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ORIGINAL CONTRIBUTIONS

Guang-Hua Li
Chang-Gi Cho

Synthesis and micellar behavior of poly(vinyl alcohol-*b*-styrene) copolymers containing PVA blocks with different syndiotacticity

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G.-H. Li · C.-G. Cho (✉)
Center for Advanced Functional Polymers,
Department of Fiber & Polymer Engineering,
Hanyang University, 17 Haengdang-dong,
Seongdong-gu, Seoul 133-791, Korea
E-mail: cgcho@hanyang.ac.kr
Tel.: +82-2-22900497
Fax: +82-2-22921053

Abstract Poly(vinyl alcohol-*b*-styrene) (poly(VA-*b*-St)) diblock copolymers with different syndiotacticity of poly(vinyl alcohol) (PVA) block were synthesized via consecutive telomerization, atom transfer radical polymerization, and saponification. These amphiphilic block copolymeric micelles were prepared by dialysis against water. Dynamic light scattering and transmission electron micrograph measurements confirmed the formation of a micelles, and the size of a micelle was less than 100 nm and increased with the molecular weight of polystyrene (PS) block. From the fluorescence emission spectrum measurements using pyrene as a fluorescence probe, the copolymers formed micelles with critical micelle concentration (CMC) in the range of 0.125–4.47 mg/l. The CMC values increase with decrease of the molecular weight of the PS block and increase of the syndiotacticity of PVA block. Kinetic stability study of micelles showed increased stability for block copolymers containing PVA block with higher syndiotacticity.

Keywords Poly(VA-*b*-St) · Syndiotacticity · Amphiphilic block copolymer · Micelle · Critical micelle concentration

Introduction

Amphiphilic block copolymers composed of hydrophilic and hydrophobic block in an aqueous phase tend to self-assemble and form microphases, i.e., micelles. These polymeric micelles have nano-scale, high thermodynamic and kinetic stability, and can solubilize hydrophobic substances, and therefore they may be applied to separation system, drug delivery system, pharmaceuticals, or emulsion stabilization [1–8].

The self-assembly behavior and micellar structure of amphiphilic block copolymers in an aqueous phase depend on the chemical composition, total molecular weight, block length ratios, architecture of the block copolymer, and relative strength of the interaction between hydrophilic and hydrophobic blocks. Therefore, it is important to systematically diversify the structure of amphiphilic block copolymers, so that their micellar characteristics can be tailored to specific applications. For the formation of micelles in an aqueous phase, most amphiphilic block copolymers are based on hydrophilic poly(ethylene oxide) (PEO) combined with various hydrophobic blocks such as polyesters [9–11], polystyrene (PS) [12–19], poly(amino acids) [20, 21], poly(propylene oxide) (PPO) [5, 22, 23], poly(tetramethylene oxide) [24, 25], and polyalkanes [26]. Among them, poly(ethylene oxide-*b*-styrene) (poly(EO-*b*-St)) block copolymers have been investigated intensively as a typical model copolymer for the study of self-assembling systems [12–19]. Poly(vinyl alcohol) (PVA) is not only water-soluble, non-toxic, and biocompatible, but also possible to form hydrogen bonds between molecular chains. However, the report on PVA as a hydrophilic block for the formation of micelles in an aqueous phase is rare [27–29], and all studies were done with atactic PVA. As PVA behaves differently in aqueous phase depending on its tacticity [30–33], a quite different micellar behavior and kinetic stability are expected with block copolymers containing PVA with different tacticity.

In this research, we prepared poly(vinyl alcohol-*b*-styrene) (poly(VA-*b*-St)) block copolymers containing PVA with different tacticity, and their micellar behaviors were studied. The poly(VA-*b*-St) block copolymers were synthesized by saponification of the corresponding poly(vinyl ester-*b*-styrene) [34]. For the preparation of poly(vinyl ester-*b*-styrene) diblock copolymer, telomerization of vinyl esters, and atom transfer radical polymerization (ATRP) with styrene were performed by following well-known established procedures [35–37]. The chain lengths of PVA and PS blocks were adjusted for the proper solubility of the block copolymers in an aqueous phase. The micellar behavior of poly(VA-*b*-St) block copolymers in an aqueous phase was investigated by means of fluorescence techniques and dynamic light scattering (DLS).

