quantum yield of the process depend also on the chemical structure of photoinitiator.

Key words: cyanine dyes borate salts, chemical structure, triacrylate, radical photopolymerization, kinetics, activity of dye photoinitiators.

The light can be used as a source of energy for the formation of a free radical that can start to build a chain. Generally, the photoinitiators of this kind of free radical polymerization can be classified into three different groups:

— the dissociative photoinitiators, such as peroxides, benzoin or acetophenone derivatives [1, 2];

— the compounds which generate free radicals in the hydrogen atom transfer reaction [3, 4];

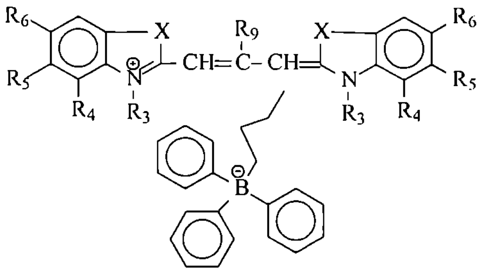
— the dyes [5] — in this case the radicals are formed in a nonclassical energy transfer process.

The panchromatic sensibilization of polymerization of vinyl monomers requires a suitable dye as a primary absorber of a radiation. The extcitation of the dye by the visible light and then the transfer of the sensitizator energy is not an efficient way of free radicals formation, because the excitation energy is not high enough for the dissociation of the majority of the chemical bonds [6]. However, a different mechanism is also possible, namely the photoinduced energy transfer process connected with an electron transfer.

In 1985 G. Schuster and co-workers noted that the laser irradiation of 1,4-dicyanonaphthalene solution containing an alkyltriphenyl borate leads to one electron oxidation of an alkyltriphenylborate salt [7, 8]. In the first step the electron transfer occurs and the 1,4-dicyanonaphthyl radical-anion and alkyltriphenylboranyl radical are formed. Next, the carbon-boron bond cleavages yielding an alkyl radical and triphenylboron. The free radical formed can be used for the initiation of the free radical polymerization in UV or visible light region. The first transfer to the dyeing system led to the preparation of cyanine borate salts. In such photoinitiator, organoborate ion possessing all aryl groups has been observed to be inefficient. The experimental results led to the general notion that aryl radicals are poor initiating species [9—11]. On the other hand the organoborate ion possessing at least one alkyl group directly bound to boron atom was found to be a very efficient part of photoinitiating ion pair. From the literature it is also known that the systems consisting of the tetraphenylborate ion and chromophores possessing covalently attached tetraalkylammonium cation effectively initiate the polymerization. However, their initiating activities are somewhat lower than those of corresponding triphenylbutylborate salts [11, 12]. The study on the ability of the photoinitiation of the free radical polymerization by cyanine borates salts is still continued [13, 14].

In this paper we present all the experimental results describing the application of the cyanine borate salts as the photoinitiators of free radical polymerization taking the triacrylate monomer as a model. We also consider the effect of the photoinitiating ion pair structure on the rate of photoinitiated free radical polymerization.

The general Formula (I) presents the salts tested in our laboratory.



(I)

or $(R_4)B^{\ominus}$

The goal of the research described in this paper was focused on the synthesis of the new dyeing photoinitiators and the study of the influence of their structure on their ability to photoinitiate of free radical polymerization. It was achieved by:

(*i*) the synthesis of the symmetrical cyanine dyes being the benzothiazole and benzoxazole derivatives,

(*ii*) the synthesis of the tetrasubstituted organoborate salts,

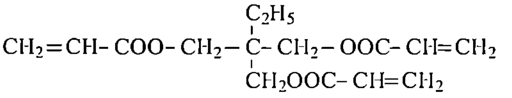
(*iii*) the study of the basic physical and chemical properties of synthesized photoinitiating pairs and the qualitative and quantitative analysis of the photochemical processes occurring during the photoinitiation process,

(*iv*) the study of the kinetics of the photoinitiated free radical polymerization.

EXPERIMENTAL — GENERAL INFORMATION

The substrates used for the synthesis of the dyes, monomers and solvents were purchased from Fluka, Merck and Aldrich. The cyanine dyes and cyanine borates were prepared in our laboratory. The purity of synthesized dyes was controlled by thin layer chromatography and their identities were checked by ^{1}H NMR, UV-VIS and IR spectroscopies.

