Synthesis of Poly(sodium styrenesulfonate-*block*-vinylnaphthalene) by Nitroxide-Mediated Free Radical Polymerization

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ABSTRACT: The new block amphiphilic copolymer, poly(sodium styrenesulfonate-*block*-vinylnaphthalene) (PSSS-*block*-VN), was synthesized by nitroxide-mediated "living" radical polymerization in homogeneous solution. The composition of the copolymer was determined by ^{1}H NMR spectroscopy and elemental analysis. On the basis of GPC, viscometric, and spectroscopic measurements, we proposed that the copolymer adopts a highly compressed, pseudomicellar conformation in aqueous solution.

Introduction

"Living" free radical polymerizations have recently attracted considerable attention as a convenient method for the synthesis of macromolecules with low degree of polydispersity, accurate molecular weight, and required architecture.[1] These new techniques overcome restrictions of traditional living polymerization methods and enable the synthesis of a variety of well-defined copolymers (statistical, block, graft, and branched).[1] Amphiphilic polymers, especially polyelectrolytes, have a wide range of practical applications. Guillet and coworkers have developed novel polyelectrolytes containing sequences of chromophores that absorb light from the near-UV−vis spectral region.[2] These polymers display very promising photocatalytic activity. The block copolymers are considerably better photocatalysts than the random copolymers of the same composition.[3] The synthesis of such copolymers by traditional methods is, however, very difficult. This paper presents the synthesis of poly(sodium styrenesulfonate-*block*-vinylnaphthalene) (PSSS-*block*-VN) via "living" free radical polymerization and describes its physicochemical properties.

Experimental Section

Materials. Sodium styrenesulfonate (SSS, Monomer-Polymer & Dajac Laboratories, technical) was purified by recrystallization from 9:1 (v/v) mixture of methanol and water at 60 °C and dried under vacuum. 2-Vinylnaphthalene (VN, Aldrich, 95%) was purified by column chromatography using aluminum oxide as the stationary phase and cyclohexane as the eluent. 4-Hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy free radical (HTEMPO, Aldrich, 98%), 6-propionyl-2-(*N*,*N*-dimethylamino)-naphthalene (PRODAN, Molecular Probes, 99%), perylene (Aldrich, gold label, 99.9%), sodium hydrogen sulfite ($NaHSO_3$, Fluka, solution for synthesis, 38−40% in water), potassium persulfate ($K_2S_2O_8$, Aldrich, 99.99%), (±)-10-camphorsulfonic acid (CSA, Aldrich, anhydrous, 98%), ethylene glycol (POCH Gliwice, 99%), methanol (POCH Gliwice, 99.8%), cyclohexane (POCH Gliwice, 99.5%), dimethyl sulfoxide (DMSO, Aldrich, 99.9%), 1-butanol (POCH Gliwice, 99%), diethyl ether (POCH Gliwice, 99%), $NaNO_3$ (Aldrich, 99.9%), NaCl (POCH Gliwice, 99.9%), and NaH_2PO_4 (POCH Gliwice, 99.9%) were used as received. Pyrene (Aldrich, 99%) was purified by zone refining. The statistical copolymer poly(sodium styrenesulfonate-*stat*-vinylnaphthalene), PSSS-*stat*-VN (47 mol % of VN), was synthesized as previously described.[4]

Synthesis of PSSS and PSSS-*block*-VN. The PSSS-*block*-VN copolymer was obtained by a two-step synthesis. In the first step, PSSS was terminated with stable nitroxy radical. In the next step, this polymer was used as a macroinitiator in synthesis of the copolymer.

a. Synthesis of PSSS. PSSS was prepared by "living" free radical polymerization using the modified method originally developed by Georges et al.[5] The procedure was modified to accelerate the reaction and reduce the amount of "dead" chains. The polymerization was carried out for 3 h in a mixture of ethylene glycol and water (75:25 v/v) under nitrogen at 125 °C. The reaction was terminated at ca. 30% conversion in order to reduce undesirable reactions. The mediator, TEMPO (2,2,6,6-tetramethyl-1-piperidynyloxy, free radical), was replaced by the more hydrophilic HTEMPO. The rate-accelerating additive, CSA, was also introduced to the polymerization mixture. The concentrations of reagents used in the polymerization were as follows: SSS (0.97 M), HTEMPO (0.097 M), $K_2S_2O_8$ (0.049 M), $NaHSO_3$ (0.049 M), and CSA (0.008 M). The resulting polymer (PSSS1) was precipitated into 1-butanol, filtered, washed with diethyl ether, and dried in a vacuum oven at 40 °C. The polymer was then dissolved in water, dialyzed (Fisher, cellulose tubing, cutoff 12 000−14 000 g mol^{-1}), and freeze-dried.

