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Studies of the antenna effect in polymer molecules. 29. Synthesis and properties of poly[sodium styrene sulfonate-*co*-(4-acryolyloxyphenyl)-10,15,20-tritolylporphyrin] in aqueous solution

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Abstract

The novel water soluble antenna polyelectrolyte: poly[sodium styrene sulfonate-*co*-(4-acryolyloxyphenyl)-10,15,20-tritolylporphyrin] (PSSS-Po) was synthesised, and its photophysical and photochemical properties were studied. Solubilisation of the various molecular probes such as pyrene or perylene in aqueous solution of the PSSS-Po proved that the polymer chain adopts the compact conformation. The interior of the polymer pseudomicelle is significantly less polar than water. The effective quenching of polymeric porphyrin fluorescence by sulfopropyl viologen (SPV) can be explained considering the possibility of electron transfer from the singlet-excited state of Po to SPV. This has been supported by measuring an absorption spectrum for PSSS-Po/SPV system after selective irradiation of Po chromophores. The formation of the new absorption bands characteristic for $SPV^{\cdot -}$ radical anion indicated that the charge separation was achieved in that system.

Keywords: Antenna polymer; Polyelectrolyte; Energy transfer

1. Introduction

Recently we have been involved in synthesis of antenna polyelectrolytes [1]. This novel group of the amphiphilic copolymers has been the subject of intensive studies [2–5]. The macromolecules of these polymers are constructed from the hydrophilic and the hydrophobic units in appropriate molar ratios. They are soluble in water but, due to the unfavourable interactions between water and hydrophobic polymeric units, they adopt the pseudomicellar conformation in aqueous solution. This allows the solubilisation of the molecules of sparingly water soluble organic compounds. The hydrophobic part of the macromolecule is usually constructed from the monomers containing chromophores which absorb light from the near UV–visible spectral region. The energy absorbed by the polymeric chromophores can migrate along the polymer chain and can be transferred to the molecule of solubilised compound and induce its photochemical reactions [6].

This paper reports the synthesis of the novel polymer, poly[sodium styrene sulfonate-*co*-(4-acryolyloxyphenyl)-10,15,20-tritolylporphyrin] (PSSS-Po). This copolymer is believed to be of special importance due to the presence of the photoactive porphyrin groups, which display the structural similarities to the chlorophyll, dye involved in natural photosynthesis [7,8].

2. Experimental

2.1. Apparatus

The UV–visible spectra of the samples were obtained using a HP 8452A Diode-Array spectrophotometer. The ^{1}H NMR spectra of the polymer were measured in solution of D_2O using Bruker AMX 500 spectrometer. Steady-state fluorescence spectra were measured at room temperature, using SLM Aminco 8100 spectrofluorometer in the L-type geometry. The phase shift and demodulation measurements of fluorescence lifetimes were done using SLM Aminco 48000S lifetime spectrofluorometer with the 450 W xenon lamp as a light source. All lifetime measurements were done at a minimum of 10 different modulation frequencies from the range of 10 to 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 results

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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). The lifetime of the excited Po chromophore was calculated as the average lifetime according to the equation [9]: $\tau = A_1\tau_1^2 + A_2\tau_2^2$, where A_1, A_2—the percentage of the component and τ_1,τ_2—the lifetimes of the components. The solutions of PSSS-Po (0.05 g/l), SPV (5×10^{-4} M) and triethanoloamine (TEA, 1×10^{-4} M) used for the photochemical experiments were also degassed by bubbling with argon. The sample was irradiated with light at $\lambda > 395$ nm (xenon lamp and cut-off filter).

2.2. Materials

K_2HPO_4 (POCH Gliwice, 99.9%) and NaH_2PO_4 (POCH Gliwice, 99.9%) (used to prepare the phosphate buffer pH = 6.9), acetonitrile (POCH Gliwice, for HPLC), hexane (POCH Gliwice, for IR, UV and HPLC), benzene (Byk-Mallinckrodt, spectro-grade), glycogen (POCH Gliwice, p.a.), methanol (POCH Gliwice, 99.8%) were used as received. Pyrene (Aldrich, 99%) was purified by zone refining. Triethanoloamine (TEA) was distilled under vacuum. 4,4-Bipyridinium-1,1-bis(trimethylenesulfonate) (SPV) was prepared according to the procedure described in the literature [10]. The solutions were prepared using deionised water.