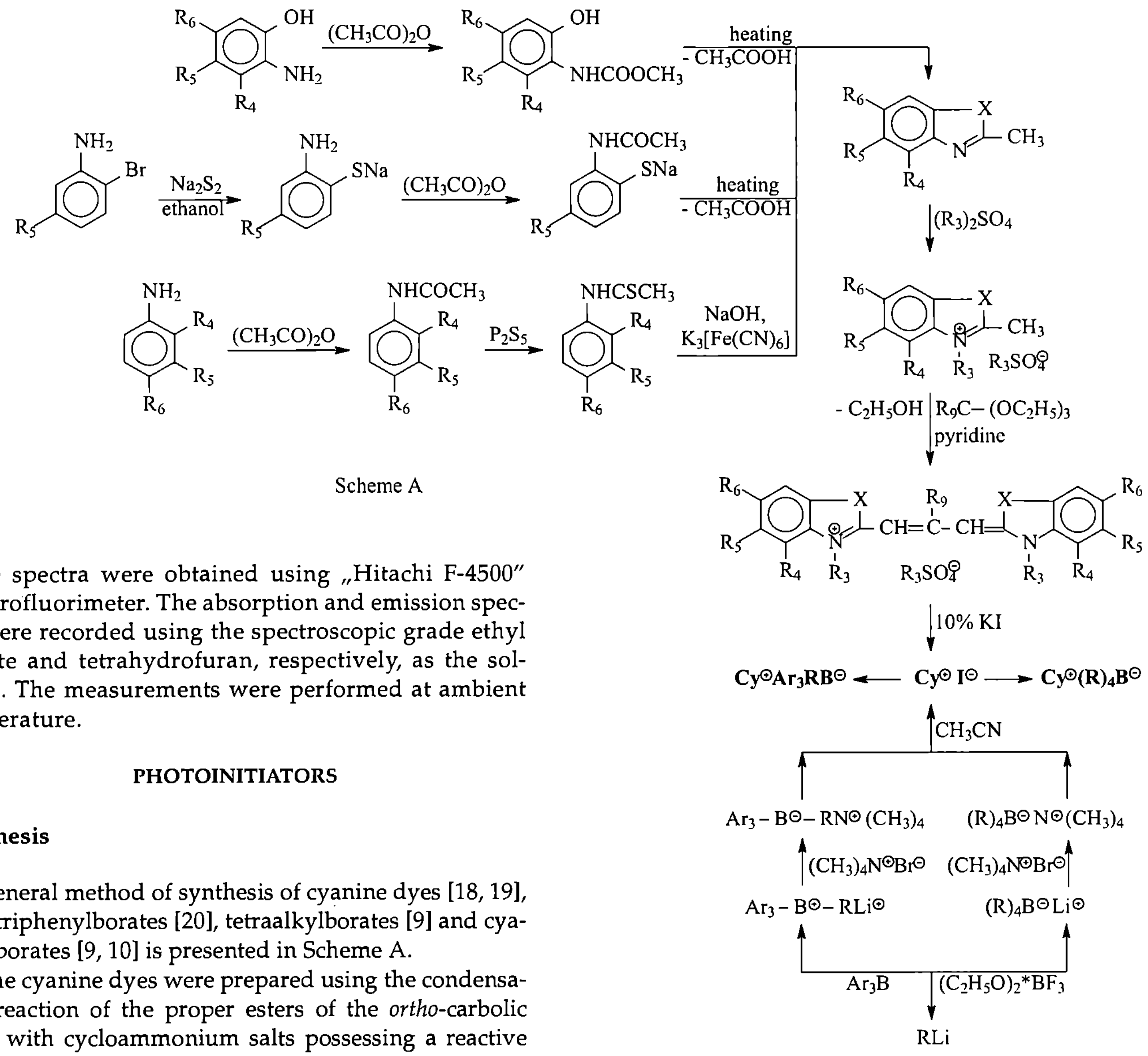
The kinetics of free radical polymerization was studied using a polymerization solution composed of 1 mL of 1-methyl-2-pyrrolidinone (MP) and 9 mL of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate [TMPTA — Formula (II)]. Cyanine borate concentration was $1 \cdot 10^{-3}$ M. As a reference sample a mixture containing



$$CH_2{=}CH{-}COO{-}CH_2{-}\overset{\displaystyle C_2H_5}{\underset{\displaystyle CH_2OOC{-}CH{=}CH_2}{C}}{-}CH_2{-}OOC{-}CH{=}CH_2 \qquad (II)$$

cyanine iodides or ethyl sulfates (dyes without an electron donor) was used. Methodology of measurements of the kinetics of free radical polymerization was described earlier [15—17]. Irradiation of the polymerization mixture was carried out using the emission of Omnichrome argon ion laser Model 543-500 MA with the intensity of light of 30 mW/0.78 cm^2.