Experimental

Materials

Vinyl pivalate (VPi) (Aldrich Chemical Co. Inc., milwaukee, WI, USA, 99%) and vinyl acetate (VAc) (Junsei Chemical Co. Ltd., Chou-ku, Tokyo, Japan, 99.5%) were washed with 25% $NaHSO_3$ aqueous solution (the pH value of the solution was adjusted to ~8 with KOH), washed three times with distilled water, dried over anhydrous $CaCl_2$, and then distilled under reduced pressure at 40 °C. Styrene (St, Kanto Chemical Co. Ltd., Tokyo, Japan, 99%) was used after passing through an alumina column to remove inhibitor. Copper(I) chloride was purified according to the established procedure [37]. CCl_4 (Duksan Pure Chemical Co. Ltd., Seoul, Korea, 99%) was distilled before use. 2,2′-Azobisisobutyronitrile (AIBN) (Wako Pure Chemical Ind., Osaka, Japan, 98%) was recrystallized from methanol. Ethyl acetate (Junsei Chemical Co. Ltd., 99.5%), acetone (Samchun Pure Chemical Co. Ltd., Seoul, Korea, 99%), methanol (Samchun Pure Chemical Co. Ltd., 99.5%), *n*-hexane (Duksan Pure Chemical Co. Ltd., 96%), tetrahydrofuran (THF, Samchun Pure Chemical Co. Ltd., 99%), 2,2′-bipyridyl (Kanto Chemical Co. Ltd., 99%), pyrene (Aldrich Chemical Co. Inc., 98%), *N*,*N*′-dimethylformamide (DMF, Junsei Chemical Co. Ltd., 99%), *N*,*N*′-dimethylacetamide (DMAc, Shinyo Pure Chemicals Co. Ltd., 99%), and 1-methyl-2-pyrrolidone (NMP, Samchun Pure Chemical Co. Ltd., 99%) were used as received.

Synthesis of amphiphilic diblock copolymers

Poly(VA-*b*-St) amphiphilic block copolymers were synthesized via consecutive telomerization of VAc and/or VPi, ATRP with styrene, and saponification as shown in Scheme 1. The synthetic procedure of poly(vinyl ester-*b*-St) block copolymers was similar to our previous study [34], except that telomerization was carried out using ethyl acetate as a solvent at 60 °C. In addition, PVAc telomer needs to be redissolved in ethyl acetate and reflux for 24 h for the decomposition of traces of unreacted initiator. Three telomers PVPi-Cl, poly(VPi/VAc)-Cl, PVAc-Cl were purified by precipitation of acetone solution into CH_3OH/H_2O (4:1, v/v), CH_3OH/H_2O (3:1, v/v), *n*-hexane, respectively; the block copolymers poly(VPi-*b*-St), poly(VPi/VAc-*b*-St), poly(VAc-*b*-St) were recovered by precipitation of THF solution into CH_3OH/H_2O (4:1, v/v), CH_3OH/H_2O (3:1, v/v), *n*-hexane, respectively. Subsequently, the poly(vinyl ester-*b*-St) copolymers were saponified by the same method as in our previous study [34]. The molecular weight and its distribution of the telomer and poly(vinyl ester-*b*-St) copolymer were determined by gel permeation chromatography (GPC). VPi/VAc ratio in the telomer, and composition of poly(VA-*b*-St) block copolymers were determined by ^{1}H-NMR.

