Porphyrin-Containing Photosensitizer Obtained via Controlled Radical Polymerization

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Summary: Block amphiphilic copolymer, poly(sodium styrenesulfonate-block-5-(4-acryloyloxyphenyl)-10,15,20-tritolylporphyrin) (PSSS-block-Po) was synthesized by nitroxide-mediated controlled radical polymerization. The polymer is soluble in water and can absorb light in the visible region. The absorbed energy migrates between the porphyrin chromophores. The polymer chains form nanospheres in aqueous solution. Their interiors are highly hydrophobic and can effectively solubilize the large hydrophobic molecules of the various organic compounds (pyrene, azulene, rubrene). The polymer photosensitizes oxidation of organic compounds via photoinduced electron transfer and/or via formation of singlet oxygen. The effect of the architecture, chain properties and Po content on the photochemical properties of the porphyrin-containing photosensitizers was also discussed.

Keywords: controlled radical polymerization; photochemistry; photosensitizer; polyelectrolytes; porphyrins

Introduction

In our previous studies we have developed a series of photosensitizers belonging to the class of so-called antenna polyelectrolytes. The macromolecules of these polymers are constructed from the hydrophilic and hydrophobic units in appropriate molar ratios. They dissolve in water but, due to the unfavorable interactions of the hydrophobic part of macromolecule with water, they adopt pseudomicellar conformation. Therefore in aqueous solutions they form hydrophobic microdomains in which the sparingly water soluble organic compounds can be easily solubilised. The hydrophobic units of macromolecules are usually constructed from the chromophores absorbing light in the near-UV spectral region. The energy absorbed by polymeric chromophores migrates along the polymeric chain and can be transferred to the solubilised compound inducing their photochemical reactions.

The amphiphilic copolymers containing defined blocks of chromophores have been shown to be especially effective photosensitizers.[1–3] For that reason we have become interested in the possibility of using controlled radical polymerization for synthesis of such polymers. Controlled radical polymerization proved to be a very useful method for synthesis of macromolecules characterized by low degree of polydispersity, accurate molecular weight, and well-defined architecture.[4] For that purpose we have used the procedure which we have developed earlier to obtain poly(sodium styrenesulfonate-*block*-N-naphthalene) (PSSS-*block*-VN) copolymer.[2] That method is a modification of the synthetic approach originally developed by Georges and coworkers.[4] We have applied that method to synthesize a new porphyrin-containing block copolymer showing a very promising photosensitizing properties. In this paper we would like to compare this polymer to the other two porphyrin-containing polyelectrolytes that we studied before and to discuss the advantages and disadvantages of each polymer in the aspect of their application as photosensitizers.

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Synthesis

The PSSS macroinitiator was prepared via ''living'' free radical polymerization using the modified method of Georges and coworkers.[5] DMSO-water (9:1 v/v) mixture was used as a solvent. A mediator, TEMPO (2,2,6,6-tetramethyl-1-piperidynyloxy, free radical) was replaced by a more hydrophilic one, HTEPMO in order to reduce the amount of mediator needed in the reaction mixture (in original procedure 10 mol % of TEMPO and 5 mol % of initiator were used). The acetic anhydride was introduced to the polymerization mixture to accelerate the reaction and reduce the amount of dead chains. The results of chain extension test indicated that obtained polymer behaves like a ''living'' system and can undergo the chain extension reaction. In the second step 5-vinyl(4-acryloyloxyphenyl-10,15,20-tritolylporphyrin) was added to PSSS macroinitiator. To obtain well-defined polymer and avoid thermal degradation, the conversion of Po was kept low (about 6%). The copolymer was dialyzed (Fisher, cellulose tubing, cutoff 12 000–14 000 g mol^{-1}) and freeze-dried. The polymer obtained as a green powder was soluble in water.

Physicochemical Properties of Synthesized PSSS-*block*-Po

The synthesized amphiphilic copolymer was well soluble in water and DMSO. It was characterized using gel permeation chromatography (GPC) and dynamic light scattering (DLS). The GPC measurements carried out for PSSS-*block*-Po with the refractive index detector and UV detector (at $\lambda_{abs} = 422$ nm, characteristic for Po absorption) have showed one, narrow chromatographic peak eluted at the same retention time (see Figure 1A and 1B). That indicated that the system consists of one polymer, not a mixture and confirms that Po units are really attached to the PSSS chain. The comparison of the traces for PSSS and PSSS-*block*-Po (Figure 1A) indicated that there was no noticeable destruction of the polymer chain at the second step of the polymerization. The M_w value for PSSS-*block*-Po was estimated to be 50 000 g/mol based on the characteristics (molecular weight and polydispersity) of PSSS macroinitiator and the polymer composition determined from its ^{1}H NMR spectrum.

