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Polymeric photosensitizers. Part 4. Synthesis of poly(sodium styrenesulfonate-*block*-*N*-vinylcarbazole) by nitroxide-mediated free radical polymerization

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Abstract

Block amphiphilic copolymer, poly(sodium styrenesulfonate-*block*-*N*-vinylcarbazole) (PSSS-*block*-VCz), was synthesized by nitroxide-mediated "living" free radical polymerization in homogenous solution. The procedure of the synthesis of poly(sodium styrenesulfonate) (PSSS) via the same technique was modified to reduce the amount of mediator and initiator needed. Camphorsulphonic acid (CSA) and acetic anhydride (AA) were used as rate-accelerating additives in polymerization of PSSS and PSSS-*block*-VCz, respectively. The physicochemical and photophysical properties of PSSS-block-VCz copolymer were determined and discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymeric photosensitizers; Poly(sodium styrenesulfonate-*block*-*N*-vinylcarbazole); Nitroxide-mediated free radical polymerization

1. Introduction

Development of the new types of water-soluble polymers is an important subject of current research. We are interested in the synthesis of water-soluble polymeric photosensitizers [1–6]. These polymers are constructed from hydrophilic and hydrophobic units. In an aqueous solution they adopt the pseudo-micellar conformation which makes possible solubilization of sparingly water-soluble molecules of organic compounds. The hydrophobic interior of such a pseudomicelle can absorb the light from the UV/Vis spectral region. The excitation energy can be used to induce a photochemical reaction with the participation of the molecule of solubilized compound. It has been shown that block copolymers are better photosensitizers than random ones [5]. However, the synthesis of the block copolymers of this kind using the classical ionic polymerization procedures is very difficult.

"Living" free radical polymerization has recently attracted considerable attention as a convenient method for synthesis of macromolecules characterized by a low degree of polydispersity, accurate molecular weight and required architecture. This new technique overcomes the restrictions of traditional living polymerization methods and makes possible the synthesis of a variety of well-defined copolymers (statistical, block, graft, branched) [7].

This paper presents the results of the studies on synthesis via "living" free radical polymerization of novel polymer of that type, poly(sodium styrenesulfonate-*block*-*N*-vinylcarbazole) (PSSS-*block*-VCz). The physicochemical and photophysical properties of this polymer were also determined and discussed.

2. Experimental part

2.1. Materials

Sodium styrenesulfonate (SSS, Monomer–Polymer & Dajac Laboratories, Trevase, USA) was purified by recrystallization from 9:1 (v/v) mixture of methanol and water at 60°C and dried under vacuum. *N*-Vinylcarbazole (VCz, Fluka, Buchs, Switzerland, pure) was twice recrystallized from methanol at 40°C and dried in a vacuum oven. Potassium peroxodisulfate ($K_2S_2O_8$, Riedel-de Haen AG Seelze-Hannover, pure) was twice recrystalized from deionized water. 4-Hydroxy-2,2,6,6-tetramethyl-1-piperidynyloxy (HTEMPO, free radical, Aldrich), 6-propionyl-2-(*N*,*N*-dimethyl)aminonaphthalene (PRODAN, Molecular Probes, 99%), perylene (Aldrich, gold label, 99.9%), sodium hydrogen sulfite ($NaHSO_3$, Fluka, pure, 38–40% aqueous

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Table 1
Concentration of the reagents for the “living” radical polymerization of SSS

Reagents	Concentration (mol/dm^3)
SSS	1.31
HTEMPO	0.0195
$K_2S_2O_8$	0.0131
$NaHSO_3$	0.0131
CSA[a]	0.0125

[a] For PSSS1.

solution, pure), (±)-10-camphorsulfonic acid, (CSA, Aldrich, anhydrous, 98%), acetic anhydride (AA, POCH, Gliwice, pure for analysis), methanol (POCH, Gliwice, pure), dimethyl sulfoxide (DMSO, Aldrich, pure), 1-butanol (POCH, Gliwice, pure), dichloromethane (Aldrich, for HPLC), $NaNO_3$ (Aldrich, pure, NaCl (POCH, Gliwice, pure for analysis), NaH_2PO_4 (POCH, Gliwice, pure for analysis) were used without further purification.