Sample preparation

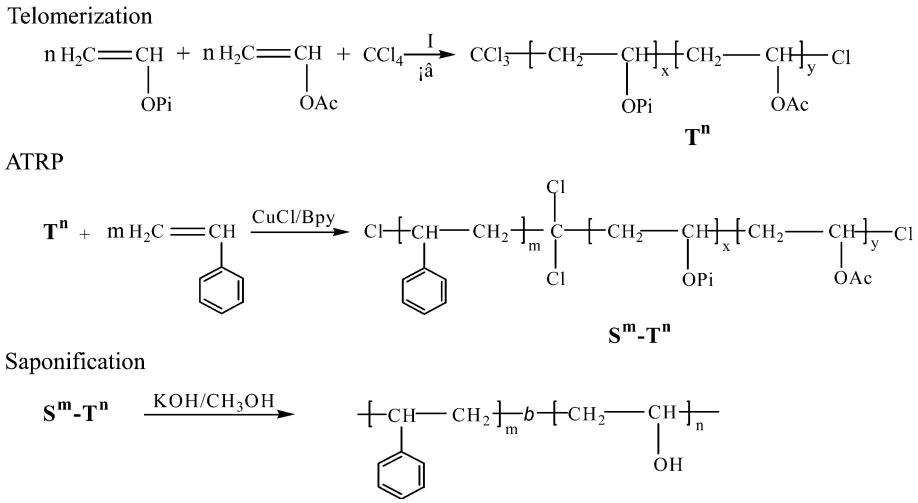
The micellar solutions of poly(VA-*b*-St) block copolymers were prepared in accordance with a dialysis method. Briefly, 10 mg of the poly(VA-*b*-St) block copolymer was dissolved in 40 ml of DMF, DMAc, or NMP, and stirred several hours for equilibration. This solution was dialyzed against distilled water (Sigma, benzoylated cellulose tubing, molecular weight cut off 1,200) for 3 days to form micelles. The water was exchanged at regular intervals. The obtained micellar solution was centrifuged to remove aggregated particles and impurities, and then diluted to prepare a solution varying in polymer concentration. In addition, the samples for dynamic light scattering (DLS) measurements were prepared by diluting stock solution with distilled water and filtering through a 0.5 μm syringe filter.

For the measurement of fluorescence spectra, the micellar solutions loaded with pyrene were prepared as follows: a known amount of pyrene in acetone was added to each of a series of 10 ml vials, and the acetone was evaporated in an oven at 65 °C. Prepared micellar solution from the above was then added to each vial, to give a pyrene concentration in the final solution of 6.0×10^{-7} M, 1.15×10^{-5} M, 2.3×10^{-5} M, 4.6×10^{-5} M. The stoppered vials were heated for 3 h (concentration of pyrene: 6.0×10^{-7} M) or 6 h (other concentrations of pyrene) at 65 °C to equilibrate the pyrene and the micelles, and subsequently allowed to cool overnight to room temperature.

Measurements

The molecular weight and its distribution of the pure telomer and the block copolymers were measured by gel

Scheme 1 Synthetic scheme of poly(VA-*b*-St)



permeation chromatography(GPC) equipped with a Waters 717plus Autosampler, Waters 515 HPLC pump, Waters 410 refractive index detector, and Waters styragel HR series (HR1, 3, 4) (eluent: THF, 35 °C, flow rate: 0.3 ml/min). Polystyrene standards were used to calibrate the columns. The number-average degree of polymerization of the telomer and the block copolymers were also determined using VARIAN 300 MHz ^{1}H-NMR spectrometer, with $CDCl_3$ or DMSO-d_6 as the solvent.

The hydrodynamic radii of block copolymer micelles were determined by a DLS using an argon ion laser (model 95-2, Lexel Laser Inc., USA) at a wavelength of 514.5 nm at 25 °C. The intensity of the scattered light was detected with a photomultiplier (Brookhaven Instrumental Co., EMI9863) at a scattering angle of 90 °.

In order to determine the critical micelle concentration (CMC) of poly(VA-*b*-St) block copolymers in an aqueous phase, and the rate of release and exchange of pyrene in the micellar solution of block copolymers, the fluorescence emission spectra of pyrene were measured at an excitation wavelength of 339 nm using a RF-5301PC spectrofluorophotometer (Shimadzu Co., Japan) at 25 °C.

For transmission electron microscopy (TEM), a drop of the dilute solution of poly(VA-*b*-St) block copolymers (0.1 g/l) was placed onto a copper micro-grid covered with carbon substrate and allowed to dry with nitrogen gas. The grids were coated with gold. TEM was performed using a JEOL-2000EX (II) instrument operating at 100 kV.

