Methylene Blue Borate Photochemical Behaviors and Application For Photopolymerization

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Methylene blue borate(MB.Ph₃RB) is a stable salt in the dark and readily proceeds electron transfer (ET) to produce a neutral radical pair upon irradiation by visible light. The unstable boranyl radical undergoes the carbon-boron cleavage to generate active alkyl radical immediately, along with MB dye bleaching. The association state of salt plays an important role in controlling the photophysical and photochemical properties. The photoinduced ET rate of MB borate in the tight ion pair state (k_{et} 9×10^{-11} s⁻¹) which predominately exists in non-polar solution, is far greater than that observed in the free solvated ion state in polar solvents. Photopolymerization of MMA in CH₃CN solution not occurs with MB borate(MB Ph₃RB) alone, but undergoes with MB Ph₃RB/Et₄NPh₃RB combination system. Addition of weak H-donor, such as methanol, results in a great rate-acceleration. The photoinitiation mechanism and different influences were also discussed.

Photoinduced electron-transfer reactions play a central role in many processes of technological importance, such as silver halide sensitization, electrophotography and photoinduced polymerization^[1]. However, the quantum yields of such reactions, in general, are very low, which means that the most part of incident photon energy is wasted^[2,3]. This is mainly due to rapid exothermic back electron transfer to reform the starting materials, which occurs within the formed radical ion pair in competition with chemical reaction^[2,3]. Recently the electron transfer reaction followed by rapidly bond cleavage, in which one or both two of ion radical in the pair is unstable with respect to fragmentation into an ion and a free radical, has attracted a great interest to design new high efficient photosensitized initiation system for visible photopolymerization^[4,5]. In the previous papers^[6,7], we have proposed a type of electron transfer sensitization system composed different xanthene dyes as electron donor and arylidonium salts as electron acceptor in the form of ion pair. The latter rapidly undergoes C-I bond cleavage through electron transfer from excited dye to iodonium salt to afford a radical species capable of initiation. In this paper we report other type of electron transfer photosensitization system for polymerization, in which triphenylalkyl borate employed as electron donating activator in combination with cationic dyes as excited electron acceptor, such as thiazene. Their spectral properties, photochemical behaviors and application for polymerization were studied kinetically.

Experiment

Triphenyl alkyl borate of tetraethylammonium ($\text{Ph}_3\text{RB NEt}_4$) (TEAB) was synthesized according to literature[8].

Methylene blue borate ($\text{MB} \cdot \text{Ph}_3\text{RB}$) (MBB) was prepared from methylene blue chloride (MBCl) and triphenyl alkyl borate (TEAB) by ion exchange method.

Methyl methacrylate (MMA) and other monomers were purified by conventional procedures and redistilled before use.

Photochemical reactions were performed in the nitrogen purged solutions. The Xenone lamp (400w) was used as light source and short wavelength light $< 320\text{nm}$ was removed by filter. The incident light intensity was measured to be 16 mw/cm^2 . Photo-bleaching rate of dye was determined by monitoring the absorption changes with irradiation time. Photopolymerization rates were measured by both dilatometry and gravimetry.

Absorption and emission spectra were recorded on spectrophotometers Hitach-330 and Hitach MPF-4 respectively.

Results and Discussion

I. Electronic Spectral Properties

The absorption spectra of different methylene blue (MBCl, MBPh_3RB) and triphenyl alkyl borate (TEAB) were shown in Fig. 1. The absorption maxima of MB dye and borate (TEAB) lie at 658nm with shoulder at 610nm (curve 3) and at UV region (curve 1) respectively. By comparison of the absorption spectra of MB chloride and MB borate in different solutions, an important observation showed that the shape and position of absorption band are independent of the sort of counter ion and the nature of solvents, but the value of molar extinction coefficient (ϵ) increases with increasing the solvent polarity and radius of anion.