b. Synthesis of the Block Copolymer PSSS-*block*-VN. VN (0.5 g) and HTEMPO-terminated PSSS1 macroinitiator (0.5 g) were dissolved in DMSO solution (10 mL). Then CSA was added at the concentration of 0.01 M, and the homogeneous solution was heated at 130 °C for 6 h under nitrogen with vigorous stirring. The resulting copolymer was soluble in water. It was treated the same way as PSSS1. Composition of the copolymer was determined by elemental analysis, ^{1}H NMR, UV−vis, and IR spectroscopy using the procedures developed earlier.[6]

Instruments and Procedures. The UV−vis spectra of the samples were obtained using a HP 8452A diode-array spectrophotometer. The ^{1}H NMR spectra of the polymers were measured in solution of deuterated DMSO using a Bruker AMX 500 spectrometer. The IR spectra of the samples were measured in KBr pellets on a Bruker IFS 48 spectrophotometer. Steady-state fluorescence spectra were measured using a SLM Aminco 8100 spectrofluorimeter. A nonlinear least-squares-fitting routine Spectra Calc was used to deconvolute experimental emission spectra of PRODAN into a sum of overlapping Gaussian functions. The spectra were fitted to obtain the minimum number of components that yielded the best fit ($\chi^2 < 0.01$). Viscosity measurements were performed in the aqueous solution of 0.5 M NaCl on 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 (pore size: 30, 40, 50 Å) columns, and the eluent was a mixture of methanol/aqueous solution of 0.3 M $NaNO_3$ 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 molec-

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Table 1. Molecular Weights, Polydispersities, and Intrinsic Viscosities of the Studied Polymers

sample	M_w[a]	M_v[b]	$[\eta]$, cm^3/g	PD
PSSS1	1.0×10^6	1.0×10^6	130	1.30
PSSS2	$>1.0 \times 10^6$	1.2×10^6	145	1.35
PSSS-*block*-VN	4.7×10^4		90	1.60

[a] Based on the GPC measurements using PSSS standards. [b] Based on the viscometry measurements and the following equation:[6] $[\eta] = 1.86 \times 10^{-2}(M_v)^{0.64}$.

ular weights (M_w) from 1500 to 780 000) obtained from Polysciences. Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA 7 thermogravimetric analyzer under a nitrogen atmosphere at a scan rate of 20° C/min.

Results and Discussion

Properties of PSSS Macroinitiator. The PSSS1 polymer was characterized by GPC, sedimentation, and viscometry techniques (see Table 1 and Figure 1). The procedure resulted in synthesis of polymer having high molecular weight, $M_w = 1.0 \times 10^6$ g/mol, and low polydispersity.

To confirm the "living" character of the synthesized polymer, a portion of the isolated PSSS1 (0.5 g) was redissolved in an ethylene glycol/water solution (5 mL) containing SSS (0.5 g) and heated at 125 °C for 2 h. The resulting polymer (PSSS2) was isolated and characterized (see Table 1). The values of the molecular weights of the polymers determined from the GPC measurements should be taken with precaution because of the limitation of the GPC columns to the range of $M_w \leq 1.0 \times 10^6$ g/mol. However, the results obtained from the viscometric measurements clearly show that molecular weight of the polymer increase after chain extension, which confirms the "living" character of PSSS1-HTEMPO terminated macroinitiator (Table 1). The unimodal chromatogram of PSSS2 indicated that the modified procedure of polymerization produces polymers with nondetectable amount of dead chains (see Figure 1).