Results and discussion

Synthesis and characterization of poly(VA-*b*-St) block copolymers

Poly(VA-*b*-St) block copolymers with different syndiotacticity of PVA block and varying composition were synthesized via consecutive telomerization of vinyl esters, ATRP with styrene, and saponification. The syndiotacticity of PVA block was adjusted by the ratio of VAc and VPi, because the polymerization of VPi is known to give a polymer rich in syndiotacticity whereas that of VAc leads to an almost atactic polymer. CCl_4 was chosen as a telogen, because of its similar chain transfer constant for both monomers (for VAc and VPi, C_{tr} is equal to 1, 1.18, respectively) [38, 39]. The structure of poly(VPi-*co*-VAc) telomer prepared with CCl_4 and AIBN was analyzed by ^{1}H-NMR spectroscopy in $CDCl_3$ as shown in Fig. 1. The signals at 2.8–3.2 (a) and 5.2–5.5 ppm (b) correspond to the methylene and methine protons adjacent to the trichloromethyl group at the α-end, respectively. The resonance at 6.25–6.5 ppm (f) corresponds to methine proton adjacent to terminal chlorine at the ω-end. The integration ratio of f/b/a is

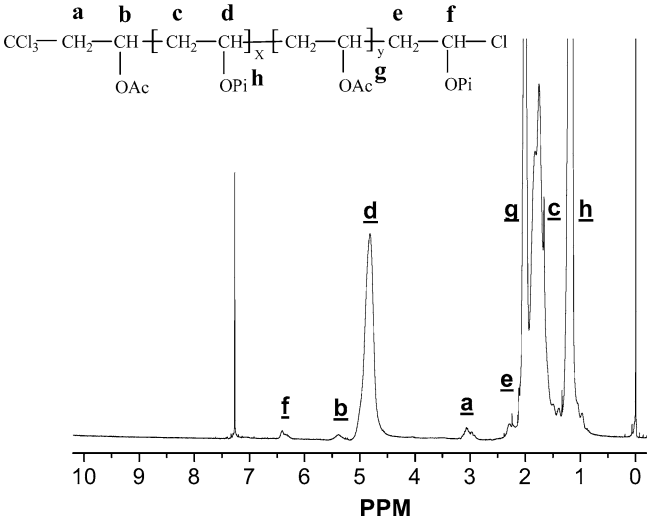


Fig. 1 ^{1}H-NMR spectrum of poly(VPi-*co*-VAc) prepared using CCl_4 as a telogen and AIBN as a initiator

Table 1 Synthetic results of telomerization of VAc or/and VPi with CCl_4

VAc/VPi in feed (mol/mol)	Time (h)	Yield (%)	VAc/VPi in polymer (mol/mol)	$M_{n,\ \mathrm{GPC}}$	$M_{n,\ \mathrm{NMR}}$	M_w/M_n
100/0	5	64.6	100/0	3,680	3,170	1.53
50/50	3.5	64.3	46/54	5,170	4,290	1.38
0/100	3	72.3	0/100	5,050	4,760	1.57

AIBN/monomer = 0.10 mol%, Reaction temperature = 60 °C, Ethyl acetate = 25 ml, Total feed monomer = 25 ml, CCl_4/monomer = 3.0 mol%

about 0.95/1/2, very close to theoretical value of 1/1/2, indicating the presence of both trichloromethyl and chlorine end groups on one polymer chain. Using the ratio of the area of the two peaks (d/a), the number-average molecular weight ($M_{n,\ \mathrm{NMR}}$) was determined. As in Table 1, $M_{n,\ \mathrm{NMR}}$ by ^{1}H-NMR shows smaller value than $M_{n,\ \mathrm{GPC}}$ by GPC. Also, the mole fraction of VPi and VAc in the poly(VPi-*co*-VAc) telomer was calculated by the ratio of the area of the two resonance peaks (h/g) in ^{1}H-NMR. The synthetic results of three telomers are shown in Table 1.

Trichloromethyl end group in the poly(vinyl ester)s is an efficient initiator for Cu-catalyzed ATRP of styrene [34, 35, 37, 40]. Trichloromethyl initiation generates a polymer structure which contains $-CH_2-CCl_2-CH_2-$, $-CH_2-CH(OAc)-Cl$, and $-CH_2CH(C_6H_5)-Cl$ groups as shown in the Scheme 1, but it is known that only $-CH_2CH(C_6H_5)-Cl$ group is active in the ATRP condition, thus generating only a diblock copolymer. ATRP is one of living radical polymerization, which is one of the most versatile methods for synthesizing homopolymers and copolymers with predetermined molecular weight and narrow molecular weight distribution. The molecular weight of PS block was adjusted via reaction time and calculated by styrene conversion. Figure 2 shows the GPC traces of PVAc-Cl macroinitiator and the resulting block polymers. The shift of chromatograms toward higher molecular weights is clearly observable with the increased polymerization time, which supports the formation of a block copolymer. In addition, the molecular weight distributions (M_w/M_n ~1.24–1.33) of the obtained block copolymers become narrower with increased polymerization time, compared to that of the macroinitiator (M_w/M_n~1.53). The GPC molecular weight of the longest PS block is only around 3,400 in Fig. 2, so the GPC traces do not tell whether the macroinitiator is consumed completely or not. In our previous research [34], the complete consumption of the macroinitiator and the shift of chromatograms toward high molecular weights were clearly observed when the molecular weight of the PS block was around 10,000.