Fig.1 Absorption spectra of MB/TPBB

1. $\text{Ph}_3\text{RB} \cdot \text{NEt}_4$ in CH_3CN , 2. $\text{MB} \cdot \text{Ph}_3\text{RB}$ in CH_3CN
3. MBCl in CH_3CN , 4. $\text{MB} \cdot \text{Ph}_3\text{RB}$ in AcEt

The fluorescence spectra of MB borate were studied in different polar solutions. We have found that the fluorescence efficiency (ϕ_f) is independent on excitation wavelength, but depends strongly on the polarity of solvents. The emission band at 674nm was only observed in CH_3CN or CH_3NO_2 polar solution, was not detectable in the less polar solution of ethyl acetate (EtAc) by steady state measurement (see table 1). These findings can be attributed to the virtual quenching of fluorescence by the fast competitive process of electron transfer via intra ion-pair, which exist predominantly in non polar solution and rarely in polar solution. The singlet excited energy of MB borate was also estimated from emission 0-0 band to be 1.86 eV. From the results reported above we can find that electronic spectral properties are obviously closely related to the dissociation state of MB borate in the solution.

As known, methylene blue borate in organic solution exists as a mixture of freely solvated ions, tight ion pairs and higher aggregates, whose relation according to the Fuoss equation (eq.1), depends on the polarity of solvents (r), temperature (T), dimension of ion pair (R) and electronic charge of ion (e) etc.

$$-\ln k_D = A \cdot e^2 / R \cdot r \cdot k_f \cdot T \quad (1)$$

By measurement the solution conductivity of MB borate in a series of concentration, the dissociation constant (k_D) and dissociation degree (α) in different polar solution were obtained as listed in Table 1.

Table 1. Physical properties of MB borate in different solutions.

Solvent	r	$k_D \times 10^5$ M	α %	Absorption		Fluorescence	
				$\lambda_{\max}$ nm	$\epsilon_{\max}$ $\text{m}^{-1} \cdot \text{cm}^{-1}$	$\lambda_{\max}$ nm	ϕ_f
CH_3CN	3.75	1.54	0.42	658	1.30	674	0.024
CH_3NO_2	36.0	1.28	0.40	658	0.91	674	0.026
EtAc	0.60	0.17	0.17	658	0.40	674	0

[MB borate] : 5×10^{-5} M

These experimentals indicate that the MB borate readily dissociates in polar solutions compared with the value for MB

chloride (k_D 0.38×10^{-5} in CH_3CN) and exists essentially exclusively as ion pair in non-polar solutions. Evidently, the dissociation state of MB borate plays an important role in their spectral properties and will affect strongly on their photochemical reactions.

II. Photochemical Reaction — Radical Photogeneration

In general, the photoinduced electron transfer (ET) reaction is expected to occur when calculated to be exergonic process using Weller's equation^[9] (eq.2).

$$\Delta G_{et} = E_D^{ox} - E_A^{red} - \Delta E^* \quad (2)$$

where E^* is the excited energy of the dye, E_D/D^+ and E_A^-/A are the oxidation potential of donor (0.92 eV for Ph_3RB^-) and reduction potential of acceptor (-0.532 eV for MB^+). Thus the values of free energy change ΔG_{et} of $\text{MB}^+/\text{Ph}_3\text{RB}^-$ system in different state were obtained to be 1.45 eV for ground state and -0.41 eV for excited singlet state or -0.32 eV for triplet state respectively. These results indicate that the electron transfer reaction of $\text{MB}^+/\text{Ph}_3\text{RB}^-$ system is unstable to occur in the dark ($\Delta G_{et} > 0$), but easily undergoes upon irradiation from either singlet state or triplet state ($\Delta G_{et} < 0$). The photoinduced ET reaction rate constant k_{et} can be predicated from the Weller's relation of k_{et} and ΔG_{et} to be above the diffusion controlled rate constant k_{dif} . Using the fluorescence quenching of MBCl by TEAB, the quenching rate constant k_{et} was obtained to be 9.4×10^{11} ($\tau_f(\text{MB})$ 0.365 ns), which reaches the value in great excess of the k_{dif} of $2.7 \times 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ in CH_3CN at same temperature. It demonstrates that in this case the intra ion-pair process plays a significant role in experimental condition, which is not limited by diffusion process and possible to gain a very high reaction rate.