Random PSSS–VCz copolymer was synthesized using a method described previously [6].

2.2. Instruments

The UV/Vis spectra of the samples were obtained using a HP 8452A Diode-Array spectrophotometer. The IR spectra of the probes were measured in KBr pellets with use of a Bruker IFS 48 spectrophotometer. The ^{1}H NMR spectra of the polymers were measured in solution of deuterated DMSO using a Bruker AMX 500 spectrometer. Viscosity measurements were performed in the aqueous solution of polymers in the presence of 0.5 M NaCl using an electronic capillary viscometer. Gel permeation chromatography (GPC) analyses were carried out using a Hewlett Packard chromatograph with a UV/Vis detector. Separation was performed with three PL-aquagel-OH 30, 40, 50 columns and the eluent was a mixture of methanol/aqueous solution of $NaNO_3$ (0.3 M) and NaH_2PO_4 (0.01 M), (pH = 9) (20:80 v:v). The columns were calibrated with PSSS standards obtained from Polysciences. Sedimentation experiments were carried out using a MOM model 3180 Analytical Ultracentrifuge.

Table 2
Molecular weights, polydispersities and yields of homopolymers of SSS

Sample	M_n[a]	M_w[a]	M_v[b]	Polydispersity		Yield (%)
PSSS1	28 000	38 000	28 000	1.36[a]	1.42[c]	40
PSSS2	36 000	61 000	38 000	1.61[a]	1.39[c]	–

[a] Based on the GPC measurements.

[b] Based on the measurements of viscosity and the data for Mark–Houwink–Sakutara equation taken from the Ref. [9].

[c] Based on the sedimentation measurements.

3. Results and discussion

The PSSS-*block*-VCz copolymer has been obtained in two step synthesis. In the first step, PSSS terminated with stable nitroxy radical was prepared. In the second step, this polymer was used as a macroinitiator.

3.1. Polymerization of SSS

The homopolymerization of SSS using the new pseudo-living technique with TEMPO (2,2,6,6-tetramethyl-1-piperidynyloxy, free radical) as a mediator was first reported by the Xerox Research Centre of Canada [8]. In our work, that procedure has been modified. A 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. It was expected that this would result in a reduction of the amount of mediator needed in the reaction mixture (in original procedure 10 mol% of TEMPO and 5 mol% of initiator were used). The rate-accelerating additive, camphorsulphonic acid (CSA), was also introduced to the polymerization mixture. The composition of the mixture used in our polymerization is given in Table 1. The reagents were placed in a glass tube and degassed. The polymerization was carried out for 4 h at 125°C. The concentrations of reagents used in the polymerization are reported in Table 1. The polymer (PSSS1) was precipitated into 1-butanol, filtered, washed with diethyl ether and dried in a vacuum oven at 40°C. The resulting polymer was dissolved in water, dialyzed (Fisher, cellulose tubing, cut-off 12 000–14 000 g mol^{-1}) and freeze-dried. The polymer was characterized by GPC, sedimentation and viscometry techniques (see Table 2 and Fig. 1). The procedure resulted in the synthesis of a polymer having relatively high molecular weight and low polydispersity.

In order to confirm the “living” character of the polymer, a portion of isolated PSSS1 (0.5 g) was dissolved in a DMSO/water solution (5 ml) containing monomer, SSS (0.5 g). The mixture was heated at 125°C for 4 h. The resulting polymer, PSSS2, was isolated and characterized (see Table 2 and Fig. 1). The chain-extension test confirmed the “living” character of PSSS1. The unimodal chromatogram of PSSS2 indicated that the modified procedure of polymerization produces polymers with a non-detectable amount of dead chains (see Fig. 1).