2.3. Polymerisation

2.3.1. Synthesis of the copolymer of sodium styrenesulfonate (SSS) and 5(acryloyloxyphenyl)-10,15,20-trirolylporphyrin(Po) (PSSS-Po)

SSS (0.2 g), 5(4-acryloyloxyphenyl-10,15,20-tritolylporphyrin (Po) (0.05 g), and 2,2-azobis(isobutyronitrile) (AIBN) (0.005 g) were dissolved in dry dimethylacetamide (4.75 ml) and placed in an ampoule. The ampoule was sealed after evacuation of air and placed in a water bath heated to 75 °C for 27 h. The resultant polymerisation mixture, a red–brown suspension, was poured dropwise into acetone (50 ml). The precipitate was filtered off, washed on the filter with fresh acetone (70 ml) and dried in vacuum over KOH at room temperature. Yield—0.23 g (92%).

2.3.2. Synthesis of 5(4-acryloyloxyphenyl)-10,15,20-tritolylporphyrin (Po) [11]

Freshly distilled acryloyl chloride (4 ml, 49.2 mmol) in dry THF (30 ml) was added dropwise to a magnetically stirred mixture of 5(4-hydroxyphenyl)-10,15,20-tritolylporphyrin (HPTTP) (1.0 g, 1.6 mmol) and dry triethylamine (12 ml, 86.3 mmol) in dry THF (80 ml). The reaction mixture was heated to reflux for 3 h. The cooled suspension was filtered. The filtrate was rotovapped, and the residue produced was redissolved in chloroform (500 ml). The solution was washed in a separatory funnel with aqueous Na_2CO_3 (pH = 11–12) (400 ml × 4 times). The organic layer was dried over anhydrous magnesium sulphate, concentrated, and separated by the column chromatography (silica, 110 g and chloroform as an eluent). The target compound was eluted as the first band. Yield—0.6 g, (52%). MS *m/z* (rel. int.) 726 ($M^+_{C50.H38.N4.O2}$, 100), 727 ($M^+_{C49.13C.H38.N4.O2}$, 55), 671 ([M − acryloyl]$^+$, 19).

2.3.3. Synthesis of 5(4-hydroxyphenyl)-10,15,20-tritolylporphyrin (HPTTP)

p-Hydroxybenzaldehyde (6.96 g, 0.057 mol) and *p*-tolylaldehyde (20.2 ml, 0.171 mol) were mixed with 750 ml of propionic acid. The reaction mixture was brought to reflux and freshly distilled pyrrole (15.8 ml, 0.228 mol) was added over a period of ca. 20 min. The resultant mixture was refluxed for another 45 min. Then the mixture was cooled to room temperature and left overnight in a refrigerator. The cold suspension was filtered and the purple crystals were washed on the filter with ethanol (250 ml) and dried in vacuum. The dried crude product (5.5 g) was dissolved in chloroform (700 ml) and chromatographed on a column of silica (550 g) using chloroform and then a chloroform/THF (95/5 v/v) mixture as eluents. The second large band was the target compound. Following rotovapping and drying in vacuum 2.34 g (5.5%) of the product, a purple crystalline solid, was yielded. MS *m/z* (rel. int.) 672 ($M^+_{C47.H36.N4.O}$, 100), 673 ($M^+_{C46.13C.H36.N4.O}$, 60), 674 ($M^+_{C45.13C2.H36.N4.O}$, 18), 336 ($M^{++}_{C47.H36.N4.O}$, 12).