Irradiation of MB borate by visible light to formation of a locally excited state of methylene blue and occurrence of an intra ion pair electron transfer from boranyl anion to MB cation, resulting in an occurrence of dye bleaching and generation boranyl radical. The boranyl radical formed is very unstable and undergoes subsequent cleavage of the alkyl carbon-boron bond to produce an alkyl radical and triphenyl borane immediately and

irreversibly[10]. These reaction processes can be described as follows:

Fig.2 shows the spectral changes of MB borate with irradiation time. It can be detected that absorption band decreases upon irradiation and an isosbestic point appears at 550 nm. Thus, the kinetical studies of electron transfer photochemical reaction of MB borate might be followed from the changes in optical density(OD) at 658 nm and the reaction rates were obtained from the plot of OD against irradiation time. To observe the influence of solvent polarity on the electron transfer reaction the experiments were carried out in mixed solution of acetonitrile (AN) and ethyl acetate(EtAc).

Fig.2 Absorption spectral change of MB borate

From data listed in Table 2, it can be seen that the photobleaching rate of MB decreases remarkably with increasing solvent polarity in which the ratio of rate constant to molar absorption coefficient (k_b/ϵ) was used in consideration of the marked absorbance change of MB borate with solvent polarity as described above.

Table 2. Effect of solvent polarity on the photobleaching of MB borate

EtAc/AN (V/V%)	100	98	95	92	90	80	70	50	25	0
k_b/ϵ	83	82	81	62	51	22.5	0.82	0.05	0.02	0.01

$$[MB\text{-}borate] = 1.5 \times 10^{-5} M$$

The results indicate that the electron transfer reaction of MB borate proceeds effectively only in non-polar solvents and becomes poor in polar solvents as a results of substantial dissociation of MB borate from tight ion-pairs to the solvated free ions. It is apparent that the strong dependence of ET reaction rate and efficiency on their dissociation state in solution will greatly affect the sequent free radical photogeneration as MB borate used to initiate vinyl polymerization.

III. Photopolymerization

The photochemical reaction of dye sensitized photoinitiation system composed of methylene blue MB and triphenyl alkyl borate as described above (eq.3-6), undergoes upon irradiation by visible light via electron transfer to generate two neutral radicals MB radical and alkyl radical($R\cdot$). The MB radical is a stable radical which acts only as a chain termination agent in polymerization processes, while the alkyl radical exhibits high reactivity. Therefore the MB^+/Ph_3RB^- system will be useful for the initiation of photopolymerization sensitive to visible light.

(1) Different systems

To observe the photoinitiation probability of MB borate, different MB^+/Ph_3RB^- systems composed of followeing compounds

(A) $MB^+Ph_3B^-R$, (B) MB^+Cl^- , (C) $Et_4N^+Ph_3BR^-$ and (D) $Et_4N^+Cl^-$ were used in our experiments. The photopolymerization of MMA was carried out in the acetonitrile in consequence of the poor solubility of borate in non-polar organic solvents. Results obtained were shown as follows:

	I	II	III	IV
System	A	B+C	A+C	A+D
Polymerization	—	—	+	—

It was observed that non polymerization occured as using MBB borate(I) alone as photoinitiator. This finding may be attributed to the substantial dissociation of MBB borate into free ions, MB^+

and Ph_3RB^- , in polar solution used. In this case photoinduced ET reaction becomes a diffusion controlled process and strongly competes with quenching of excited MB by monomers as shown below:

Of particular importance is the excited state quenching in the condition of vinyl polymerization. In this case the monomer concentration is far higher than that of MBB borate and the ET induced radical generation is predominantly inhibited by monomer. Therefor no polymerization could be observed. The same result was also obtained in the bimolecular system (II) of MBCl and $\text{Et}_4\text{NPh}_3\text{BR}$. When tetraethylammonium borate (TEAB) added to the MBB borate solution (system III), polymerization occurred readily. Whereas addition of tetraethylammonium chloride to MBB borate solution (IV) has not any positive effect detected. Obviously, addition of TEAB borate to reaction system leads to an increase in concentration of boranyl anions and turns the dissociation balance in favor of formation of MBB borate ion pair. Since electron transfer via intra ion-pair is a much fast process with rate constant of the order of 10^{11} s^{-1} that is far greater than the value of diffusion controlled quenching, so that the polymerization occurs efficiently with the initiation system III.