3.2. Synthesis of the block copolymer PSSS–VCz

VCz (2 g) and HTEMPO-terminated PSSS1 macroinitiator (3 g) were dissolved in DMSO/water solution (7/1 v/v, 40 ml) and placed in a four-neck round bottom flask. Oxygen was removed by bubbling with oxygen-free nitrogen for 30 min. Water present in the polymerization mixture

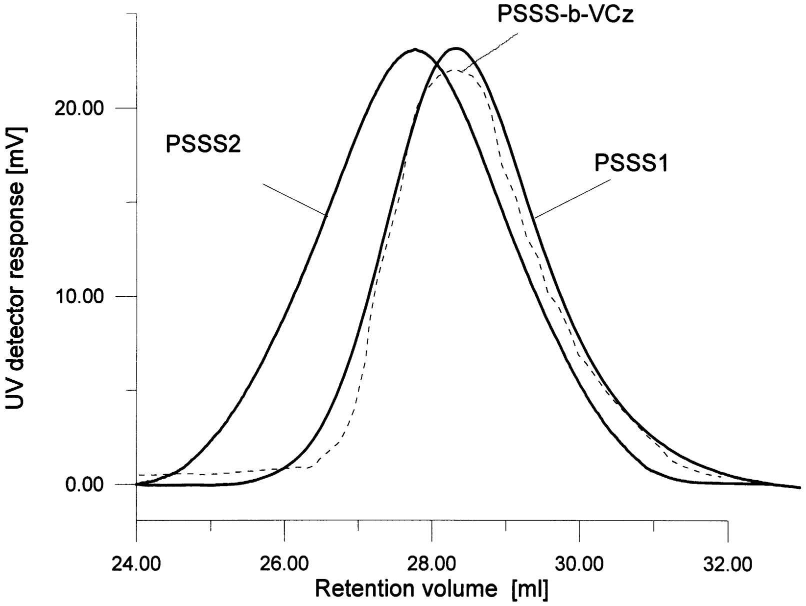

Fig. 1. GPC chromatograms for PSSS1, PSSS2 and PSSS-*block*-VCz.

was quantitatively removed by distillation before adding the rate-accelerating agent acetic anhydride (AA, 0.2 ml) (at 125°C). Then the homogenous solution was heated at 135°C for 24 h under nitrogen with vigorous stirring using a mechanical stirrer. The resulting copolymer was soluble in water. It was treated in the same way as PSSS1. Composition of the copolymer was determined by the elemental analysis and ^{1}H NMR, UV/Vis and IR spectroscopies using the methods described earlier [6].

3.3. Properties of the PSSS-block-VCz copolymer

The measurements carried out allowed us to estimate that PSSS-*block*-VCz contains about 5 mol% of carbazole.