3. Results and discussion

3.1. Properties of the PSSS-Po copolymer

PSSS-Po copolymer was soluble in water, DMSO and methanol. It was characterised by NMR, UV and fluorescence spectroscopy. The UV absorption spectrum of PSSS-Po in aqueous solution, as well as in methanol, displays the bands characteristic for the porphyrin chromophore. The composition of the copolymer was determined based on its ^{1}H NMR 500 MHz spectrum in D_2O (more specifically on the ratio of the ending methyl groups of the porphyrin sharp signal integration ($\delta = 2.01$ ppm, s, 9H) to the PSSS broad aromatic signals integration ($\delta = 6.7$ and 7.5 ppm, m, 4H)). It was found that the polymer contains 81 wt% of SSS and 19 wt% of Po.

Fig. 1 shows the steady state fluorescence and excitation spectra of PSSS-Po in aqueous solution. The excitation spectrum is in good agreement with the absorption spectrum and does not display any additional bands. The fluorescence spectrum of PSSS-Po in methanol is very similar to that measured for tetraphenylporphyrin (TPP) in the same solvent. The quantum yield for the fluorescence of Po chromophores in PSSS-Po (φ_f) was determined, using TPP as a standard ($\varphi_f = 0.11$ in benzene) [12]. In aqueous solution (phosphate buffer, pH = 6.9) it was found that $\varphi_f = 0.07 \pm 0.005$ and in methanol $\varphi_f = 0.09 \pm 0.005$. The value of φ_f

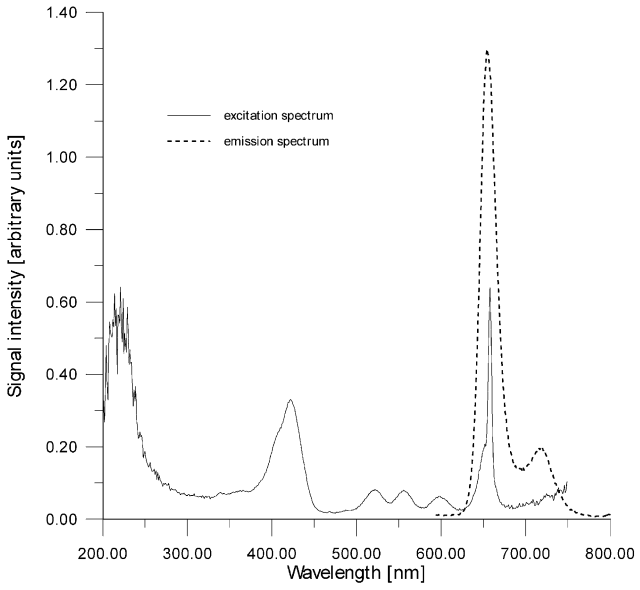

Fig. 1. Excitation ($\lambda_{em} = 656$ nm) and emission ($\lambda_{exc} = 422$ nm) spectra of PSSS-Po in aqueous solution (pH = 6.9).

found for PSSS-Po in aqueous solution is in good agreement with the respective value for model compound [5,10,15,20-tetra (4-carboxyphenyl) porphyrin], $\varphi_f = 0.09 \pm 0.005$ in methanol [13].

The absorption and fluorescence spectra of PSSS-Po are strongly dependent on a pH of the aqueous solution. Fig. 2 shows the changes in the Soret band of Po induced by the changes in pH. The presence of the isosbestic point indicates coexistence of two different forms of Po chromophore in aqueous polymer solution. This is related to the existence of the pH dependent equilibrium between protonated and diprotonated porphyrin in aqueous polymer solution. The

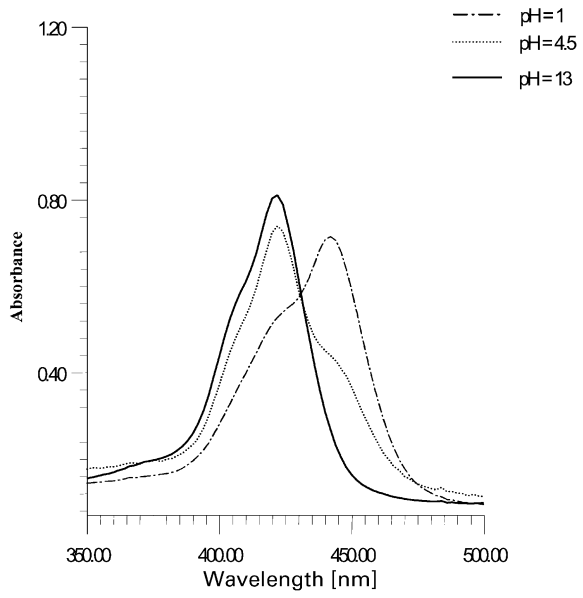

Fig. 2. The influence of pH of the aqueous solution on the absorption spectra of PSSS-Po.