The NMR spectrum, measured in D_2O, confirmed the presence of the porphyrin block. There are no sharp signals from Po units in the range characteristic for aromatics (6.0–8.0 ppm) as we observed earlier in the NMR spectrum of the random PSSS-*stat*-Po copolymer.[6] This is due to a strong coupling of Po units in the block. We have also observed the shift of the signal characteristic for three outer methyl groups of Po from 2.01 ppm in random copolymer spectrum to 2.70 ppm in block copolymer, suggesting the presence of highly hydrophobic microdomains in aqueous solution of PSSS-*block*-Po. The composition of the copolymer was determined on the basis of the integrations of selected signals in its ^{1}H NMR spectrum and it was found that the polymer contains 87 wt % SSS and 13 wt % Po.

The effective polymeric photosensitizer should adopt the compact, pseudomicellar conformation in water, forming the hydrophobic microdomains of chromophores. We have tested three different Po-containing polyelectrolytes to analyze and compare the hydrophobicity of the pseudomicelles formed by their macromolecules in water: PSSS-*block*-Po, PSSS-*stat*-Po (19 wt % Po units), and polymer where Po chromophore was covalently attached to the end of the poly- (methacrylic acid) chain (PMA-Po). In these studies pyrene was used as a polarity-sensitive probe. It is known that the intensity of the vibronic fine structure in pyrene monomer fluorescence strongly depends on solvent polarity.[7] The ratio of the intensity of peaks III and I is generally used to measure the micropolarity of the environment.

The microdomain hydrophobicity of the PSSS-*block*-Po copolymer was found to be higher than that that for PSSS-*block*-Cz[3]

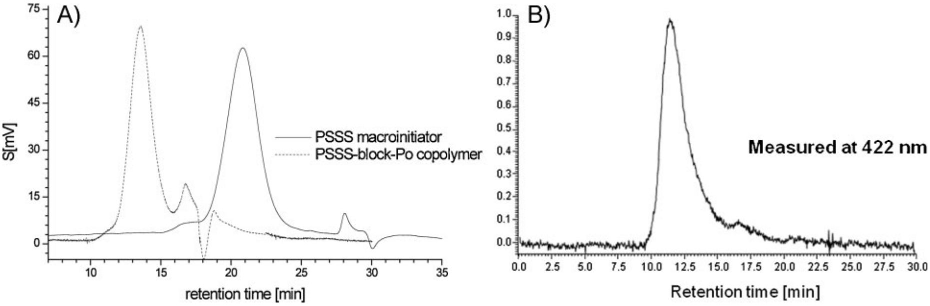


Figure 1.
The comparison of the chromatograms for PSSS macroinitiator and PSSS-block-Po copolymer from the refractive index detector (A) and the chromatogram for the PSSS-block-Po copolymer from the UV/Vis detector measured at 422 nm (B).

but lower than that for PSSS-*block*-VN.[2] That reflects the effect of the content of hydrophobic units in the block as well as the nature of the monomer used. The micropolarity of PSSS-*block*-Po was also much higher than for the random copolymer (PSSS-*stat*-Po) and was comparable to that of toluene. Very interesting results were obtained for PMA-Po. Due to the fact that conformation of the PMA chain is strongly pH-dependent, the micropolarity of the polymer microdomains changes dramatically with the pH of its aqueous solution. Therefore in basic conditions the porphyrin end-group is exposed to surrounding water whereas in acids the chain will adopt compact conformation with the Po chromophore ‘‘hidden’’ inside the hydrophobic microdomain.