Figure 3 represents ^{1}H-NMR spectrum of the poly (VAc-*b*-St) block copolymer at 6.4% styrene monomer conversion. In the spectrum, it is possible to calculate the molecular weight of the PS block based on the resonance peaks of aromatic protons and methine proton of vinyl ester unit. Obtained value matches well with the theoretical molecular weight, $M_{n,\mathrm{th}}$, which is calculated

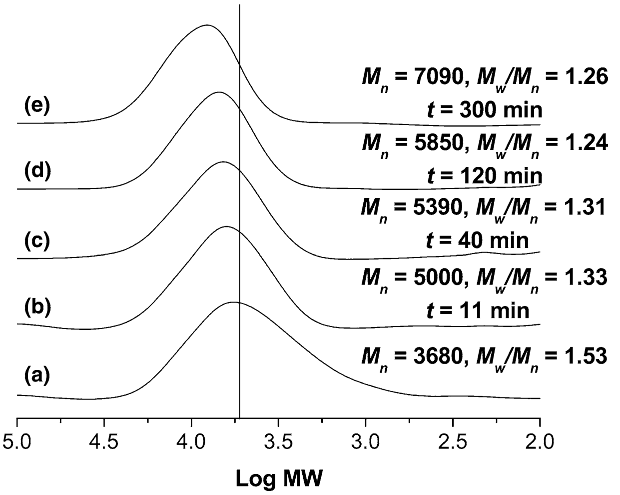


Fig. 2 Gel permeation chromatography traces of PVAc macroinitiator (**a**) and poly(VAc-*b*-St) copolymers ((**b**)–(**e**)). Polymerization conditions: [St] = 8.7 M, [Macroinitiator]/[CuCl]/[Bpy]/[St] = 4:1:2:300, 130 °C

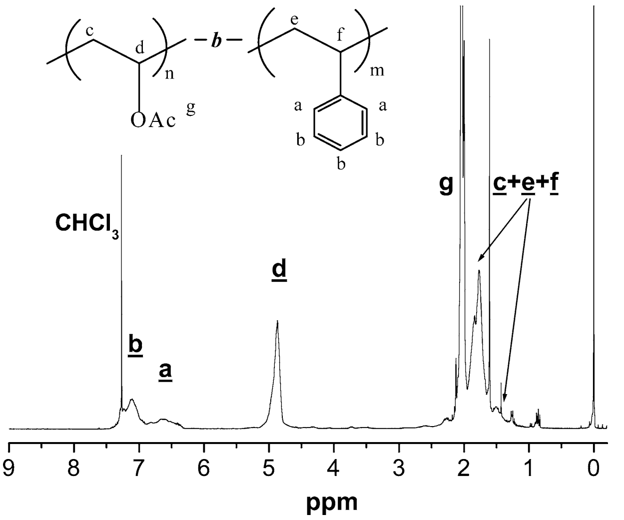


Fig. 3 ^{1}H-NMR spectrum of poly(VAc-*b*-St) (time = 11 min, St conversion = 6.4%). Conversion (%) = (Product weight − Macroinitiator weight)/St weight×100%

