Synthesis and Properties of Water-Soluble Poly(sodium styrenesulfonate-*block*-5-(4-acryloyloxyphenyl)-10,15,20-tritolylporphyrin) by Nitroxide-Mediated Free Radical Polymerization

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ABSTRACT: The new block amphiphilic copolymer, poly(sodium styrenesulfonate-*block*-5-(4-acryloyloxyphenyl)-10,15,20-tritolylporphyrin) (PSSS-*block*-Po), was synthesized by nitroxide-mediated "living" radical polymerization. The polymer is soluble in water and can absorb light in the visible region. The absorbed energy migrates between the porphyrin (Po) polymeric 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.

Introduction

"Living" free radical polymerization has recently attracted considerable attention as a very useful method for synthesis of macromolecules characterized by low degree of polydispersity, accurate molecular weight, and well-defined architecture.[1] The possibility of applying that technique for synthesis of block copolymers is especially attractive as it allows to overcome restrictions of traditional living polymerization methods. We have become interested in the possibility of using "living" free radical polymerization for synthesis of water-soluble polymeric photosensitizers. The amphiphilic copolymers containing defined block of chromophores have been shown to be especially active photosensitizers.[2,3]

This paper reports on the synthesis and properties of the novel amphiphilic block copolymer containing porphyrin chromophores, poly(sodium styrenesulfonate-*block*-5-(4-acryloyloxyphenyl)-10,15,20-tritolylporphyrin) (PSSS-*block*-Po). The polymers containing porphyrin chromophores are intensively studied due to their special importance, both as effective photosensitizers and as models for natural systems involved in photosynthesis.[4−8] There are, however, very few examples of water-soluble systems and *none* in which the porphyrin chromophores are present as a block.

Experimental Section

Instruments and Procedures. Gel permeation chromatography (GPC) analyses were carried out using a Waters chromatograph with diode-array UV/vis and refractive index detectors. Separation was achieved with three PL−aquagel−OH (pore size: 30, 40, 50 Å) columns, and the eluent was a mixture of methanol/aqueous solution of 0.3 M NaCl and 0.01 M NaH_2PO_4 at pH = 9 (20/80 v/v). The columns were calibrated with PSSS standards (10 samples with the molecular weights, M_w, from 1500 to 780 000) from Polysciences.

The light scattering measurements were performed using Malvern Instruments ZETASIZER 3000HS. The sample was dissolved in 0.1 M NaCl aqueous solution at pH = 7.0 and at room temperature. UV/vis spectra of the samples were obtained using a HP 8452A diode-array spectrophotometer. The ^{1}H NMR spectra for the polymer were measured in D_2O and DMSO solutions and for the model porphyrin in $CDCl_3$, using a Bruker AMX 500 spectrometer. Steady-state fluorescence spectra were measured at room temperature, using a SLM Aminco 8100 spectrofluorometer with L-type geometry. The phase shift and demodulation measurements of fluorescence lifetimes were done using a SLM Aminco 48000S lifetime spectrofluorometer with the 450 W xenon lamp as a light source. All lifetime measurements were done at least at 10 different modulation frequencies from the range of 10−110 MHz using glycogen as a reference ($\tau = 0.0$ ns). The solutions used for the lifetime measurements were degassed by bubbling with argon. All fluorescence decay profiles showed two components: the short one (small fraction, in the range of picoseconds) and the long one (fraction reaching 80%, in the range of nanoseconds) and were fitted to double-exponential function $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. The mean values of the fluorescence lifetimes for porphyrin (Po) chromophores were calculated according to the equation[8] $\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

The irradiation of the samples in photochemical experiments was carried out using medium-pressure mercury lamp ASH-400. The interference filter at $\lambda = 425$ nm was used to obtain the monochromatic light absorbed only by the porphyrin chromophores. The light intensity was measured using ferrioxalate actinometer[9] to be $I = (2.7 \pm 0.1) \times 10^{-9}$ einstein/s.