Photochemical Properties of PSS-Po Photosensitizers

The fluorescence spectrum of Po in PSSS-block-Po ($pH = 9$) shows two Q porphyrin bands with maxima at 656 and 720 nm, while the spectrum for its acidic form ($pH = 1$) displays only one band with maximum at 701 nm. In both cases the fluorescence emission is weak. The quantum yield for the fluorescence of Po chromophores in aqueous solutions of PSSS-*block*-Po was determined (using tetratolylporphyrin as a standard; $\varphi_f = 0.11$ in benzene[8]) to be $\varphi_f = 0.0012 \pm 0.0001$. The value is very low, most probably due to the highly compact conformation of the copolymer with Po chromophores squeezed in a small volume. That induces their strong mutual interactions which are manifested by the quenching of the fluorescence. The micropolarity measurements suggest that the polymer chains of the statistical copolymer form less compact pseudomicelles which can be easily penetrated by water. For the PSSS-*stat*-Po the fluorescence quantum yield for Po chromophores was found to be higher than that for the block copolymer ($\varphi_f = 0.070 \pm 0.005$). That fact rules out the possibility of quenching of excited singlet state of Po by water and indicates that the mutual interactions between Po chromophores are responsible for observed lowering of Po emission. Since the Po chromophores in PMA-Po are placed only at the end of the polymeric chain there is no mutual quenching observed, porphyrin units are protected by surrounding PMA units and the quantum yields are much higher. Quantum yield values for Po chromophores of PMA-Po are also pH dependent and while at $pH = 13.0$ the φ_f value was found to be 0.295, at $pH = 3.5$ the extremely high values close to 1.0 were obtained ($\varphi_f = 0.993$). Such high quantum yield may be justified by the fact that under these experimental conditions Po chromophore are well isolated from the surrounding environment by the compact and highly hydrophobic pseudomicelle formed by PMA chain.

Photoinduced Electron Transfer

To demonstrate the usefulness of our polymeric system as a photosensitizer in photoinduced electron transfer processes, we have carried out the experiment in which the electron donor (polymeric Po chromophores) is trapped in hydrophobic polymeric microdomain while electron acceptor resides in water. We have chosen the SPV (4,4′-bipyridyl-1,1′-bis(propanesulfonate) as the electron acceptor, because it is well soluble in water, and it is electrostatically neutral. The process can be described by equation:

$$^{1}Po^{*} + SPV = Po^{\bullet +} + SPV^{\bullet -} \tag{1}$$

The measurements of the steady-state fluorescence spectra of PSSS-Po copolymers in aqueous solution in the absence and in the presence of SPV have shown that SPV quenches efficiently the emission of porphyrin polymeric chromophores. The quenching process can be described by the Stern-Volmer kinetic equation expressed as a dependence of the ratio of the fluorescence intensities (I_0/I) of Po on the SPV concentration. The values of the quenching constant of Po polymeric chromophores in aqueous solutions of polymers studied, calculated from the linear fit, are presented in Table 2.

Table 1.
Micropolarity of the pyrene in various environments (in solvents and in the polymeric microdomains formed in water).

Environment	I_{III}/I_{I} *
PMA-Po in basic conditions	**0.56**
Water	0.63
Methanol	0.75
PSSS-*stat*-Po	**0.77**
PSSS-block-VCz	**0.81**
Toluene	0.90
PSSS-*block*-Po	**0.92**
PMA-Po in acidic conditions	**1.01**
PSSS-*block*-VN	**1.08**
n-Hexane	1.65

*The ratio of the intensity of the peaks III and I in the fluorescence spectrum of pyrene in various environments

Table 2.
Quenching constant values calculated from the linear fits to the Stern Volmer equation.

Polymer	Quenching constant [M^{-1} s^{-1}]
PSSS-*stat*-Po	$(3.10 \pm 0.30) \times 10^{11}$
PSSS-*block*-Po	$(1.29 \pm 0.04) \times 10^{11}$
PMA-Po at pH = 3.5	$(1.50 \pm 0.30) \times 10^{10}$
PMA-Po at pH = 13.0	$(5.40 \pm 0.20) \times 10^{10}$

For all the polymeric photosensitizers studied an effective quenching of the fluorescence of Po chromophores by SPV was observed indicating that in all systems the photoinduced electron transfer occurs.

Process of the photoinduced electron transfer is reversible and in homogenous solutions the formation of the products is very difficult to be observed. In our systems, however, the back reaction should be retarded. The SPV radical anion, once formed in the primary photochemical process, should be expelled from the polyanion chain. That should result in the separation of the charges in the $_{\text{pair}}$ Po-SPV pair, as schematically presented in Figure 2.

Since the radical anion of SPV shows a characteristic absorption spectrum with the maxima at 399 nm and 610 nm the process of charge separation can be followed by spectrophotometric measurements in the UV/Vis region. Figure 3 shows the absorption spectra for the PSSS-*stat*-Po + SPV + TEA system before and after 2 and 15 minutes of irradiation with the light of 425 nm absorbed only by the Po chromophores. TEA (triethanoloamine) acts in our system as an additional, sacrificial electron donor. The new bands are observed at the wavelengths confirming the presence of the SPV radical anion and the solution color changes from yellowish to blue.