The absorption spectra were recorded using „Varian Cary 3E" Spectrophotometer, and the fluores-



Scheme A

cence spectra were obtained using „Hitachi F-4500" Spectrofluorimeter. The absorption and emission spectra were recorded using the spectroscopic grade ethyl acetate and tetrahydrofuran, respectively, as the solvents. The measurements were performed at ambient temperature.

PHOTOINITIATORS

Synthesis

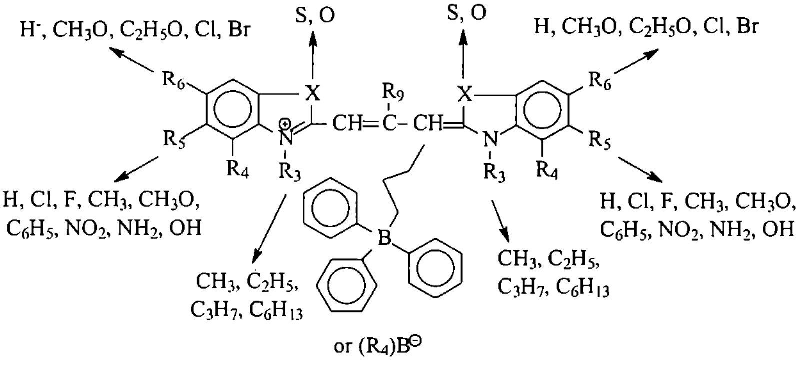
General method of synthesis of cyanine dyes [18, 19], alkyltriphenylborates [20], tetraalkylborates [9] and cyanine borates [9, 10] is presented in Scheme A.

The cyanine dyes were prepared using the condensation reaction of the proper esters of the *ortho*-carbolic acids with cycloammonium salts possessing a reactive methyl group [18, 21].

For the study the following borate anions were used as electron donors:

— *n*-butyltriphenylborate (B2),
— *sec*-butyltriphenylborate (B3), } Scheme A, Ar3RB⁻
— *tert*-butyltriphenylborate (B4),
— tetra-*n*-butylborate (B5). } Scheme A, (R)4B⁻

The lithium salts of an alkyltriphenylborate and tetraalkylborate were synthesized in a reaction of the butyl lithium with trialkylboron or triarylboron, respectively. The stable alkyltriphenylborates were prepared by the exchange of lithium cation to tetramethylammonium cation.



(III)

The exchange of a halogen or ethylsulfate anion in the dye molecule to borate anion yields cyanine borate salts.

32 Carbocyanine and thiacarbocyanine dyes were synthesized. Formula (III) shows their structures.

The structures of the dyes were modified by: (*i*) the change of a heteroatom X type (sulfur or oxygen); (*ii*) the change of a substituent type in the phenyl ring and (*iii*) the change of a substituent R_9 in the *meso* position of polymethine chain (H, CH_3, C_2H_5). The above mentioned modifications of the dye structure gave the possibility to change the spectroscopic properties of the compounds studied and allowed the examination of the rate of free radical polymerization as a function of free energy of activation of electron transfer reaction in the relatively wide range of its value without the change of the type of the initiating free alkyl radical.

The spectroscopic and photophysical properties of the cyanine borate salts

The tested thiacarbocyanine dyes show an intensive absorption band localized in the range of 550—600 nm. The second band is less intense and shifted to the blue region of the spectrum by about 60—70 nm. Oxacarbocyanines depict their absorption bands in the range between 480—510 nm. The position of the absorption maximum, as it is shown in Figure 1, does not depend on the type of a borate anion.

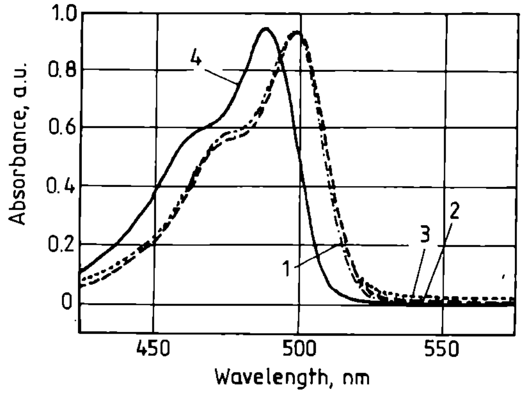


Fig. 1. Electronic absorption spectra of an example of cyanine dye recorded in EtAc: 1 — Cy25B2, 2 — Cy25B3, 3 — Cy25B4, 4 — Cy25 with different anions (for symbols see Table 1)

The main difference observed between cyanine and its *meso* analogue is reflected by the value of the molar absorption coefficient that for alkyl substituted *meso* dyes is approximately one order of magnitude lower than for the non-substituted derivatives. It is assumed that this phenomenon is caused by a destabilization of the all-*trans* isomer being a result of the introduction of an alkyl substituent into the *meso* position [21, 22].