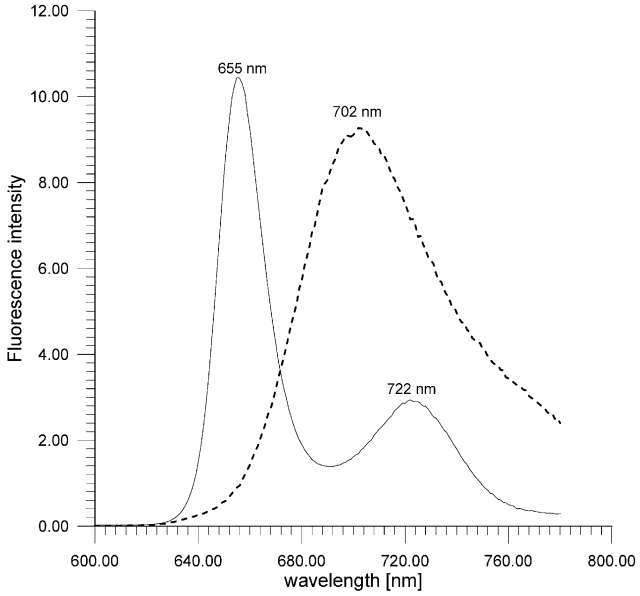

Fig. 3. Steady-state fluorescence spectra of PSSS-P in aqueous solution at pH = 1 (- -) and at pH = 13 (—).

extinction coefficients determined from the absorption spectra of PSSS-Po at the wavelength characteristic for the respective forms (at $\lambda_{max} = 422$ nm, at pH = 13) and at $\lambda_{max} = 442$ nm, at pH = 1) are practically the same: $\varepsilon = (6.0 \pm 0.1) \times 10^4$ M^{-1} cm^{-1}. The fluorescence spectrum in basic solution (pH = 13) shows two maxima at 655 and 722 nm whereas in acidic medium (pH = 1) there is only one maximum at 702 nm of the much lower intensity (see Fig. 3).

The appearance of these two forms of PSSS-Po in aqueous solution has been confirmed by significant difference in lifetimes of fluorescence polymeric Po in this copolymer at different pH ($\tau_0 = 2.7 \pm 0.2$ ns at pH = 1) and ($\tau_0 = 7.7 \pm 0.2$ ns at pH = 13). For a comparison, the lifetime of Po chromophore in PSSS-Po in methanol solution was found to be 8.5 ± 0.2 ns and for model compound (TPP) in hexane 7.9 ± 0.2 ns. Both values are similar to the lifetime of polymeric Po in its basic form.

The absorption and emission spectra of Po in PSSS-Po are also dependent on the ionic strength of the aqueous solution, especially at pH lower than 7 (see Fig. 4a). This is characteristic for the behaviour of porphyrin chromophores in the aqueous solutions at pH $\leq$ 7. Under these conditions the diacid, monocation and free base forms of Po are present in solution. Both pK values which characterise diacid–monocation and monocation–free base equilibria increase with an increase in ionic strength [14]. The shift in pK values manifests itself in the change in the absorption and emission spectra of PSSS-Po with the change in the ionic strength (addition of NaCl) because each of these species has different spectral characteristics. On the other hand, little change in spectra is observed upon addition of salt to the solution at pH = 6.9 (see Fig. 4b), where both pK values are about 4 units below, even at high ionic strengths.