Materials. Sodium styrenesulfonate (SSS, Monomer-Polymer & Dajac Laboratories, technical) was purified by recrystallization from 9:1 mixture of methanol and water at 60 °C and dried under vacuum. 5,10,15,20-Tetra-*p*-tolyl-21*H*,23*H*-porphine (dye content 97%, Aldrich) and 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (TPP) (99+%, Aldrich) were used as received. 5-Vinyl(4-acryloyloxyphenyl-10,15,20-tritolylporphyrin) (Po) was synthesized as described eariler.[6] Sodium hydrogen sulfite ($NaHSO_3$, Fluka, solution for synthesis, 38−40% in water), potassium persulfate ($K_2S_2O_8$, Aldrich, 99.99%), dimethyl sulfoxide (DMSO, Aldrich, 99.9%), acetic anhydride (Aldrich, 99+%), 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy free radical (HTEMPO, Aldrich, 98%), K_2HPO_4 (POCH Gliwice, 99.9%), NaH_2PO_4 (POCH Gliwice, 99.9%) (used to prepare the phosphate buffer pH = 6.9), hexane (POCH Gliwice, for IR, UV, and HPLC), benzene (Byk-Mallinckrodt, spectro-grade), glycogen (POCH Gliwice, p.a.), and methanol (POCH Gliwice, 99.8%) were used as received. Pyrene (Aldrich, 99%) was purified by zone refining. Triethanolamine (TEA) was distilled under vacuum. 4,4′-Bipyridyl-1,1′-bis(propanesulfonate) (sulfopropyl viologen, SPV) was prepared according to the procedure described in the literature.[10] The aqueous solutions were prepared using deionized water.

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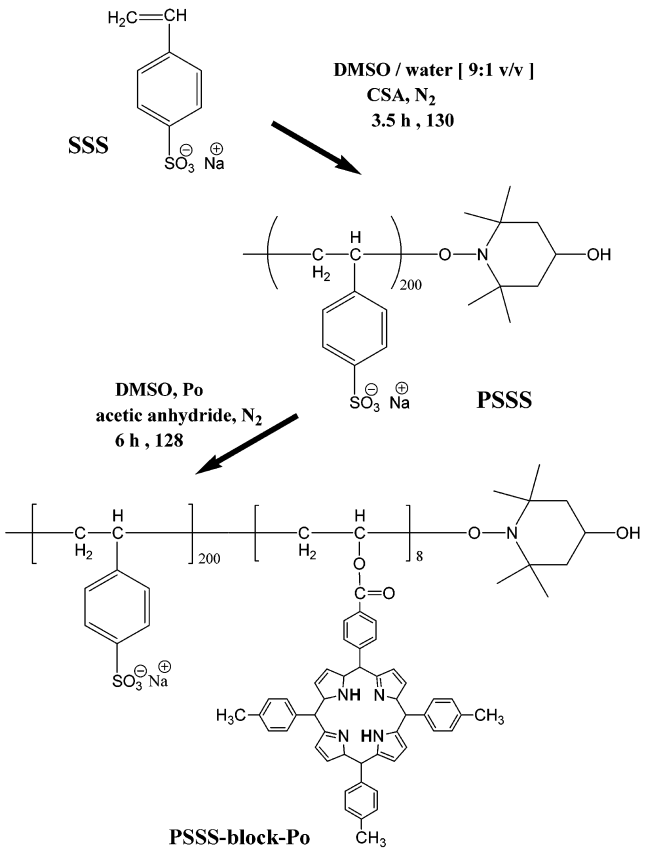
Scheme 1



Synthesis of Copolymer. The PSSS-*block*-Po copolymer was obtained by a two-step synthesis (see Scheme 1). In the first step poly(sodium styrenesulfonate) (PSSS) terminated with HTEMPO was synthesized. In the second step, this polymer was used as a macroinitiator in synthesis of the copolymer.