The fluorescence spectra of the dyes tested are roughly a mirror image of the absorption spectrum. The typical room temperature absorption and emission spectra (for 3,3′-diethyl-5,5′-diphenyl-9-methylcarbocyanine) salts in ethyl acetate solution are shown in Figure 2.

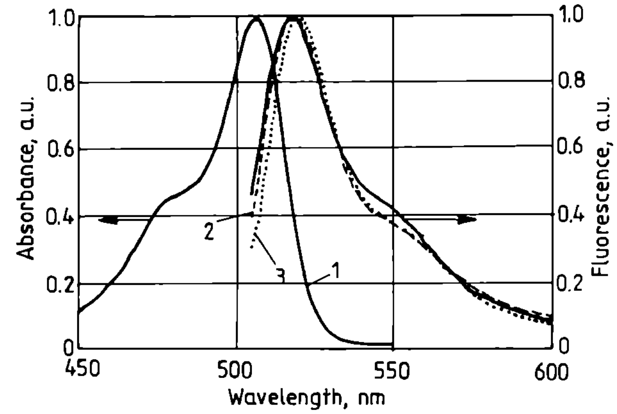


Fig. 2. Electronic absorption and fluorescence spectra (recorded in EtAc) of an example of cyanine borate tested (Cy52): 1 — n-BuPh3B⁻, 2 — sec-BuPh3B⁻, 3 — tert-BuPh3B⁻

The fluorescence emission in tetrahydrofuran solution exhibits a maximum which is redshifted in comparison to the absorption maximum by less than 1000 cm^{-1}. The value of the Stockes shift only slightly depends on the type of a borate anion and is the highest for cyanine *n*-butyltriphenylborates. Since the Stockes shift is not large and the half width of the absorption and emission bands are almost the same, therefore one can conclude that the geometry of the dye molecule is almost the same in its ground and its emitting excited states.

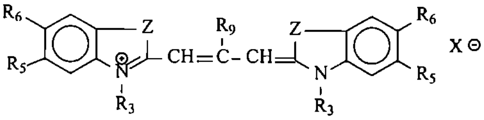
THE STRUCTURE EFFECT OF THE PHOTOINITIATING DYE-BORATE PAIR ON THE RATE OF POLYMERIZATION

It is well known that the irradiation of cyanine borate salts with visible light results in the efficient sensitization of the borate anion and the generation of free alkyl radicals [10].

$$Cy^+[R-B(Ph_3)]^- \xrightarrow{h\nu} [Cy^\bullet] + R^\bullet + Ph_3B \qquad (1)$$

This reaction is useful for the photoinitiation of the polymerization of vinyl monomers. Four various electron donors and two different groups of electron acceptors were used in our study. The irradiation of these binary systems with visible light may generate three types of free radicals (*n*-butyl, *sec*-butyl and *tert*-butyl) that can initiate free radical polymerization of triacrylate monomers. Considering the mentioned earlier properties of cyanine dyes and taking into account the properties of borate anions one can expect that the efficiency of the photoinitiation of free radical polymerization can be affected by:

Table 1. Measured relative rates of the polymerization — for cyanine borates tested[*)]