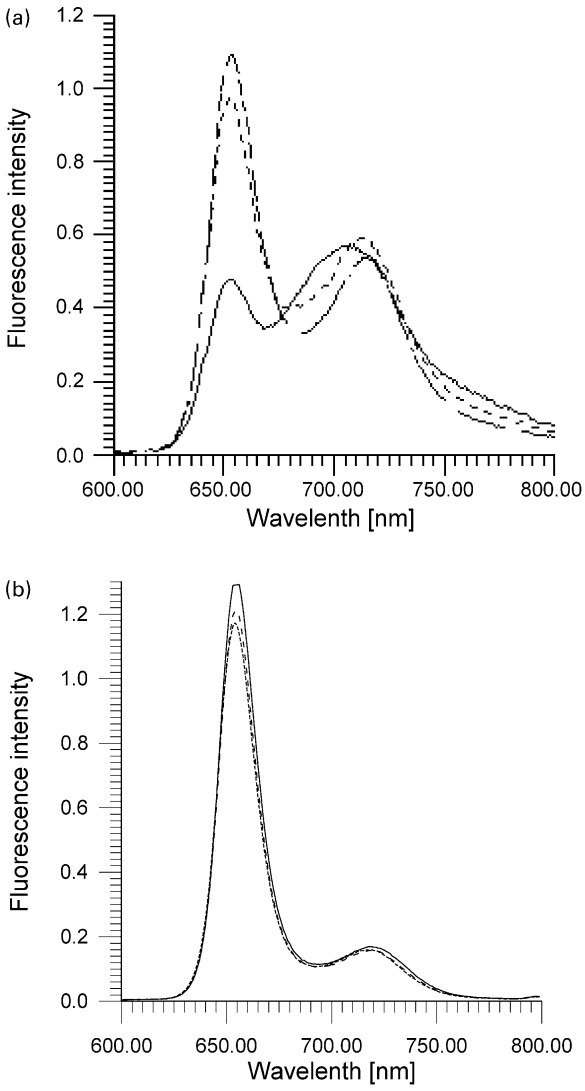

Fig. 4. Steady-state fluorescence spectra of PSSS-Po aqueous solutions at various concentration of NaCl ($c = 5 \times 10^{-3}$; 1×10^{-2}; 5×10^{-2} M), at (a) pH = 5.5 and (b) pH = 6.9.

It was found that in aqueous solution (pH = 6.9), even without salt added, the PSSS-Po polymer chain adopts a pseudomicellar conformation which results in formation of hydrophobic microdomains. The pyrene was used as a molecular probe to determine the polarity of the microdomains. It is known [15], that the ratio of the intensities of bands III to I of its emission spectrum allows characterisation of the relative polarity of the interior of the pseudomicelle. For our copolymer this ratio of I_{III}/I_I was found to be 0.66 ± 0.1 in a solution of pH = 6.9, without salt added, and it increased with the increase in concentration of NaCl in solution (Table 1). This indicates that the polarity of polymeric microdomains is significantly lower than in water where the ratio of I_{III}/I_I is equal to 0.59 ± 0.1.

Due to the presence of hydrophobic polymeric microdomains in aqueous solution the solubilisation of the sparingly water soluble hydrophobic molecules, such as perylene can be observed. Based on the experimental data and using the method described earlier [16], the distribution coefficient K (defined as the ratio of the weight fraction of perylene in the polymeric pseudophase and aqueous phase) was determined to be equal to $(1.5 \pm 0.5) \times 10^5$. The value is quite high, considering the relatively low content of hydrophobic Po units present in polymer.

