New polymeric photosensitizers*

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Abstract: Novel polymeric photosensitizers for singlet oxygen production in water are described. The polymers contain rose bengal (4,5,6,7-tetrachloro-2',4',5',7'–tetraiodo-fluorescein) chromophores covalently attached to the polymer chain. The quantum yields of singlet oxygen formation and photooxidation of phenol in water have been determined. The methods of separation of photosensitizer from the reactants after completion of reaction have been established.

INTRODUCTION

Many photochemical processes of practical importance have to be photosensitized. It has been shown, however, that in some cases the photosensitizer interacts chemically with the substrates or products formed. The other problem is related to the difficulties in separation of the photosensitizer from the reaction mixture when the reaction is completed. It has been demonstrated that these problems are much less important when the chromophore acting as a photosensitizer is covalently attached to a polymer chain [1].

The current paper describes our attempts for development of novel polymeric photosensitizers for oxidation of organic compounds with participation of singlet oxygen. This reaction is intensively studied due to its biological, medical, chemical, and technical importance. Rose bengal (RB) is very often used as the efficient photosensitizer in these studies. Apart from the above-mentioned difficulties connected with the separation of that dye from the reaction mixture there are some problems with its aggregation and bleaching on exposure to the light. It has been demonstrated that RB can be easily attached to the polymeric chain following the general procedure developed by Merrifield [2]. Several different types of the heterogenous photosensitizers as well as polymeric photosensitizers soluble in organic solvents have been prepared [3]. Although the heterogenous photosensitizers are quite convenient for practical applications, their usage is limited due to the relative low photochemical activity of the RB (low quantum yield of singlet oxygen formation) in such systems.

We have recently synthesized and studied several different types of water-soluble polymeric photosensitizers containing RB chromophores covalently attached to the polymeric chain. They include: homogenous photosensitizer: poly[(sodium styrenesulfonate-*co*-vinylbenzyl chloride)/rose bengal] (PSSS-VBC/RB) [4], microheterogenous systems such as: poly[(sodium styrene sulfonate-*co*-styrene-vinylbenzyl chloride)/rose bengal] (PSSS-S-VBC/RB) or poly [(sodium styrene sulfonate-*co*-2-vinyl-naphthalene-*co*-vinylbenzyl chloride)/rose bengal] (PSSS-VN-VBC/RB) [5] and the thermo-responsive photosensitizers combining advantages of homo- and heterogenous systems: poly[(*N*-isopropylacryl-amide-*co*-vinylbenzyl chloride)/rose bengal] (PNIPAM-VBC/RB) with various amounts of RB attached.

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EXPERIMENTAL

Rose bengal (RB, Aldrich, 92%) was used without further purification. Vinylbenzyl chloride (VBC, Fluka, 30 mol% of *para* and 70 mol% of *meta* isomer) was distilled under vacuum. DMF (POCh, analytical grade) was dried with $MgSO_4$. α,α'-Azoisobutyronitrile (AIBN, Merck, 98%) was crystallized from methanol in 40 °C under nitrogen. *N*-isopropylacrylamide (NIPAM, Aldrich, 97%) was purified by dissolving in benzene and precipitating in hexane. *t*-Butanol (Fluka, analytical grade) was used as received. 1,3-Diphenylisobenzofuran (DPBF, Aldrich, 98%) was purified by threefold recrystallization from benzene in the dark. Phenol (PhOH, POCh, Poland, pure) was purified by sublimation twice. Imidazole (Aldrich, 97%) and *N,N*-dimethyl-4-nitrosoaniline (RNO, Aldrich, 97%) were used as received.

Irradiation of the samples

Irradiations were carried out using a medium-pressure mercury lamp (ASH 400, Hanau) and interference filters (554 or 546 nm) or a glass filter with cut-off at $\lambda > 535$ nm. The intensities of the incident light were determined by means of the potassium reineckate actinometer [6]. During irradiation the solutions were bubbled with oxygen.

Determination of the quantum yields of singlet oxygen formation

The quantum yields of singlet oxygen formation by the RB chromophores attached to polymer chain were determined by reactions with an acceptor. DPBF and the system of imidazole and RNO were used as a singlet oxygen acceptor in methanol and aqueous solution, respectively. The procedure with DPBF was described earlier [4]. The measurements in aqueous solution with imidazole $(0.008–0.01 \text{ mol/dm}^3)$ and RNO $(4 \times 10^{-5} \text{ mol/dm}^3)$ were carried out according to the method described in literature [7,8].