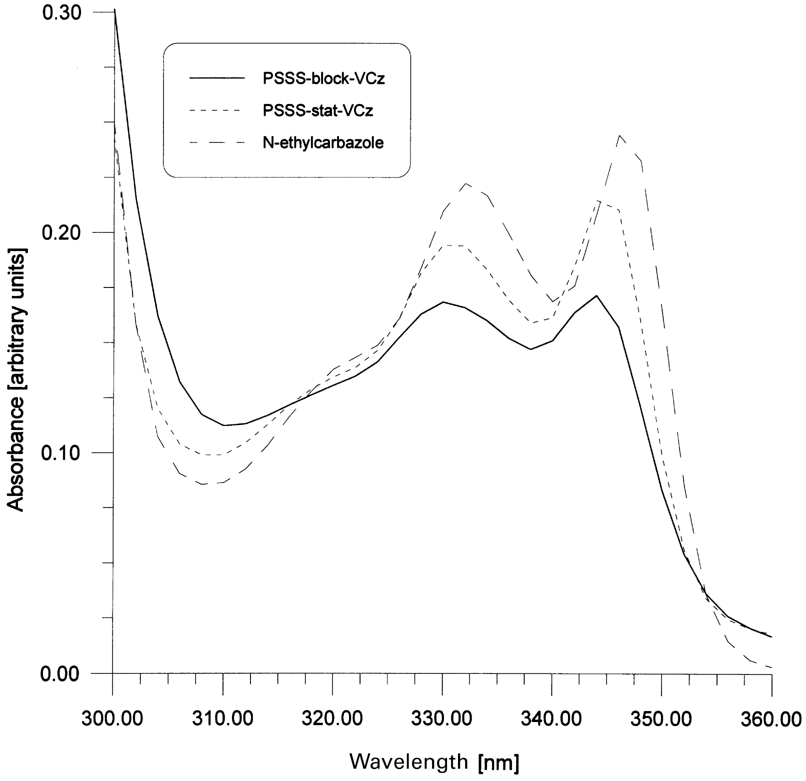

Fig. 2. UV absorption spectra of *N*-ethylcarbazole in THF and statistical and block copolymers of PSSS–VCz in water.

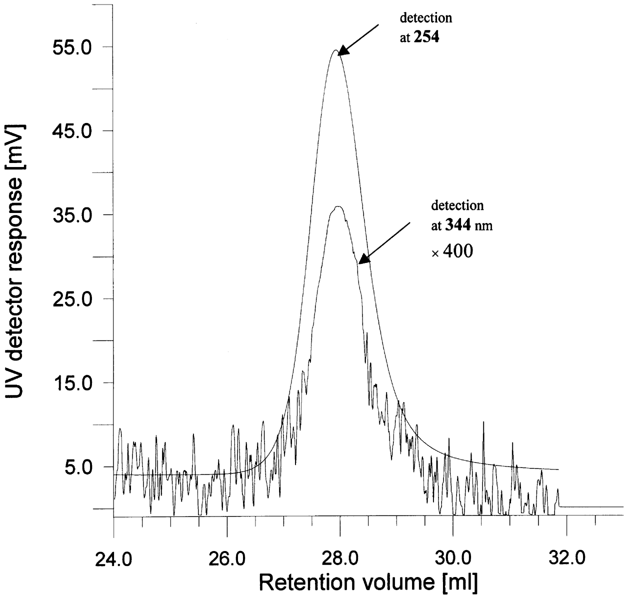

Fig. 3. Dual detection GPC chromatograms for PSSS-*block*-VCz.

Taking into account the value of the number average molecular weight of the PSSS macroinitiator, $M_n = 2.8 \times 10^4$ g/mol, and the content of VCz monomer in a copolymer, one can estimate the statistical length of the carbazole segment for 6 units. It should be pointed out that the block of VCz in a copolymer is rather short, although VCz monomer was introduced to the reaction mixture in considerable excess. This observation corresponds well with the previous literature report that VCz could not be homoplymerized by a "living" process (initiation with benzoyl peroxide, mediation with TEMPO) [10]. This effect can be explained assuming high stability of the VCz radical-TEMPO adducts formed during the reaction. The rate-accelerating agent, AA, used in our experiments played a crucial role. We have found that the formation of VCz block was possible only when polymerization was carried out in the presence of AA. The reaction did not occur even in the presence of CSA. Most likely AA increases the probability of dissociation of VCz-TEMPO adducts making possible the addition of the VCz units. More work is needed to explain the mechanism of that process.