Table 1
Ratio of the I_{III}/I_I determined from the steady-state fluorescence spectrum of pyrene solubilised in aqueous solution of PSSS-Po (pH = 6.9, $c_{Po} = 1.3 \times 10^{-5}$ M) in an absence and in the presence of NaCl at various concentrations

Concentration of NaCl (M)	I_{III}/I_I
0	0.6609
0.01	0.6897
0.02	0.8055
0.04	0.8628
0.06	0.9227
0.08	1.0282
0.10	1.0336
0.20	1.0552

3.2. Photochemical activity of PSSS-Po

3.2.1. Energy transfer

In order to test the possibility of the energy transfer from the Po chromophores in aqueous solution of PSSS-Po, the azulene was solubilised in the system as the possible energy acceptor. The azulene was chosen in order to ensure that the singlet–singlet energy transfer is termodynamically possible (E_s (Po) = 1.9 eV, E_s (azulene) = 1.76 eV). [17] Fig. 5 shows the fluorescence emission spectra recorded for aqueous solution of PSSS-Po in the absence and in the presence of azulene. The efficiency of the energy transferred from Po^* to azulene (χ) was calculated using the equation

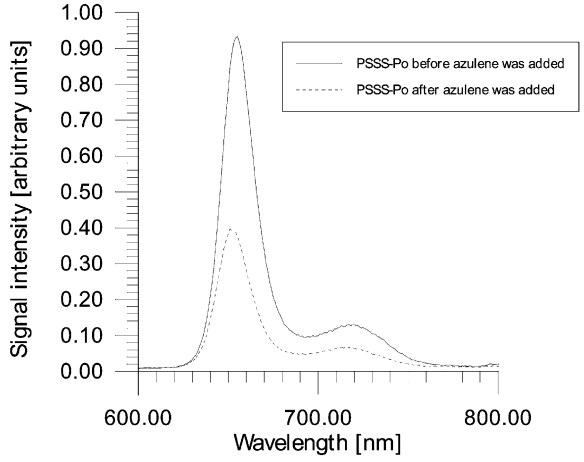

Fig. 5. The fluorescence emission spectra recorded for aqueous solution of PSSS-Po in the absence (—) and in the presence (- - -) of azulene ($c_{PSSS\text{-}Po} = 0.078$ g/dm^3, $c_{azulene} = 5 \times 10^{-5}$ M).

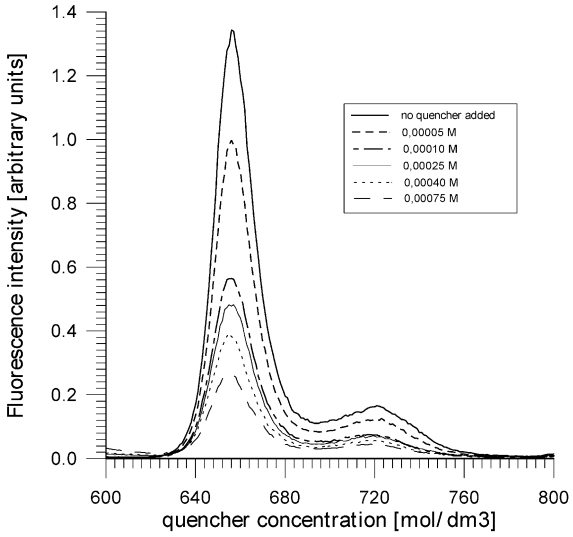

Fig. 6. The steady-state fluorescence spectra of aqueous solutions of PSSS-Po at different quencher (SPV) concentration and at pH 6.9.

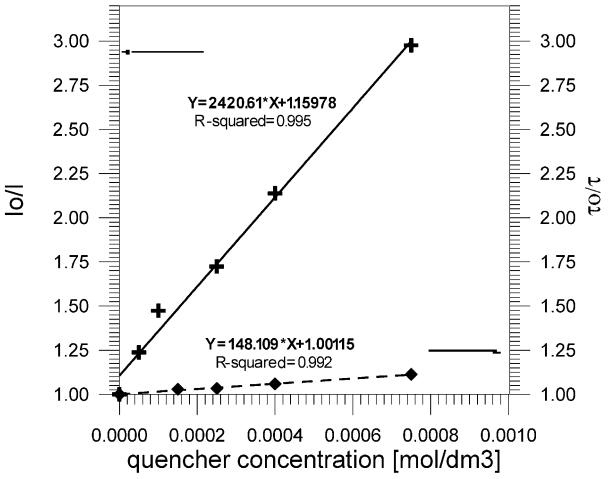

Fig. 7. The Stern–Volmer kinetics: the dependence of the ratio of the fluorescence intensities (I_0/I) or the ratio of the fluorescence lifetimes (τ_0/τ) of polymeric Po on the SPV concentration.