Dye	Z	R_5	R_6	R_9	R_3	1 + ln R_p*), a.u. CyB2	1 + ln R_p*), a.u. CyB3	1 + ln R_p*), a.u. CyB4	1 + ln R_p*), a.u. CyB5
Cy3	S	H	H	H	C_2H_5	5.27	4.46	4.57	1.67
Cy4	S	H	H	CH_3	C_2H_5	3.75	4.47	3.10	—
Cy6	S	H	H	H	C_3H_7	5.22	5.40	2.88	2.71
Cy8	S	F	H	H	C_2H_5	5.61	5.37	3.16	3.25
Cy9	S	CH_3	H	H	C_2H_5	5.36	5.03	4.93	3.18
Cy10	S	H	CH_3O	H	C_2H_5	4.67	5.36	2.80	2.64
Cy11	S	CH_3O	H	C_2H_5	CH_2CH_2OH	3.21	2.15	1.00	2.68
Cy18	O	H	H	H	CH_3	5.12	5.65	5.76	1.99
Cy19	O	H	H	H	C_2H_5	5.05	6.01	5.67	2.67
Cy20	O	H	H	H	C_3H_7	5.12	1.30	2.48	1.00
Cy21	O	H	H	H	C_6H_{13}	5.25	5.51	2.20	1.38
Cy22	O	Cl	H	H	C_2H_5	5.43	4.62	6.29	2.51
Cy23	O	CH_3	H	H	C_2H_5	4.71	5.22	6.00	3.05
Cy24	O	CH_3O	H	H	C_2H_5	3.72	5.25	5.07	—
Cy25	O	C_6H_5	H	H	C_2H_5	5.24	4.19	4.86	—
Cy27	O	CH_3O	H	C_2H_5	C_2H_5	3.50	—	—	—
Cy28	O	C_6H_5	H	C_2H_5	C_2H_5	3.51	3.75	5.47	—
Cy33	S	H	C_2H_5O	H	C_2H_5	4.63	2.53	2.92	2.43
Cy36	S	NO_2	H	H	C_2H_5	5.30	1.38	2.39	2.29
Cy41	O	H	H	CH_3	C_2H_5	4.18	1.29	2.57	2.45
Cy45	O	H	H	C_2H_5	C_2H_5	5.53	6.06	2.60	—
Cy46	S	CH_3	H	CH_3	C_2H_5	3.50	1.00	2.22	2.54
Cy47	S	CH_3	H	C_2H_5	C_2H_5	3.25	3.55	2.79	1.08
Cy48	O	Cl	H	CH_3	C_2H_5	1.88	—	—	—
Cy49	O	Cl	H	C_2H_5	C_2H_5	1.17	1.46	2.18	2.29
Cy50	S	H	H	C_2H_5	C_2H_5	3.95	4.79	3.23	—
Cy51	O	CH_3	H	CH_3	C_2H_5	4.07	3.94	1.69	1.38
Cy52	O	C_6H_5	H	CH_3	C_2H_5	3.80	4.14	1.98	2.58
Cy53	O	C_6H_5	H	C_2H_5	C_2H_5	4.06	—	1.86	1.36
Cy54	S	H	H	CH_3	C_3H_7	3.78	2.65	2.43	1.00
Cy55	S	H	H	C_2H_5	C_2H_5	3.74	—	2.13	—
Cy56	S	F	H	CH_3	C_2H_5	4.29	1.71	2.41	3.07
Cy57	S	F	H	C_2H_5	C_2H_5	—	4.31	1.86	—
Cy58	S	OH	H	H	C_2H_5	2.07	1.30	2.85	2.70
Cy59	S	OH	H	CH_3	C_2H_5	—	4.31	1.86	—
Cy60	S	OH	H	C_2H_5	C_2H_5	—	—	—	—
Cy61	S	CH_3O	H	H	C_2H_5	3.91	3.99	—	1.36
Cy63	S	H	Cl	H	C_2H_5	5.49	6.85	4.40	—
Cy64	S	H	Br	H	C_2H_5	—	—	—	—
Cy65	S	H	Cl	CH_3	C_2H_5	3.63	4.97	3.67	3.11
Cy66	S	H	Cl	C_2H_5	C_2H_5	4.27	5.09	2.88	1.17

[*)] R_p — the relative rate of polymerization, symbols B_2—B_5 denote *n*-, *sec*-, *tert*-butyltriphenylborate salts and tetra-*n*-butylborate, respectively.

(*i*) the type of heteroatom in the dye molecule,

(*ii*) the type of substituent in phenyl ring of dye molecule,

(*iii*) the type of substituent in the *meso* position of the polymethine chain,

(*iv*) the type of free alkyl radical formed from the borate anion.

The data illustrating the kinetics of free radical polymerization of TMPTA initiated by the tested cyanine borate salts tested are summarized in Table 1.

The sensitivity of cyanine borate salts depends on the structure of the dye as well as on the structure of the borate anion. This is illustrated in Figures 3 and 4 as well as is summarized in Table 1.

From the inspection of Figures 3 and 4 and the data summarized in Table 1, it is clear that there is little difference between the reactivities of the free alkyl radicals formed. In many cases the highest sensitivity is observed for the systems possessing *n*-butyltriphenylborate (B2) or *sec*-butyltriphenylborate (B3) as an electron donor.