VBC/RB monomer synthesis

VBC/RB monomer was obtained by reacting 0.55 g (100% excess) of VBC with 1.83 g of RB in 35 ml of DMF. The reaction was carried out for 24 h in 40 °C under nitrogen. The reaction mixture was freeze-dried, the product was washed a few times with ether and dried in vacuum. The purity of the product was confirmed by HPLC.

Polymer synthesis

The synthesis of PSSS-VBC/RB, PSSS-S-VBC/RB, and PSSS-VN-VBC/RB were described earlier [4,5]. The PNIPAM-VBC/RB polymers were synthesized as follows. VBC/RB and NIPAM were dissolved in 25 ml of *t*-butanol in three different ratios to obtain three polymers with different RB chromophore content. The reaction mixtures contained 1 mol%, 0.5 mol%, and 0.2 mol% of VBC/RB. The amounts of NIPAM and VBC/RB reacted were: 1.819 g and 0.181 g (1 mol%), 1.906 g and 0.094 g (0.5 mol%), and 1.961 g and 0.039 g (0.2 mol%), respectively. The amount of AIBN used was 0.5 mol% based on total concentration of monomers. The reaction mixtures were degassed by three freeze-pump-thaw cycles and sealed in glass ampoules. The polymerization reaction was carried out for 30 h in 60 °C. The solvent was removed from the reaction mixture by freeze-drying and the polymers were washed with hexane and three times with ether, dissolved in methanol, and freeze-dried. The yields ranged from 35 to 78%.

RESULTS AND DISCUSSION

All synthesized polymers were soluble in water and in methanol. It has been shown that the attachment of RB to the polymeric chain does not influence considerably the photophysical properties of the dye. The absorption and emission spectra display the band characteristics of RB chromophore (see Fig. 1 and Table 1). All absorption spectra have one band with well-defined maximum and a shoulder at a shorter wavelength. The position of the absorption maximum and the ratio of the absorption at the maximum and at the shoulder (A_1/A_2) provide the information about the microenvironment experienced by RB chromophore. In methanol solutions the shape and position of the absorption and emission bands are almost the same for all the polymers. The main absorption band has a maximum at 559 ± 5 nm, and the emission band has a maximum at 577 ± 4 nm. The ratio A_1/A_2 does not change considerably; the highest limit is about 25%.
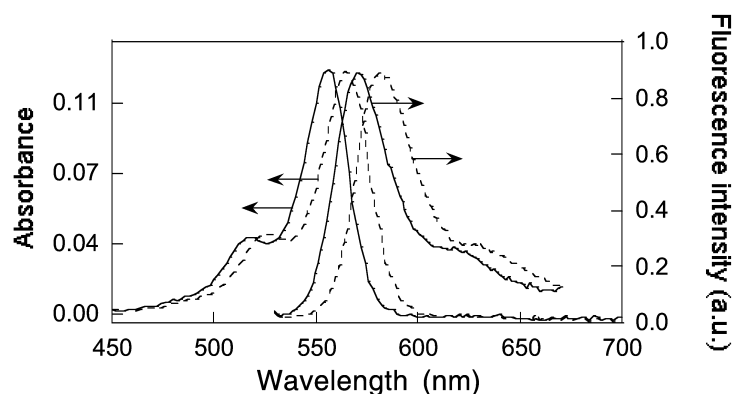

Fig. 1 Electronic absorption and emission spectra in visible spectral region of PNIPAM-VBC/RB1 (dashed line) and RB (solid line) in aqueous solution.

Table 1 Spectral characteristics of rose bengal chromophores.

Polymer	Content of RB (wt.-%)	Methanol			Water		
		λ_{max}^{Ab} (nm)	λ_{max}^{Fl} (nm)	A_1/A_2	λ_{max}^{Abs} (nm)	λ_{max}^{Fl} (nm)	A_1/A_2
PSSS-VBC/RB	55.0	555	573	2.64	546	564	2.48
PSSS-S-VBC/RB	3.30	554	579	3.04	546	568	2.49
PSSS-VN-VBC/RB	4.50	554	576	2.68	540	563	2.11
PNIPAM-VBC/RB1	1.27	564	581.5	2.99	568	592.5	2.10
PNIPAM-VBC/RB2	4.0	564	581.5	2.93	568	592.5	1.91
PNIPAM-VBC/RB3	9.04	564	581.5	2.92	566	589.5	1.81
PNIPAM-VBC/RB4	26.0	556	581	2.9	562	569.5	1.5
RB	—	556	570	3.15	548	564.5	3.05

This finding confirms that the attachment of RB to the polymer chain does not influence considerably the properties of the dye chromophore. The situation is, however, more complicated when polymers are dissolved in water. Generally, the A_1/A_2 ratios for the RB chromophores attached to the polymer chain are lower. Interestingly, the blue shift is observed for PSSS-VN-VBC/RB, and the red shift for PNIPAM-VBC/RB.