a. Synthesis of PSSS. The PSSS macroinitiator was prepared via "living" free radical polymerization using the modified method originally developed by Georges and coworkers.[11] The procedure was modified to accelerate the reaction and reduce the amount of dead chains, as described earlier.[3] The concentrations of reagents used in the polymerization were as follows: SSS (1.39 M), HTEMPO (0.021 M), $K_2S_2O_8$ (0.014 M), $NaHSO_3$ (0.014 M), and CSA (0.01 M). The polymerization was carried out in a mixture of DMSO and water (9:1 v/v) under nitrogen at 130 °C for 3.5 h. The conversion of SSS was deliberately kept low (30%). The resulting polymer (PSSS) was precipitated into 1-butanol, filtered, washed with diethyl ether, and dried in a vacuum oven at 40 °C. The polymer was dissolved in water, dialyzed (Fisher, cellulose tubing, cutoff 12 000−14 000 g mol^{-1}), and freeze-dried. The results of chain extension test indicated that obtained polymer behaves like a "living" system and can undergo the chain extension reaction.

b. Synthesis of PSSS-*block*-Po. 5-Vinyl(4-acryloyloxyphenyl-10,15,20-tritolylporphyrin) (75 mg) and PSSS macroinitiator (30 mg) were dissolved in DMSO solution (2 mL). To accelerate the reaction, the acetic anhydride was added at the concentration of 2×10^{-4} M, and the homogeneous solution was heated at 128 °C for 6 h under argon with vigorous stirring. To obtain well-defined polymer and avoid thermal degradation, the conversion of Po was kept low (about 6%). The resulting copolymer was soluble in water. It was first precipitated into acetone, filtered, and dried. Then the polymer was dissolved in water, dialyzed (Fisher, cellulose tubing, cutoff 12 000−14 000 g mol^{-1}), and freeze-dried. The polymer in a form of green powder was obtained.

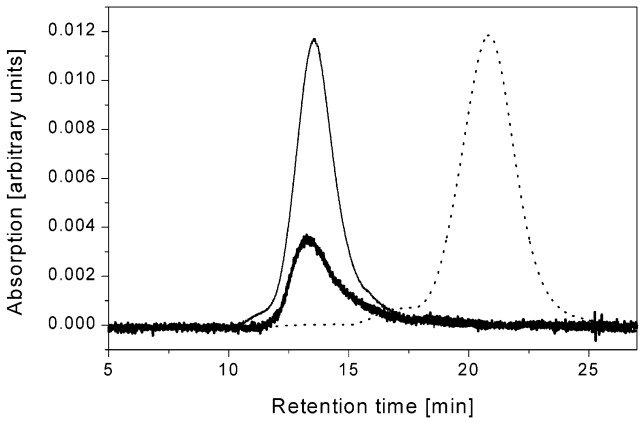


Figure 1. GPC chromatograms for PSSS macroinitiator (···) and PSSS-*block*-Po (UV detector, absorbance measured at two wavelengths, $\lambda = 262$ nm for SSS (—) and $\lambda = 422$ nm for Po (—).

Results and Discussion

Physicochemical Properties of PSSS-*block*-Po. PSSS-*block*-Po copolymer was soluble in water and DMSO. It was characterized by GPC, light scattering techniques, NMR, and UV/vis (absorption and emission) spectroscopy. The GPC analyses of PSSS-*block*-Po were performed by the measurements of PSSS macroinitiator synthesized in the first stage of reaction. It was found that the PSSS macroinitiator is characterized by the weight-average molecular weight (M_w) of 44 000 g/mol and the polydispersity of 1.35. The GPC measurements carried out for PSSS-*block*-Po with the refractive index detector and UV detector have indicated clearly that the system consists of one polymer, not a mixture (see Figure 1). The traces recorded with the UV detector (simultaneously at two wavelengths) indicated the presence of the Po chromophores ($\lambda_{abs} = 422$ nm) as well as SSS chromophores ($\lambda_{abs} = 262$ nm). This proves that Po units are really attached to the PSSS chain. The comparison of the traces for PSSS and PSSS-*block*-Po indicated that there was no noticeable destruction of the polymer chain at the second step of the polymerization. The molecular weight of PSSS-*block*-Po copolymer could not be determined from our GPC measurements. One has to take into account the expected change in the effective hydrodynamic volume of PSSS-*block*-Po polymer chain due to the presence of hydrophobic Po units. 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 as described below.