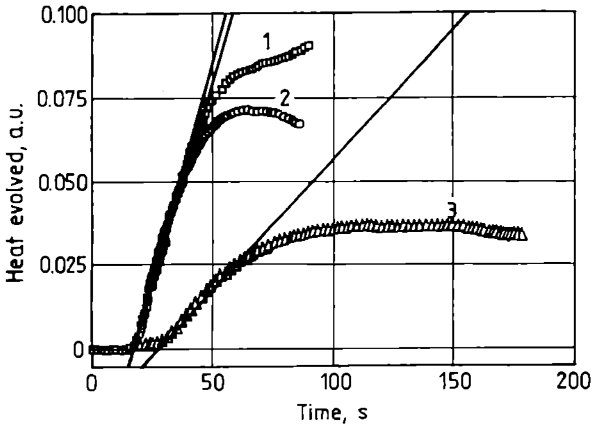


Fig. 3. Time dependence of heat evolved during argon-laser photoinitiated polymerization of TMPTA in MP, initiated by selected cyanines tert-butyltriphenylborate: 1 — Cy18B4, 2 — Cy8B4, 3 — Cy10B4 (for symbols — see Table 1)

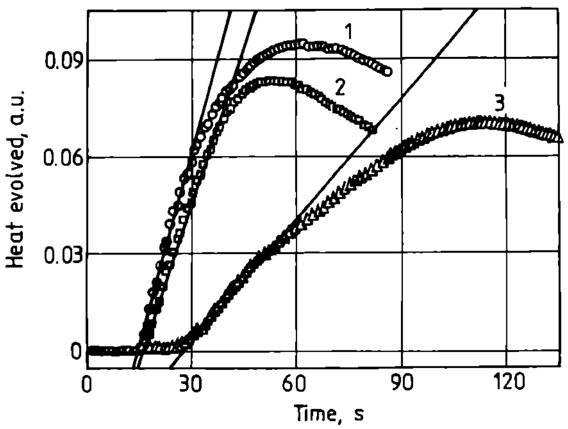


Fig. 4. The effect of the borate type on the rate of heat evolution during argon-laser photoinitiated polymerization of TMPTA in MP, initiated by Cy9: 1 — Cy9B4, 2 — Cy9B2, 3 — Cy9B3 (for symbols see Table 1)

It is known from the literature that the efficiency of cyanine radicals formation depends on the structure of an alkyl group bound to boron atom [10]. Generally, in series in which the stability of the formed alkyl radicals decreases, the quantum yield of the free radicals formation decreases. Based on the experimentally determined by Schuster [10] correlation between the efficiency of free radical formation and the hydrogen-carbon bond dissociation energy of alkyl radicals formed, and the experimentally determined electron transfer efficiency (which for the *n*-butyl radical is about 1), by the comparison one can establish the quantum yields of *sec*-butyl and *tert*-butyl radicals formation. For the tested salts the quantum yields of radicals formation for *sec*-butyl and *tert*-butyl are 0.78 and 0.83, respectively. This result explains why one can observe essentially no influence of the quantum yield of the radical formation on the rate of free radical polymerization initiated by cyanine-borate salts (Table 1).

It is also surprising that for the two series, which generate the same type of free radicals, the rates of free radical polymerizations initiated by these salts substantially differ (Table 1). On the basis of the data summarized in Table 1 one can conclude that the activity of investigated systems in photoinitiation of free radical polymerization is controlled by other factors than the structure of co-initiator (anions B2, B3, B4 or B5). It is also well documented that the photochemical efficiency (f) of the initiator affects the kinetics of free radical polymerization. Its value depends on the relationship between rate constant of free radical escape from the solvent cage (k_{sp}) and the rate constant of recombination of free radicals in the cage (k_{rec}).

$$f = k_{sp}/(k_{sp} + k_{rec}) \qquad (2)$$

It should be noted that observed photoinitiator efficiency depends not only on the structure and geometry of free radicals formed but also on the nature of a monomer. In the present study the cage effect is the same for every tested series because we used the same monomer (TMPTA) and solvent (MP). In one series of measurements the rates of free radical polymerization were compared only for one type of electron donor (borate). Taking this into consideration, one can conclude that the differentiation in activity of cyanine borate salts in initiation of radical photopolymerization results from the structure of the dye. As it was mentioned earlier, the rate of photoinitiated polymerization can be affected by the type of heteroatom in dye molecule, the type of an alkyl group at nitrogen atom, the type of substituent in phenyl ring and the type of substituent in the *meso* position of the polymethine chain.