Quantum yields of singlet oxygen formation

The quantum yields of singlet oxygen formation by rose bengal chromophores attached to the polymer chains were determined in methanol and in aqueous solution. It was found that all polymers display the high efficiency of singlet oxygen formation. In a series of PNIPAM-VBC/RB polymers the quantum yield reaches the highest value for the polymer with the lowest loading with RB, and it decreases while the amount of the RB present in the polymer increases. This can be explained considering the growing probability of aggregation of the RB chromophores in polymers containing higher content of the dye (see Table 1).

Photosensitized oxidation of organic compounds by polymeric RB

The possibility of the practical application of polymeric photosensitizers with RB chromophores was tested using the oxidation of phenol in aqueous solution as the example. It was found that all polymers photosensitize the oxidation of phenol (see Table 2). *p*-Benzoquinone was identified as the primary product of that reaction. The rate and quantum yield of the reaction are strongly dependent on pH of the solution, reaching the highest value in alkaline solution. The values of quantum yield of photosensitized oxidation of phenol at pH = 10.3 are given in Table 2.

Table 2 Quantum yields of singlet oxygen formation by the polymers ($\Phi_{^1O_2}$) and quantum yields of the oxidation processes for: DPBF in methanol (Φ_{DPBF}) and phenol in water (Φ_{PhOH}).

Polymer	Content of RB [wt.-%]	Methanol		Water	
		$\Phi_{^1O_2}$	Φ_{DPBF}	$\Phi_{^1O_2}$	Φ_{PhOH} [c]
PSSS-VBC/RB	55.0	0.73	0.17[a]		0.212
PSSS-S-VBC/RB	3.30	0.75	0.19[b]		
PSSS-VN-VBC/RB	4.50	0.77	0.20[b]		
PNIPAM-VBC/RB1	1.27	0.73	0.18[b]	0.84	0.24
PNIPAM-VBC/RB2	4.0	0.71	0.18[b]	0.78	0.23
PNIPAM-VBC/RB3	9.04	0.69	0.17[b]	0.75	0.21
PNIPAM-VBC/RB4	26.0	0.55	0.14[b]	0.36	0.10
RB	—	0.76		0.75	

[a]concentration of DPBF 5×10^{-5} mol/dm^{-3}
[b]concentration of DPBF 8×10^{-5} mol/dm^3
[c]concentration of phenol 5×10^{-5} mol/dm^3, pH = 10.3

Separation of photosensitizer

The possibility of separation of the polymeric photosensitizers from reactants after completion of reaction is an essential problem. Several different methods were developed and demonstrated to be useful for a given system. The PSSS-VBC/RB, PSSS-S-VBC/RB, and PSSS-VN-VBC/RB polymers can be removed by column chromatography and dialysis [4,5]. It seems that the easiest one is the thermal method, which can be used for removing the PNIPAM-VBC/RB polymers. The method is based on the observation that the polymer displays the low critical solubility temperature (LCST) (Fig. 2). It can be easily removed from the reaction mixture by heating the reaction mixture up to about 35 °C, which is not difficult from a technological point of view.
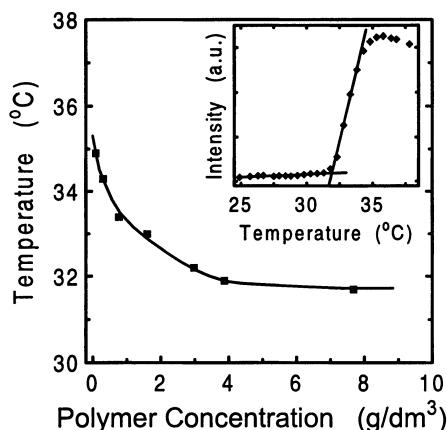
Fig. 2 Phase diagram for PNIPAM-VBC/RB4 – water system. Insert: dependence of the intensity of the scattered light on temperature of the solution for the PNIPAM-VBC/RB at the concentration 4.0 g/dm^3.

CONCLUSIONS

The new efficient photosensitizers for the oxidation of organic compounds were synthesized. The polymers contain rose bengal chromophores attached to the polymer chain. They are very efficient generators of singlet oxygen in methanol and in aqueous solutions. The polymers can be used as photosensitizers in oxidation of such compounds as phenol in water. The PNIPAM-VBC/RB polymers are the most promising. They are homogenous photosensitizers in aqueous solutions at room temperature. That is why they are very efficient generators of singlet oxygen and very efficient photosensitizers in oxidation reaction. What is important, they can be very easily removed from the reaction mixture.

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