Properties of PSSS-*block*-VN Copolymer. The TGA curve for PSSS-*block*-VN is shown in Figure 2. Although the shape of the curve is not perfect, it confirms that the sample used for analysis is a copolymer, not a blend of homopolymers of PSSS and PVN. It is noteworthy that there is no degradation step at 485 °C which could be expected for PSSS homopolymer.[7,8]

The content of naphthalene chromophores in PSSS-*block*-VN was 20 mol % by ^{1}H NMR spectroscopy and 22 mol % by elemental analysis. Using the average molecular weight of the PSSS1 precursor, this corresponds to an average of about 4850 SSS units and 1300 VN units which are present by average in the PSSS-*block*-VN polymer chain. Interestingly, despite very high molecular weight and the high content of hydrophobic chromophores in the PSSS-*block*-VN, the polymer is highly soluble in water (up to the 5 g/dm^3 at ambient temperature). This may indicate that the polymer chain adopts a pseudomicellar conformation in aqueous solution in which the hydrophobic core of naphthalene block is surrounded by a hydrophilic shell created by the SSS polymeric units. This is supported by GPC and viscometric measurements, both of which depend on the hydrodynamic volumes of the polymer chain. Both methods show that there is a dramatic decrease in the hydrodynamic volume of the polymer chain coming from PSSS1 macroinitiator to the PSSS-*block*-VN. The intrinsic viscosity of PSSS-*block*-VN ($[\eta] = 90$ cm^3/g) is

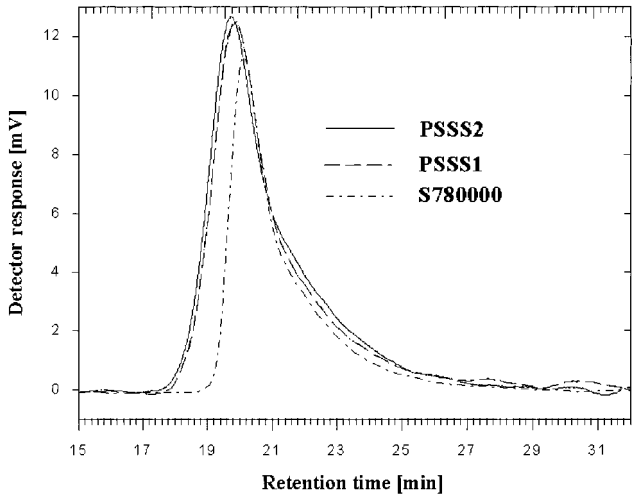

Figure 1. GPC chromatograms of polymers PSSS1, PSSS2, and S 780 000 (PSSS standard, $M_w = 780\,000$ g/mol, PD = 1.1).

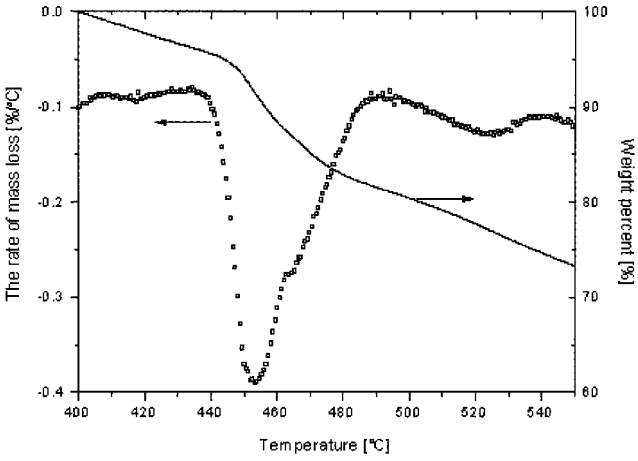

Figure 2. Thermogravimetric analysis of PSSS-*block*-VN.

considerably smaller than that of the macroinitiator, PSSS1 ($[\eta] = 130$ cm^3/g). While the GPC-determined molecular weight of the PSSS1 precursor was $M_w = 1.0 \times 10^6$ g/mol, *the apparent* molecular weight of PSSS-*block*-VN determined by the same method and at the same conditions was *lower* (4.7×10^4 g/mol) (see Table 1).

The effective hydrodynamic volume (V_{eff}) of the PSSS-*block*-VN polymer chain in aqueous NaCl solution (0.5 M) was estimated from the viscometric measurements using the following equation[9] (assuming $M_v = 1.2 \times 10^6$ g/mol):

$$V_{eff} = \frac{M_v[\eta]}{0.025N} \quad (1)$$

where N is Avogadro's number.