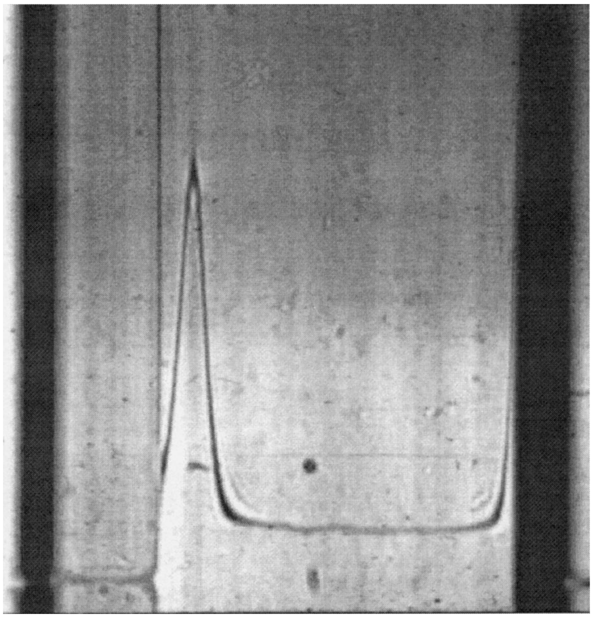

Fig. 4. The sedimentation curve obtained for PSSS-*block*-VCz copolymer in aqueous solution.

UV/Vis spectrum of PSSS-*block*-VCz copolymer in aqueous solution contains bands characteristic for carbazole chromophore. They are, however, strongly blue-shifted with respect to the absorption bands characteristic for the statistical copolymers and a model compound *N*-ethylcarbazole (see Fig. 2). This can be explained in terms of the hypochromic effect [11]. The interactions between adjacent chromophores lead to the shift in the position of their absorption bands and to the decrease in their absorption coefficients. The effect is expected to be much more pronounced for carbazole chromophores in a block than for those existing in short sequences, like in statistical copolymer. Data presented in Fig. 2 clearly illustrate the difference between the copolymers. The ^{1}H NMR spectrum for PSSS-*block*-VCz in D_2O displays the characteristic peak of shielded aromatic proton at 5.4 ppm, typical for longer sequences of carbazole chromophores [12,13]. All the above observations confirm the presence of a block of carbazole in the synthesized copolymer. The result of GPC measurement for PSSS-*block*-VCz copolymer carried out with dual detection provides one more piece of evidence. The GPC traces for the copolymer obtained by measuring the absorbance at $\lambda = 254$ nm (characteristic for both SSS and VCz blocks) and at $\lambda = 344$ nm (characteristic for VCz block) show the peaks at the same retention time (Fig. 3). Their relative intensities reflect both the composition of the polymer and the differences in the values of extinction coefficient characteristic for the respective components [6].

The sedimentation analysis (see Fig. 4) and GPC traces for PSSS-*block*-VCz copolymer have indicated that the copolymer is characterized by the narrow distribution of the molecular masses. Interestingly, the value of the intrinsic viscosity $[\eta]$ of the copolymer PSSS-*block*-VCz in aqueous solution, in the presence of 0.5 M. NaCl was found to be lower than the value for PSSS precursor determined under the same conditions ($[\eta] = 13$ cm^3/g for PSSS and $[\eta] = 10$ cm^3/g for PSSS-*block*-VCz). Similarly, the apparent molecular weight of the PSSS-VCz determined by GPC technique (see Fig. 1) was lower for PSSS-*block*-VCz than that for PSSS precursor ($M_n = 1.9 \times 10^4$ g/mol and $M_n = 2.8 \times 10^4$ g/mol, respectively). Both of these observations can be explained considering that the effective hydrodynamic volume of the polymer coil decreases while hydrophobic VCz units are introduced to the polymer chain. Thus, it can be suggested that the polymer coil of