[18] and the experimental data:

$$\chi = 1 - (I/I_0) \tag{1}$$

where: I and I_0 are the intensities of fluorescence of Po in the presence and absence of azulene, respectively.

Under the experimental conditions ($c_{\text{PSSS-Po}} = 0.078$ g/dm^3, $c_{\text{azulene}} = 5 \times 10^{-5}$ M) the value of χ was found to be 0.575 ($I_0 = 0.934$ and 0.397, at $\lambda = 656$ nm). This means that 57.5% of the absorbed by PSSS-Po energy is transferred to azulene and indicates that PSSS-Po can act as efficient energy donor.

3.2.2. Electron transfer

In order to demonstrate particular usefulness of our polymeric system for the studies of photoinduced electron transfer we have carried out the experiments in which the electron acceptor (polymeric Po chromophores) is trapped in hydrophobic polymeric microdomains while electron acceptor resides in water. The sulfopropyl viologen (SPV) was thus chosen as the electron acceptor because it is well soluble in water and it is electrostatically neutral.

Measurements of the steady state fluorescence spectra of PSSS-Po in aqueous solution in the absence and in the presence of SPV have shown that SPV quenches efficiently the emission of porphyrin polymeric chromophore (see Fig. 6). The excitation emission spectra recorded for the system indicated that there is no complex formation in a ground electronic state between PSSS-Po and SPV. Measurements of the fluorescence lifetime of PSSS-Po in the absence and in the presence of SPV have confirmed the occurrence of quenching of Po chromophores in their electronically excited singlet state by SPV. 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) or the ratio of the fluorescence lifetimes (τ_0/τ) lifetimes of Po on the SPV concentration (see Fig. 7). One can observe that there is a substantial difference in the slopes of these two dependencies. Thus the value of the quenching rate constant of Po polymeric chromophores in aqueous PSSS-Po solution was determined to be $k_{qs} = (3.1 \pm 0.3)10^{11}$ M^{-1} s^{-1} ($k_{qs}\tau_0 = 2.4 \times 10^3$ M, $\tau_0 = 7.7 \pm 0.2$ ns). The value of the same rate constant determined from the lifetime measurements was found to be $k_{qd} = (1.9 \pm 0.25)10^{10}$ M^{-1} s^{-1} ($k_{qd}\tau_0 = 1.48 \times 10^2$ M, $\tau_0 = 7.7 \pm 0.2$ ns). The value is close to the diffusion controlled bimolecular rate in water and confirms that the electron is transferred to the molecule of acceptor located in aqueous phase. The difference observed in the values of k_{qs} and k_{qd} indicates, however, that the considerable static interactions between polymeric Po chromophores and SPV exist in their aqueous solutions (SPV is electrostaticaly neutral so the electrostatic interactions are excluded).

Taking into account that the energy transfer from Po chromophores to SPV is unfavourable due to the values of the energy levels of these compounds, ($\Delta E = E(\text{SPV}) - E(\text{Po}) = 4.97 - 2.94 = 2.03$ eV) the quenching of Po by SPV can be explained considering the possibility of electron transfer from the singlet excited state Po to SPV. In order to check whether the process is thermodynamically possible, the driving force (ΔG^0) for photoinduced electron transfer should be determined. Weller has shown that ΔG for photoinduced electron transfer in a polar solvent and at a relatively large donor–acceptor separation can be calculated using Rhem–Weller equation [19]:

$$\Delta G = E_{\text{D}}^{\text{ox}} - E_{\text{A}}^{\text{red}} - E^* - C \tag{2}$$

where: E_{D}^{ox} is the oxidation potential of the donor ($E_{\text{D}}^{\text{ox}} = 1$ eV for TTP [20]), $E_{\text{A}}^{\text{red}}$ the reduction potential of the acceptor ($E_{\text{A}}^{\text{red}} = -0.37$ eV for SPV [10]), E^* the energy