The composition of the copolymer was determined on the basis of the integrations of selected signals in its ^{1}H NMR spectrum. The sharp signal of three methyl groups of Po chromophore ($\delta = 2.6$ ppm, s, 9H) and PSSS broad aromatic signals ($\delta = 6.7$ and 7.5 ppm, m, 4H) were taken for calculations. It was found that the polymer contains 87 wt % SSS and 13 wt % Po—this gives the molar ratio of 25:1 (SSS:Po). Taking into account the molecular weight of the PSSS precursor, one can estimate that statistically each polymer chain of PSSS-*block*-Po contains 8 Po units, on average. The NMR spectra confirmed also the presence of the porphyrin block. Only two broad bands can be observed in the range characteristic for aromatics (6.0−8.0 ppm). There are no sharp signals from Po units observed earlier in the NMR spectrum of the random copolymer

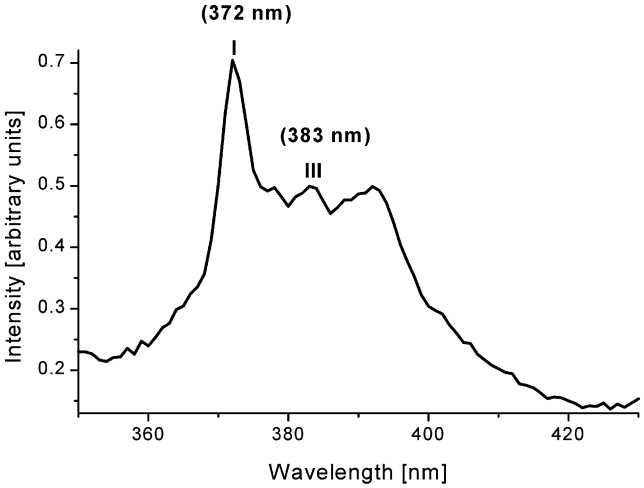


Figure 2. Fluorescence emission spectrum of pyrene solubilized in the PSSS-*block*-Po microdomains.

(PSSS-*stat*-Po).[6] This is due to a strong coupling of Po units in the block. Furthermore, the signal of three outer methyl groups of Po is shifted from 2.01 ppm in random copolymer spectrum to 2.70 ppm in block copolymer. That signal for the model porphyrin (TPP) in $CDCl_3$ was also observed at 2.70 ppm. This can be explained considering that the microenvironment of the Po units in aqueous solution of PSSS-*block*-Po is quite hydrophobic.

The presence of highly hydrophobic microdomains in aqueous solution of PSSS-*block*-Po was confirmed using pyrene 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.[12] The ratio of the intensity of peak III to peak I is generally used as a sensitive measure of the environmental micropolarity. Thus, pyrene was solubilized in aqueous solution of PSSS-*block*-Po, its fluorescence spectrum was measured (see Figure 2), and the ratio of I_{III}/I_I was determined to be 0.92. The value is considerably higher than that in water ($I_{III}/I_I = 0.59$) and higher than that characteristic of typical micelles (e.g., in hexadecyltriethylammonium bromide micelles the I_{III}/I_I ratio was 0.72). It is comparable with toluene ($I_{III}/I_I = 0.90$). This provides another evidence for the high hydrophobicity of the interior of PSSS-*block*-Po copolymer. Thus, the polymer is expected to solubilize molecules of various organic compounds.

We suggest that the polymer chain of PSSS-*block*-Po adopts a pseudomicellar conformation in which the hydrophobic Po units form the hydrophobic core which is surrounded by the hydrophilic shell created by the SSS polymeric units. The light scattering measurements indicated that the polymer chains are organized as the nanospheres with the diameter of 72 nm (see Figure 3).