(2) Effect of concentration

On the basis of results above, the MBB borate/TEAB borate combination system is used to further study photopolymerization. The influence of concentration of TEAB borate on polymerization of MMA was shown in Fig.3. A linear dependence of polymerization rate R_p on concentration of TEAB borate was observed after a certain concentration added at a fixed MBB borate content of $3 \times 10^{-5} \text{ M}$.

Fig.3 Dependence of R_p on the concentration of TEAB borate

The variation in R_p with concentration of MBB borate at constant concentration of TEAB borate is listed in Table 2. It can be seen that with increasing concentration of MBB borate the polymerization rates increase in the low concentration range and decrease in the high concentration range. This negative concentration effect frequently observed in the photosensitized polymerization and is considered as the dramatic increase in excited state decay.

Table 4. Polymerization rate (R_p) as function of MBB borate and light intensity

MB Ph_3BR	$R_p \times 10^5 (M^{-1}.s^{-1})$	T%	$R_p \times 10^5 (M^{-1}.s^{-1})$
3.0×10^{-5}	5.63	100	5.01
3.0×10^{-4}	8.15	50	6.27
2.8×10^{-3}	3.13	39	4.07

$[MMA]: 3.7 \text{ M}$, $[TEAB]: 1 \times 10^{-3} \text{ M}$, $[MBB]: 3 \times 10^{-5} \text{ M}$

Influence of incident light intensity on the polymerization rate was performed using grey films with different transmittance (T%). The experimental results listed in Table 4 demonstrate that with reducing incident light intensity rate of polymerization (R_p) increased in a certain degree at start range then dropped down quickly. It is apparent that intensive light is not favorable to the generation of free radicals from the photoinduced ET reaction of MB borate. Because the high local concentration of active intermediates formed in primary photoreaction results significantly in an enhancement of photophysical and photochemical deactivations.

(3) Addition of weak proton donor

Addition of weak proton donor, such as MeOH, H₂O, to the polymerization system initiated with MBB borate/TEAB borate combination was examined in the aprotic polar solution of CH₃CN. The data in Table 5 show that adding methanol to reaction system the polymerization rate and polymer yield increased obviously, while photobleaching rate becomes lower.

Table 5. Photopolymerization rate (R_p)
as function of methanol content

MeOH%	0	0.1	10
$R_p \times 10^5 (M^{-1} \cdot s^{-1})$	6.27	10.7	16.9

To understand the rate-enhancement of methanol in polymerization a comparative study was performed in protic and aprotic solution separately. We observed that photoreaction of MB borate in net acetonitrile solution gave a red color with absorption at 482 nm (curve 1) as shown in Fig.4. addition of a small amount of methanol or water to the red solution formed results in loss of the red color and reconversion to the blue color, whose absorption band at 642 nm is blue shifted about 16 nm compared with that of original MB dye. This observation was not found in the mixed solution of CH₃CN and CH₃OH. The mixed solution of MB borate will eventually bleach, but no red color is formed.

Fig.4 Spectral change of photobleached solution
of MB borate with addition of CH₃OH

[MB borate]: 1.5×10^{-5} M in CH₃CN

(1) Before and (2) after addition of CH₃OH

Obviously, addition of methanol to system leads to part regeneration of photoreduced MB to the starting blue form and reduces the chain termination by MB radicals, resulting an enhancement of polymerization rate.

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* This work was supported by National Science Foundation of China.