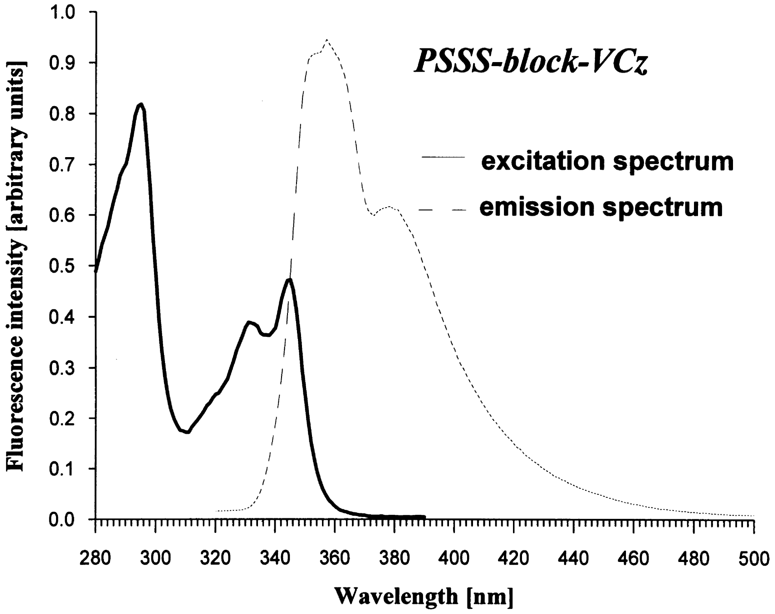

Fig. 5. Emission ($\lambda_{ex} = 280$ nm) and excitation ($\lambda_{em} = 400$ nm) spectra of PSSS-*block*-VCz in aqueous solution.

PSSS-*block*-VCz adopts a compact pseudomicellar conformation in aqueous solution.

The measurements of the fluorescence spectra support that suggestion. Fig. 5 shows the excitation and emission spectra of PSSS-*block*-VCz copolymer. It can be observed that the emission spectrum consists of three bands characteristic for the monomeric carbazole chromophores (at 354 nm), high energy excimer (partially overlapped, so called second excimer, at 357 nm) and normal, fully overlapped excimer (at 378 nm) [14]. The spectrum is dominated by the fluorescence of the second excimer. This indicates that the Cz chromophores are in close proximity

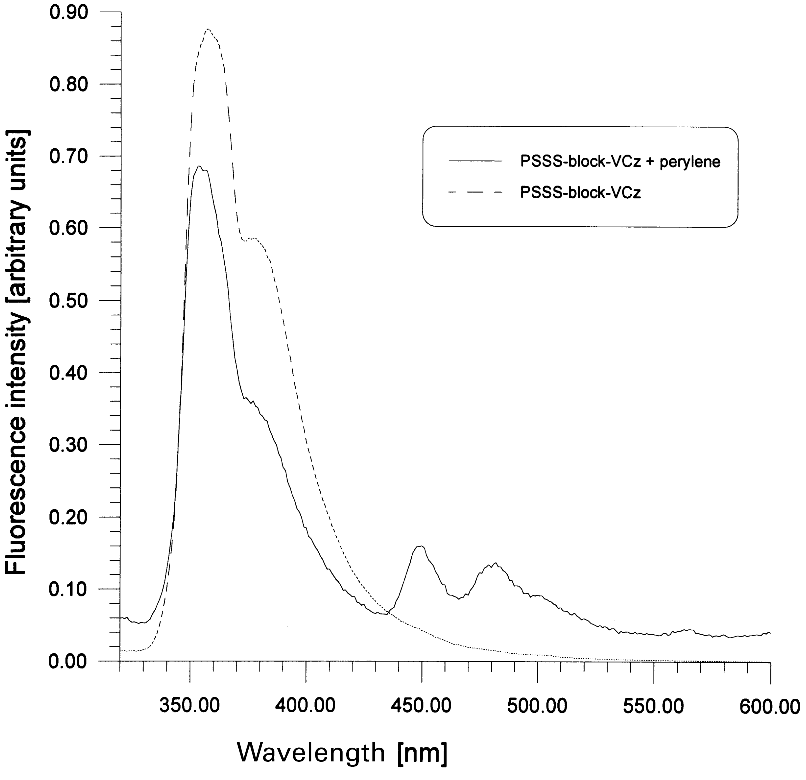

Fig. 6. Steady-state emission spectra of PSSS-*block*-VCz in the absence and in the presence of perylene ($\lambda_{ex} = 280$ nm).