Photochemical Properties of PSSS-*block*-Po. Figure 4 shows the characteristic for porphyrin macrocycle band (Soret band) in the absorption spectrum of aqueous solution of PSSS-*block*-Po. The shape of the spectrum and the positions of the absorption bands are dependent on the pH of the solution. The Soret band displays a maximum at 422 nm for the solution of pH from 3.5 to 13 and shows two maxima at 422 and 444 nm for the solution of pH below 3.5. It was noticed, however, that the absorption spectrum characteristic of the Po chromophores in PSSS-*block*-Po is considerably less pH-sensitive than that for random copolymer PSSS-*stat*-

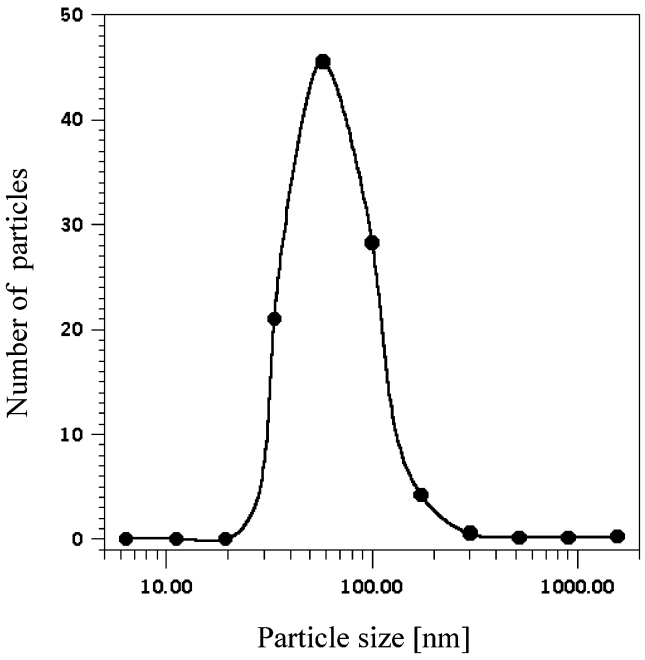


Figure 3. Particle size distribution for aqueous solution (0.1 M NaCl) of PSSS-*block*-Po measured by dynamic light scattering.

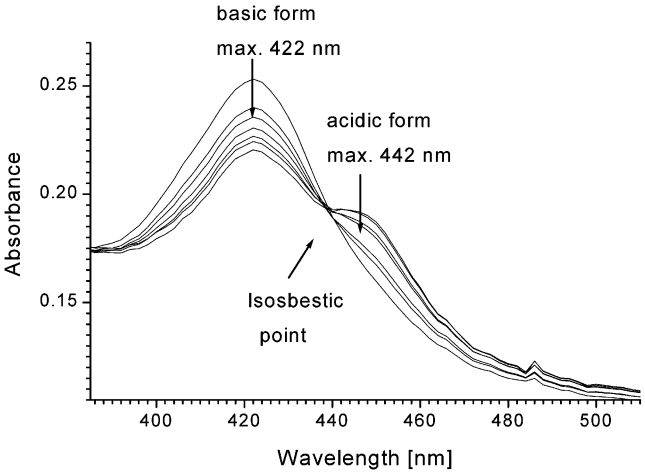


Figure 4. UV/vis absorption spectrum of PSSS-*block*-Po in aqueous solution at various pH.

Po. For random copolymer the isosbestic point was observed at pH values in the range 5.5−7, and the change from the basic form to the acidic form with decreasing pH was fast and complete. Although for the block copolymer the two forms, acidic and basic, are also clearly distinguishable, the isosbestic point is observed at the considerably lower pH values being in a range from 3.5 to 1.0 (even for more acidic solutions two forms are still present). This suggests again that the PSSS-*block*-Po in aqueous solution forms pseudomicelles whose interior is highly hydrophobic and therefore difficult to be penetrated by protons.

The fluorescence spectrum of the basic form of Po in PSSS-*block*-Po (pH = 9) shows two 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 (see Figure 5). In both cases the fluorescence emission is weak. The quantum yield for the fluorescence of Po chromophores in PSSS-*block*-Po (φ_f) in water (at pH ≈ 6.0) was determined using tetratolylporphyrin