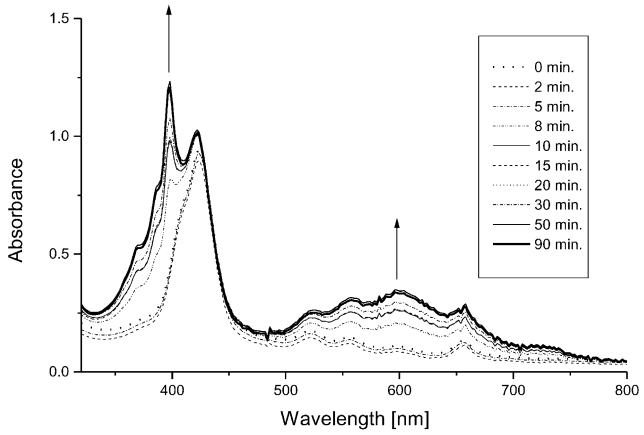

Fig. 8. The changes in the absorption spectrum of PSSS-Po/SPV/TEA system during the selective irradiation of the Po chromophores with light at $\lambda > 395$ nm; ($c_{\text{PSSS-Po}} = 0.07$ g/dm^3, $c_{SPV} = 5 \times 10^{-4}$ M, $c_{TEA} = 2.5 \times 10^{-3}$ M).

of electronically excited state of the excited species ($E^* = 1.9$ eV for TTP) [17] and C an electrostatic correction term, which is typically about 0.1 eV in the polar solvent. Using these values one can find that:

$$\Delta G = -0.63 \text{ eV} \quad (3)$$

This indicates that the process of electron transfer between Po and SPV is thermodynamically favourable. The process can be described as follows:

$$^1\text{Po}^* + \text{SPV} \rightarrow \text{Po}^{\cdot+} + \text{SPV}^{\cdot-} \quad (4)$$

It is well known that the process of photoinduced electron transfer is reversible and in homogenous solution it is very difficult to observe the formation of the products. One can expect, however, that in our microheterogenous polymeric system the back reaction should be retarded. The $\text{SPV}^{\cdot-}$ radical anion formed in a primary photochemical process should be expelled from the negatively charged polymer chain (polyanion). This should result in net separation of the charges in the pair Po-SPV. The process can be followed by the measurements of the absorption spectra in the near UV–Visible spectral region. It is known [21] that $\text{SPV}^{\cdot-}$ displays a characteristic spectrum with the maxima at 399 and 610 nm. Fig. 8 shows the absorption spectra for the PSSS-Po + SPV aqueous solution (in a presence of TEA as a sacrificial electron donor) after various times of irradiation with the light absorbed only by the Po chromophores (cut-off filter 395 nm). One can observe that the $\text{SPV}^{\cdot-}$ is indeed formed in the system studied.

Model studies carried out in homogenous solution of TTP + SPV + TEA in acetonitrile have shown that although the charge separation could occur in such system, there was no stable charge separation. One could not observe formation of $\text{SPV}^{\cdot-}$ in model system irradiated under the same conditions as the polymeric one. This clearly demonstrated the essential role of polyanion in a process of charge separation.

4. Conclusions

In this paper we report the synthesis of a new type of photoactive water-soluble polymer containing porphyrin chromophores and able to absorb light from the visible spectral region. The electronic absorption and emission spectra are strongly dependent on pH of the aqueous solution. The copolymer can solubilise molecules of sparingly water-soluble organic compounds (pyrene, perylene). We observe the quenching of Po chromophores in their electronically excited singlet state by SPV and from the substantial difference in the slopes of Stern–Volmer static and dynamic dependencies we suggest that the considerable static interactions between polymeric Po chromophores and SPV exist in their aqueous solutions. The possibility of electron transfer from the singlet excited state Po to SPV, which may explain the quenching of Po chromophores by SPV, was confirmed by the formation of the $\text{SPV}^{\cdot-}$ radical upon irradiation of exclusively Po chromophores in the presence of TEA as a sacrificial electron donor.

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