From the data presented in Table 1 it is clear that activity of cyanine borate salts in initiation of TMPTA polymerization indeed depends on the structure of the dye. In almost all cases the highest rates of free radical polymerization are observed for the dyes without the substituent in the phenyl ring ($R_5 = R_6 = H$). This relationship is observed for both series, *i.e.* for thiacarbocy-

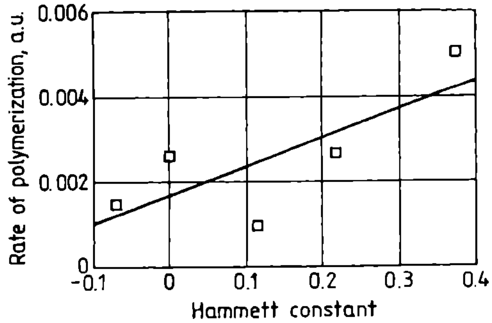


Fig. 5. The relationship between the rate of free radical polymerization of TMPTA initiated by n-butyltriphenylborate salts of oxacarbocyanine dyes and the Hammett's constants; experimental points in turn from below to the top: Cl, H, CH_3, OCH_3, C_6H_5

anine and carbocyanine dyes. Also the introduction of an electron-withdrawing atoms, for example chloride and fluoride, into the phenyl ring causes an increase in the rate of polymerization in all tested series. The weakly activating substituents, *e.g.* methyl, metoxy and phenyl groups, cause a decrease in the rate of free radical polymerization. The rates of polymerization initiated by different borate salts of the selected cyanine dye with different substituent in *N*-3 position are very similar. All these observations can be easily illustrated by applying the classical Hammett's relationships shown in Figures 5 and 6.

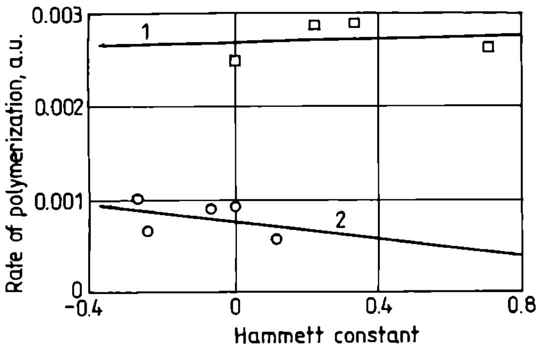


Fig. 6. The relationship between the rate of free radical polymerization of TMPTA initiated by n-butyltriphenylborate salts of thiacarbocyanine dyes and the Hammett's constants; experimental points in turn: 1 — H, F, NO_2, Cl; 2 — CH_3, OCH_3, OC_2H_5, OH (two dyes have the same substituent OCH_3 but in different positions: as R_5 or R_6)

The type of substituent in *meso* position of the polymethine chain strongly affects the rate of free radical polymerization in all tested series. The disturbance of coplanarity of the electron acceptor molecule (cyanine dye) by the introduction of methyl or ethyl group into the *meso* position (R_9) of the polymethine chain causes a distinct decrease in the rate of photoinitiated polymerization. The relationship is shown in Figure 7.

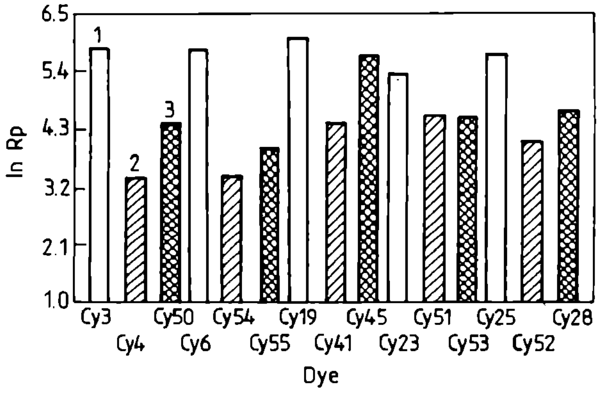


Fig. 7. The effect of the R_9 group [see Formula (III)] on the relative rates of an argon-laser photoinitiated polymerization of TMPTA in MP, initiated by selected cyanine n-butyltriphenylborates; 1 — H, 2 — CH_3, 3 — C_2H_5

It was also found that the polymerization rates, recorded using the thick layer technique, indicate the conversion of monomer in the range from 3% to 20%, while the quantum yields of photopolymerization oscillate between 20 and 60 for almost all tested series (Table 2). The exception is the ion pair marked as Cy63B3 showing the fastest initiation rate of TMPTA polymerization with quantum yield of polymerization of about 122. It was also found that the degree of the monomer conversion depended on the structure of the photoinitiator. The highest degrees of monomer conversions were reached when the polymerization of TMPTA was photoinitiated by cyanine dyes without the substituents in the phenyl rings for all the carbocyanine dyes tested.