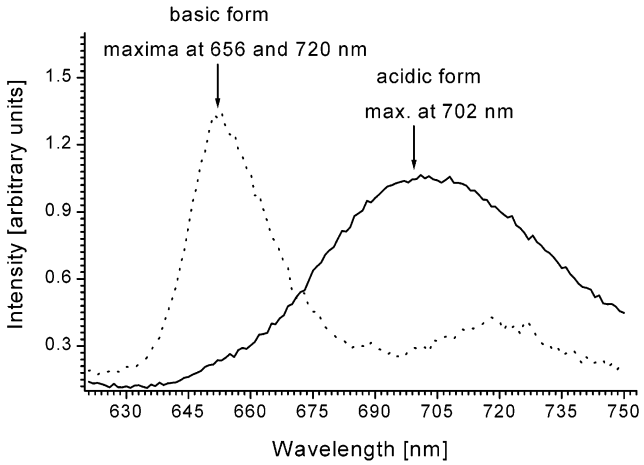


Figure 5. Fluorescence emission spectra of the basic (pH = 9) and acidic (pH = 1) forms of PSSS-*block*-Po in aqueous solution.

(TTP) as a standard ($\varphi_f = 0.11$ in benzene).[13] In aqueous solution it was found that $\varphi_f = 0.0012 \pm 0.0001$. The value is very low. This confirms the assumption that the conformation of the polymer is indeed highly compact. The Po chromophores are squeezed in a small volume. This induces their strong mutual interactions which are manifested by the quenching of the fluorescence of Po chromophores. The nonradiative processes are the most probable energy dissipation channels in that system. Such an explanation is supported by the observation that for the statistical copolymer of SSS and Po (PSSS-*stat*-Po,19 wt % Po), which we have synthesized and studied before,[6] the quantum yield for the fluorescence of Po chromophores was much higher ($\varphi_f = 0.070 \pm 0.005$) than for the block copolymer. The polymer chains of the statistical copolymer form pseudomicelles which can be easily penetrated by water, considerably easier than these formed by the block copolymer. Despite the presence of water, the fluorescence quantum yield for statistical copolymer is much higher. This 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.

The measurements of the degree of fluorescence polarization for solubilized rhodamine B were carried out to confirm the energy migration between porphyrin chromophores in PSSS-*block*-Po. Soutar and Philips[14] showed that energy migration in polymers can be monitored by determining the degree of polarization, p, of directly and indirectly (via energy transfer) excited probe molecule that has been solubilized by the polymer. Rhodamine B was chosen for its spectral properties, which were most suitable for our studies. It was possible to excite its molecules either directly (at 552 nm) or indirectly (at 422 nm) through the energy transfer from polymeric Po chromophores. The degree of polarization, p, can be calculated using the following equation:[15]

$$p = (I_{VV} - GI_{VH})/(I_{VV} + GI_{VH}) \qquad (1)$$

where $G = I_{HV}/I_{HH}$ is the instrument correction factor; the first index in the subscript represents the position of the excitation polarizer (H = horizontal, V = vertical), and the second index represents the position of the emission polarizer.

The values of $p_d = 0.169 \pm 0.001$ for direct and $p_i = 0.046 \pm 0.007$ for indirect excitation were found. The fluorescence anisotropy r[15]

$$r = (I_{VV} - GI_{VH})/(I_{VV} + 2GI_{VH}) \qquad (2)$$

was found to be $r_d = 0.119 \pm 0.001$ for direct and $r_i = 0.031 \pm 0.005$ for indirect excitation.

These results show a significant depolarization of the fluorescence emission of rhodamine B solubilized in the PSSS-*block*-Po microdomains. These data suggest that the effective energy migration between Po chromophores occurs in our copolymer. The value of p_d determined for our system is comparable with these found for micelles of surfactants (sodium dodecyl sulfate),[16] which indicates that the rigidities of these two environments are similar. For comparison, the intrinsic fluorescence polarization (p_0) of rhodamine B is known to be nearly the maximum possible value of 0.5.[17]