The similarly effective charge separation occurred when PMA-Po (at pH = 3.5) was tested as photosensitizer. On the other hand for our block copolymer (PSSS-*block*-Po) due to the high mutual quenching of the Po chromophores the concentration of the

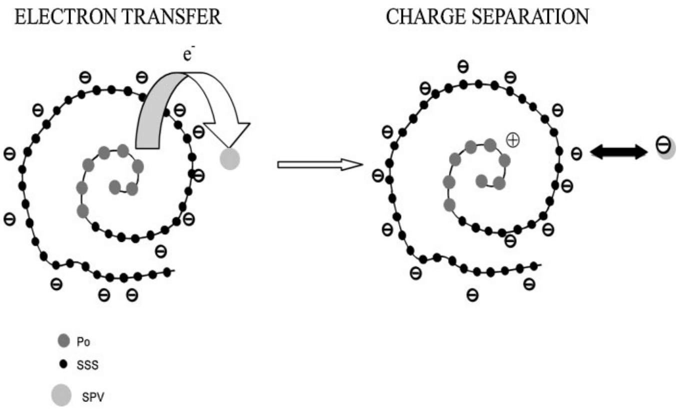


Figure 2.
Schematic illustration of the Po/SPV ion pair formation by the photoinduced electron transfer and charge separation.

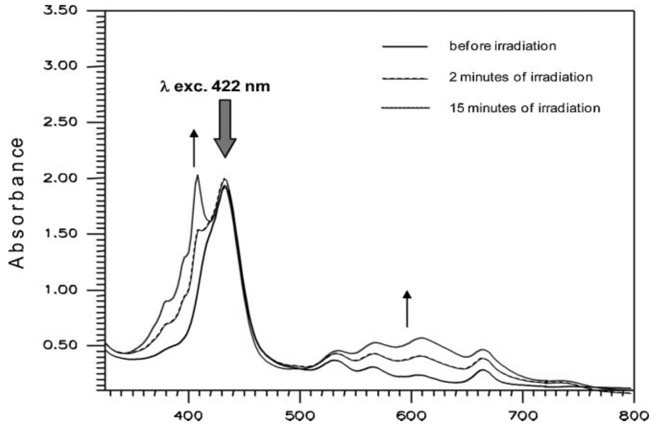


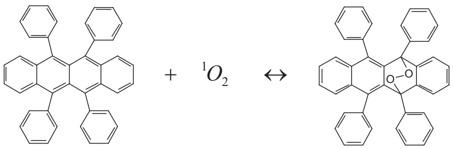
Figure 3.
UV/VIS spectra of the PSSS-*stat*-Po + SPV + TEA system before and after 2 and 15 minutes of irradiation with the light of 425 nm.

SPV radical anion formed was too low to be detected.

Photooxidation of Rubrene

The advantages of the highly compact conformation of the PSSS-*block*-Po photosensitizer, however, are well pronounced in the studies of the process of photosensitized oxidation of rubrene. The highly hydrophobic microdomains formed by the blocks of Po units of this copolymer in aqueous solutions provide good solubilizing medium, low sensitivity of the chromophoric groups to pH and effective migration of absorbed energy along the polymeric chain. The photooxidation of rubrene was induced by irradiation with monochromatic light at 425 nm and most likely occurs with the participation of singlet oxygen according to the equations:

$$Po^{3*} + {}^{3}O_2 \rightarrow Po^{0} + {}^{1}O_2 \qquad (2)$$



(3)

The reaction was again followed by measuring the absorption spectra of the system upon irradiation. The disappearance of the rubrene bands due to its oxidation was observed. The reaction kinetics could be best fitted by the second-order kinetics and the kinetic constant was found to be $k_{ox} = (3{,}1 \pm 0{,}1) \times 10^{-2}$ $[M^{-1}\ min^{-1}]$. The quantum yield of this reaction was calculated to be 5.16×10^{-3}. PSS-*stat*-Po was found to be less effective photosensitizer in the photooxidation process and the PMA-Po polymer was rather ineffective due to its low Po chromophores content.

Conclusion

Block copolymer containing porphyrin chromophores (PSSS-*block*-Po) was synthesized using controlled radical method and its properties were compared with previously obtained block copolymers containing the same ionic sequences (PSS) and various hydrophobic ones; VN and VCz, respectively. The amphiphilic PSSS-*block*-Po copolymer displays interesting physicochemical properties such as very high hydrophobicity of the microdomains formed by its compact chains in aqueous solutions and high solubilizing properties of the sparingly water soluble compounds. It has been shown to be more effective photosensitizer in the photoinduced oxidation of rubrene then its statistical analogue. The effect of the architecture, chain properties and Po content on the photochemical properties of the porphyrin-containing photosensitizers was established. with the special emphasis on the photoinduced electron transfer processes.

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