Table 2. The quantum yield (Φ) and degree of monomer conversion for selected photoinitiating ion pairs*)

CyX Dye	Conversion of monomer CyB2, %	Conversion of monomer CyB3, %	Conversion of monomer CyB4, %	$\Phi_{polymer}$ CyB2	$\Phi_{polymer}$ CyB3	$\Phi_{polymer}$ CyB4
Cy3	5.67	—	—	24.86	—	—
Cy6	3.49	4.61	—	22.92	33.06	—
Cy8	4.39	3.32	—	28.89	21.86	—
Cy9	3.41	4.22	3.82	9.29	23.78	8.14
Cy10	—	6.39	—	—	29.67	—
Cy36	4.42	—	—	21.81	—	—
Cy63	5.30	12.42	—	27.91	122.45	—
Cy18	12.11	21.70	13.34	23.88	48.91	35.07
Cy19	—	—	17.29	—	—	31.71
Cy45	8.78	20.74	—	26.64	56.40	—
Cy21	14.76	12.30	—	32.33	19.80	—
Cy22	—	—	7.46	—	—	20.27
Cy23	—	—	4.70	—	—	14.81
Cy25	7.23	—	—	17.82	—	—

*) For symbols of the dyes see Table 1.

CONCLUSIONS

Butyltriphenylborates as co-initiators forming with cyanine dyes ion pairs can be used for visible-light-induced polymerization of acrylates. The comparative analysis of the rates of the polymerizations photoinitiated by cyanine-borate salts showed that the activity of the photoinitiation of free radical polymerization by cyanine borates only slightly depends on the reactivity of the butyl radical formed. However, it strongly depends on the structure of the cyanine dye.

ACKNOWLEDGMENT

This research was sponsored by the State Committee for Scientific Research (KBN), grant No 4 T09A 051 22.

LITERATURE

1. Carblom L. H., Pappas S. P.: *J. Polym. Sci. A1* 1997, **15**, 1301.
2. Monitz W. B., Sojka S. A., Porański C. F., Birkle D. L.: *J. Am. Chem. Soc.* 1978, **100**, 7940.
3. Sandner M. A., Osborn R. M., Trecker D. J.: *J. Polym. Sci. A1* 1972, **10**, 3173.
4. Neckers D. C., Hassoon S., Klimtchuk E.: *J. Photochem. Photobiol., A: Chem.* 1996, **95**, 33.
5. Oster G.: *Nature* 1954, **173**, 300.
6. Pączkowski J., Kucybała Z.: *Macromolecules* 1995, **28**, 269.
7. Lan J. Y., Schuster G. B.: *J. Am. Chem. Soc.* 1985, **107**, 6710.
8. Lan J. Y., Schuster G. B.: *Tetrahedron Letters* 1986, **36**, 4261.
9. Murphy S., Yang X., Schuster G. B.: *J. Org. Chem.* 1995, **60**, 2411.
10. Chatterjee S., Davis P. D., Gottschalk P., Kurz M. E., Sauerwein B., Yang X., Schuster G. B.: *J. Am. Chem. Soc.* 1990, **112**, 6329.
11. Sato T., Takahashi T., Seno M., Mirano T.: *J. Polym. Sci., Part A* 2002, **39**, 4206.
12. Popielarz R., Sarker A. M., Neckers D. C.: *Macromolecules* 1998, **31**, 952.
13. Zhang S., Li B., Tang L., Wang X., Liu D., Zhou Q.: *Polymer* 2001, **42**, 7575.
14. Zhang S., Li B., Tang L.: *Acta Polym. Sin.* 2001, **1**, 114.
15. Pączkowski J., Kucybała Z.: *Macromolecules* 1995, **28**, 269.
16. Pączkowski J., Pietrzak M., Kucybała Z.: *Macromolecules* 1996, **29**, 5057.
17. Kabatc J., Kucybała Z., Pietrzak M., Ścigalski F., Pączkowski J.: *Polymer* 1999, **40**, 735.
18. Hamer F. M.: *J. Chem. Soc.* 1927, 2796.
19. Turicina N. F., Levkoev I. I.: *Zh. Obshch. Khim.* 1950, **22**, 309.
20. Damico R.: *J. Org. Chem.* 1964, **29**, 1971.
21. Markocki W.: „Chemia organiczna procesu fotograficznego", PWN, Warszawa 1958.
22. Sheppard S. E., Lambert R. H., Walker R. D.: *J. Phys. Chem.* 1941, **45**, 107.

Received 25 VI 2002.