Azulene was used to study the possibility of the energy transfer from the polymeric Po chromophores to the probe solubilized in aqueous solution of PSSS-*block*-Po. Azulene was used as an energy acceptor to ensure that the energy transfer will be energetically favorable ($E_S = 184$ kJ/mol for TTP[18] (model for Po chromophores) and $E_S = 170$ kJ/mol for azulene[9]). Thus, one can expect that the intensity of fluorescence of Po chromophores in the polymer should decrease in the presence of azulene. However, quite the puzzling effect was observed in our system. When a very small amount of azulene (total concentration up to 5×10^{-5} M) was added to aqueous solution of PSSS-*block*-Po, the emission intensity of Po chromophores increased. The addition of azulene at higher concentration led to the expected decrease in the intensity of fluorescence for Po. That strange behavior may be explained considering the possibility that solubilized azulene induces less compact conformation and/or disturbs the mutual interactions between Po chromophores. This limits their "concentration" quenching. One can assume that when azulene is solubilized in aqueous solution of PSSS-*block*-Po, two opposite effects can occur in the system. The first involves an increase of the efficiency of Po emission due to the effect of "loosening" of the micellar core after addition of azulene. The second one involves the decrease of Po emission due to the energy transfer to azulene. It seems that at very low concentration of azulene the first one predominates. However, when more azulene is solubilized, the process of energy transfer from Po to azulene becomes more important and the intensity of Po emission decreases, as expected.

To demonstrate the usefulness of our polymeric system for the studies of photoinduced electron transfer, we have carried out the experiment in which the electron donor (polymeric Po chromophores) is trapped in hydrophobic polymeric microdomains while electron acceptor resides in water. We have chosen the SPV as the electron acceptor because it is well soluble in water, and it is electrostatically neutral. To check whether the process of electron transfer between excited Po chromophores and SPV is thermodynamically possible, ΔG for such reaction was calculated using the Rehm−Weller equation:[19]

$$\Delta G = E_D^{ox} - E_A^{red} - E^* + C \qquad (3)$$

where E_D^{ox} is the oxidation potential of the donor ($E_D^{ox} = 1$ eV for TTP),[20] E_A^{red} is the reduction potential of

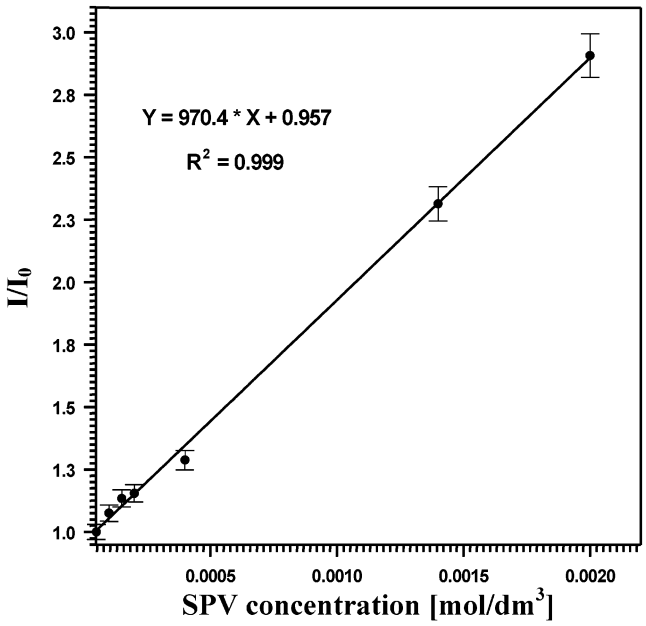


Figure 6. Stern−Volmer kinetics: the dependence of the ratio of the fluorescence intensities (I_0/I) of polymeric Po on the SPV concentration.

the acceptor ($E_A^{red} = -0.37$ eV for SPV),[21] E^* is the energy of electronically excited state of the excited species ($E^* = 1.9$ eV for TTP),[18] and C is an electrostatic correction term, which is typically about 0.1 eV in the polar solvent.

Using these values, it was found that

$$\Delta G = -0.63 \text{ eV} \quad (4)$$

This indicates that the process is thermodynamically favorable.