The calculated parameters $V_{eff} = 7.17 \times 10^{-17}$ cm^3 and effective hydrodynamic radius, $r_{eff} = 25.8$ nm, characterize the polymeric coil present in solution at high concentration (0.5 M) of ions which screen repulsion between sulfonic groups. For solutions of lower ionic strength one should expect much larger V_{eff}. (The V_{eff} of PSSS-*stat*-VN increases more than 10-fold in solutions of ionic strength from 10^{-2} to 2×10^{-6}.[10])

The fluorescence spectra of PSSS-*block*-VN and PSSS-*stat*-VN are considerably different (Figure 3). There are three bands characteristic of the isolated naphthalene

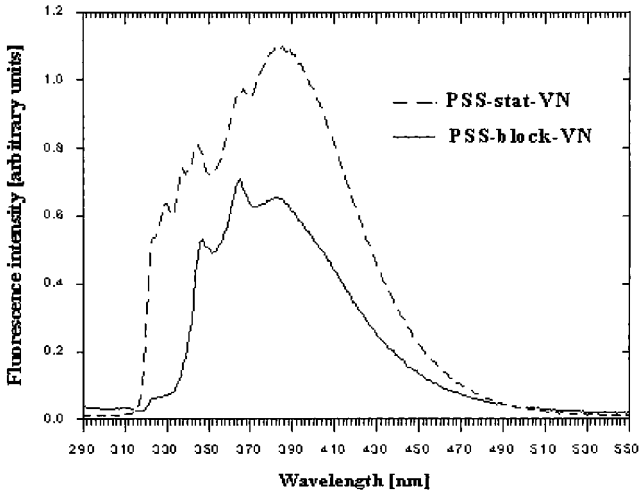

Figure 3. Corrected fluorescence spectra of PSSS-*stat*-VN and PSSS-*block*-VN copolymers (λ_{ex} = 280 nm).

chromophores at 330 nm ("monomeric emission"), partially overlapped excimer at 365 nm ("second excimer"), and fully overlapped excimer at 385 nm ("normal excimer").[11] The relative intensity of the band characteristic of the second excimer is the highest. This indicates that the block of naphthalene chromophores forms a microenvironment in which the chromophores interact strongly, but their rearrangement to a lower energy excimer is difficult.

To characterize the interior of the polymeric coil, molecular probes such as perylene, pyrene, and PRODAN were solubilized in aqueous solutions of PSSS-*block*-VN. The photophysical properties of these molecules are very sensitive to their environment. The solubilizing ability of the PSSS-*block*-VN copolymer toward perylene in aqueous solution is very high. The distribution coefficient (K) of perylene molecules between the polymeric pseudophase and the aqueous phase (defined as the ratio of molar fraction of perylene in the polymeric pseudophase and aqueous phase) was determined using a method described earlier.[12] The very high value of $K = 2.1 \times 10^{10}$ indicates that the polymeric microenvironment is very hydrophobic.

The presence of the hydrophobic microdomains in aqueous solution of PSSS-*block*-VN was confirmed using pyrene as a polarity-sensitive probe. The intensity of the vibronic fine structure in pyrene monomer fluorescence strongly depends on solvent polarity.[12,13] The ratio of the intensity of peak III to peak I is generally used as a sensitive measure of the environmental micropolarity.[12,13] The ratio of the emission intensities III/I of pyrene is equal to 1.08 in the presence of PSSS-*block*-VN in aqueous solution (see Figure 4), while in water it is only 0.63.[12] The former value is comparable to that of common aromatic solvents (e.g., the III/I ratio is equal to 0.88 in benzene and 1.00 in *p*-xylene solutions)[12] and is significantly higher than that found in typical micelles (e.g., in the hexadecyltriethylammonium bromide micelles the III/I ratio was 0.72).[12]

To probe possible solubilization sites for aromatic molecules within the polymeric coil of PSSS-*block*-VN in aqueous solution, we investigated the fluorescence emission spectra of PRODAN/polymer mixtures. The position of the emission maximum of PRODAN depends strongly on the polarity of the medium.[14] Usually the emission spectrum of PRODAN in microheterogeneous systems is broad.[15,16] Deconvolution of the spectrum into

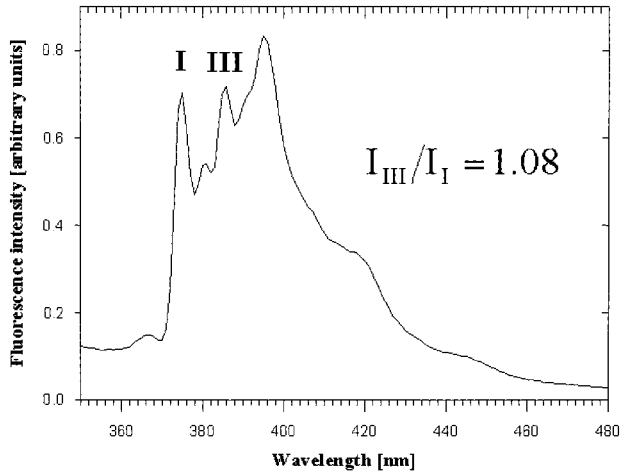

Figure 4. Fluorescence emission spectrum of pyrene solubilized in aqueous solution of PSSS-*block*-VN.