Table 3
Fluorescence depolarization measurements for perylene via direct and indirect excitation

Excitation wavelength (nm)	Degree of polarization (*P*)
280	0.0090 ± 0.0005
415	0.2410 ± 0.0010

but due to the sterical hindrance their mobility is restricted, which gives the preference for formation of excimers that are not fully overlapped.

It was found that the PSSS-*block*-VCz copolymer in aqueous solution solubilizes molecules of organic compounds sparingly soluble in water. The process is efficient. For example, the distribution coefficient (K_x) for the perylene between polymeric pseudophase and water ($K = x_p/x_{aq}$, where x_p and x_{aq} are the mole fraction of perylene in the polymeric pseudophase and in water, respectively) [15] was found to be very high, $K = (8.5 \pm 0.5) \times 10^7$. This indicates that the interior of the polymeric pseudomicelle is quite hydrophobic. The properties of the interior of polymeric pseudomicelles can be determined by solubilization of environment-sensitive probes. It is well known that the intensity of the vibronic fine structure in pyrene monomer fluorescence, in particular the ratio of the intensities of peak III to peak I, displays a strong dependence on solvent polarity [16,17]. In polar solvents, the value of the III/I ratio is low and it increases considerably in hydrophobic media. Using this method, the relative polarity of solubilizing microdomains in PSSS-*block*-VCz copolymer was determined. It was found that the ratio III/I is equal to 0.81. The value is close to that for tetrahydrofuran and higher than that found for typical micelles formed by the surfactant molecules (e.g. in the hexadecyltriethylammonium bromide micelle it was found to be 0.72) [17].

In order to answer the question regarding the possibility of using PSSS-*block*-VCz as the photosensitizer, studies on the energy transfer and energy migration within the polymer were carried out. It has been shown (see Fig. 6) that the excitation energy is transferred to the solubilized perylene molecules. The quantum yield of this process (ϕ_{ET}) can be calculated as follows:

$$\phi_{ET} = 1 - I_Q/I_0 \qquad (1)$$

where I_0 and I_Q are the carbazole fluorescence intensities in the aqueous polymer solution in the absence and in the presence of solubilized perylene, respectively. The value was determined to be 0.26 ± 0.02.

To determine whether energy migration plays an important role in the system, steady-state fluorescence depolarization studies were performed. Fluorescence depolarization has been shown to be a useful method for studying energy migration [18]. The studies involved monitoring the depolarization of the perylene fluorescence by direct excitation and indirect excitation via energy transfer. Data presented in Table 3 indicate that for the perylene excited via the energy transfer for the excited VCz polymeric chromophores ($\lambda_{ex} = 280$ nm) there is virtually complete depolarization of the incident light whereas substantial retention of polarization occurs on direct excitation of perylene ($\lambda_{ex} = 415$ nm). The large value of P for directly excited perylene shows that the molecular probe does not undergo significant rotational motion during its fluorescence lifetime ($\tau = 6$ ns [19]). This suggests that the perylene is solubilized in rather viscous polymeric microenvironment, resembling that of glycerol [20]. More importantly it confirms that the perylene rotational motions do not influence the observed depolarization. These results lead to the conclusion that the observed fluorescence depolarization is due to the energy migration among the carbazole polymeric chromophores prior to the energy transfer of the solubilized perylene.

4. Conclusions

The PSSS-*block*-VCz copolymer has been synthesized using a nitroxide-mediated pseudoliving free radical polymerization in the presence of AA as accelerator. The copolymer is soluble in water. The macromolecules of that polymer adopt in aqueous solution a compact pseudomicellar conformation. The interior of this pseudomicelle has been shown to be quite hydrophobic and rigid. Due to the presence of carbazole polymeric chromophores, PSSS-*block*-VCz absorbs light from the UV/Vis spectral region. The excitation energy migrates along the polymeric chromophores before being transferred to a suitable energy acceptor. Although the VCz segment in PSSS-*block*-VCz is quite short, the polymer displays promising properties as a potential photosensitizer.

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