The measurements of the steady-state fluorescence spectra of PSSS-*block*-Po 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[22] (Figure 6). The value of the quenching constant of Po polymeric chromophores in aqueous PSSS-*block*-Po solution, calculated from the linear fit, was determined to be $k_{qs} = (1.29 \pm 0.04) \times 10^{11}$ M^{-1} s^{-1} ($k_{qs}\tau_0 = 9.7 \times 10^2$ M^{-1}, $\tau_0 = 7.5 \pm 0.2$ ns). The value is high, and it indicates that the system can be very useful for studies of photoinduced electron-transfer processes in aqueous solution.

To study the effectiveness of our copolymer as a photosensitizer, the kinetics of the photosensitized oxidation of rubrene solubilized in aqueous solution of PSSS-*block*-Po was studied. The changes at the maximum of the absorption band characteristic of rubrene (at 302 nm) were monitored after various irradiation times. The reaction was induced by irradiation with monochromatic light at 425 nm (absorbed only by the Po polymeric chromophores—absorption of incident radiation by rubrene is negligible under our experimental conditions), and it most likely occurs with participation of singlet oxygen. It is known that quenching of excited Po with oxygen results in formation of singlet oxygen and rubrene reacts readily with singlet oxygen. The second-order kinetics gave the best fit to the experimental data (see Figure 7). The quantum yield of this reaction (ϕ) has been found to be 5.16×10^{-3}.

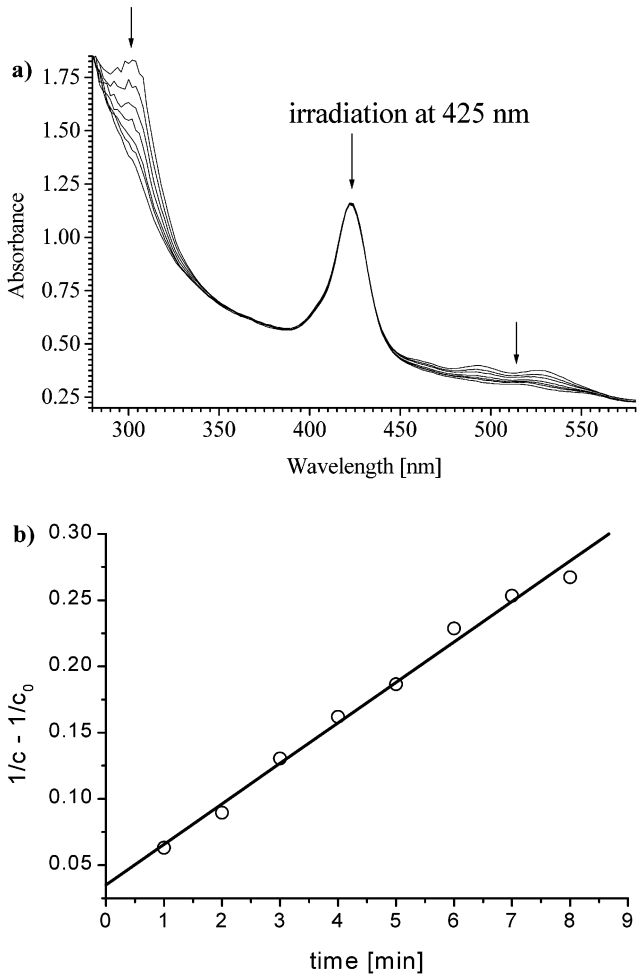


Figure 7. Photosensitized oxidation of rubrene solubilized in aqueous solution of PSSS-*block*-Po (irradiation with light at λ = 425 nm): (a) absorption spectra recorded after various irradiation times; (b) fit of the experimental data to the second-order kinetic equation.

Conclusions

The "living" free radical polymerization was used to obtain a novel block copolymer of well-defined architecture containing porphyrin chromophores. This polymer is soluble in water and can absorb light in the visible spectral region. In aqueous solution it forms nanospheres with highly hydrophobic interior in which the large molecules of sparingly water-soluble hydrophobic compounds (pyrene, rubrene, azulene) can be solubilized. The excitation energy absorbed by the polymer can migrate along the porphyrin polymeric chromophores. It can be also transferred to the molecules of solubilized organic compounds such as azulene or used in photoinduced electron-transfer processes. Thus, the macromolecules of PSSS-*block*-Po can form the nanophotoreactors dispersed in aqueous solution.

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