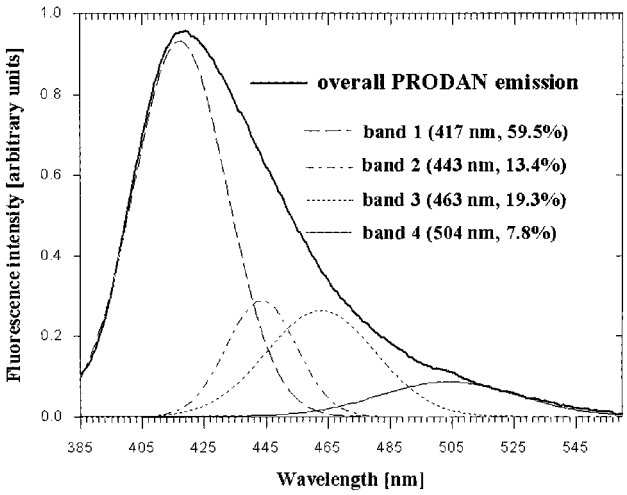

Figure 5. Overall emission of PRODAN, solubilized in aqueous solution of PSSS-*block*-VN, deconvoluted into four Gaussian bands. (The values in the parentheses are the wavelength of maxima and percentages of total emission for the calculated bands.)

a sum of overlapping Gaussian bands shows that there are four solubilization sites for PRODAN in the interior of the polymeric core. About 60% of its overall emission originates from the emission of the molecules which experience a polarity similar to that of benzene[14] (a band with maximum at λ_{em} = 417 nm) (see Figure 5). Three other bands characteristic of microenvironments of higher polarity participate in the remaining 40% of the emission. Moreover, penetration of the hydrophobic microdomain by water molecules may be ruled out by the lack of band characteristic for PRODAN in aqueous solution (λ_{em} = 526 nm).[14] Therefore, these results obtained using PRODAN as a molecular probe also indicate that the polymeric microdomain is highly hydrophobic, and that it is quite homogeneous.

The degree of polarization of fluorescence of perylene (p, p = 0.25, λ_{ex} = 415 nm, λ_{em} = 450 nm) embedded in PSSS-*block*-VN micelles is an order of magnitude higher than that of surfactant micelles[17] and is closer to the value of 0.46 obtained for perylene under conditions at which the rotational motions of the molecule are eliminated (propylene glycol at −50 °C).[18] This indicates that the microviscosity of the polymeric domain in PSSS-*block*-VN is high.

Conclusions

A new amphiphilic block copolymer, PSSS-*block*-VN, has been synthesized by a homogeneous nitroxide-mediated free radical polymerization. To the best of our knowledge, this is the first report on the synthesis of block amphiphilic polyelectrolyte in a simple two-step procedure using TEMPO-mediated radical *homogeneous* polymerization. Chaleux et al. have reported the synthesis of block amphiphilic copolymers using "living" radical polymerization in emulsion.[19]

The rate-accelerating additive, CSA, was used successfully to synthesize the PSSS macroinitiator and in its subsequent copolymerization to generate PSSS-*block*-VN. CSA has been used previously as a rate-accelerating additive in the "living" radical polymerization of styrene.[20] Even at relatively low concentration (ca. 0.01 M), the presence of CSA increases the number of chain-ends capped with the mediator fragments.[20] In this work we have shown that CSA can also be applied in polymerization and copolymerization of hydrophilic monomers.

Despite the high molecular weight and high content of hydrophobic units, the PSSS-*block*-VN block copolymer is readily soluble in water. The copolymer chain adopts a pseudomicellar conformation in aqueous solution. Molecular probes such as perylene, pyrene, and PRODAN show that the interior of the polymeric pseudomicelle is viscous, hydrophobic, and relatively homogeneous.

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