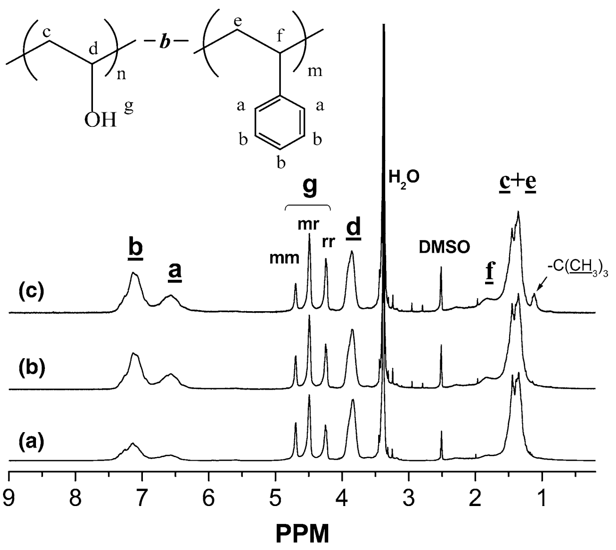


Fig. 4 ^{1}H-NMR spectra of poly(VA-*b*-St) prepared by the saponification of poly(vinyl ester-*b*-St). **a** by poly(VAc-*b*-St), **b** by poly(VPi/VAc-*b*-St), **c** by poly(VPi-*b*-St)

based on styrene conversion (%) ($M_{n,\mathrm{NMR}} = 620$; $M_{n,\mathrm{th}} = 500$; total $M_{n,\mathrm{GPC}}$ by GPC = 5,000).

Obtained poly(vinyl ester-*b*-St)s were saponified and the resultant poly(VA-*b*-St)s were analyzed by ^{1}H-NMR in DMSO-d_6. Figure 4 shows a benzene ring proton peak at 6.2–7.4 ppm and –OH proton peak at 4.2–4.8 ppm, which indicate the presence of PVA and PS blocks, and the calculated syndiotacticity (diad%) from three –OH peaks is 53.0% (A), 56.1% (B), 59.1% (C), respectively. Also, the presence of the pivaloyl proton peak at 1.1 ppm, indicates that the PVPi block was not completely saponified, which maybe ascribed to the different solubility of highly syndiotactic PVA and PS blocks in the THF solvent. From the ratio of the area of the methine protons peak (d) adjacent to the –OH and the pivaloyl proton peak in the spectrum (C), the calculated degree of saponification is 97.8%. The small amount of unsaponified pivaloyl group may influence the self-assembling properties in solution. Table 2 shows the synthetic results of poly(VA-*b*-St) block copolymers.

Size and morphology of poly(VA-*b*-St) block copolymer micelles

Since the direct preparation of poly(VA-*b*-St) block copolymeric micelles in an aqueous solution was difficult via dispersion or "co-precipitation", a dialysis method was employed to prepare the micelles [10]. The formation and morphology of micelles were investigated by DLS and TEM. The size distribution of the PVA$_1$-PS$_{970}$ polymeric micelles was obtained by histogram analysis and is shown in Fig. 5. From Fig. 5, narrow and unimodal distributions were observed and the average diameter of the PVA$_1$-PS$_{970}$ polymeric micelles was determined to be about 47 nm. Other results are listed in Table 2. As seen from Table 2, the size of a micelle is less than 100 nm and increases with the molecular weight of the PS block. However, the PVA$_1$-PS$_{500}$ shows micelles with bimodal distribution, which may be ascribed to the partial aggregation of smaller micelles. In addition, in the case of poly(VA-*b*-St) copolymers with medium syndiotacticity, its size was larger than the others, and the reason is not clear at present.

A typical TEM of a sample prepared from a dilute solution of the PVA$_3$-PS$_{1030}$ is shown in Fig. 6. Spherical shapes with some irregularities are clearly observed, and their diameters are approximately the same as that determined by DLS.

CMC of poly(VA-*b*-St) block copolymers

The amphiphilic block copolymers, poly(VA-*b*-St)s form micelles in an aqueous phase. The CMC of the block copolymers were determined by a fluorescence technique using pyrene as a probe. Pyrene is probably the most widely used fluorescence probe, because its vibrational fine structure is sensitive to polarity [13, 22, 41–43] and

Table 2 Synthetic results, CMC, and average micelle size of poly(VA-*b*-St) copolymers

Precursor		PVA	PS		Syndio- tacticity (diad%)	Sample	CMC (mg/l)	Average micelle size (nm)
	$M_{n,\mathrm{GPC}}$	$M_{n,\mathrm{NMR}}$	$M_{n,\mathrm{th}}$	$M_{n,\mathrm{NMR}}$				
Poly(VAc-*b*-St)	5,000	1,540	500	620	53.0	PVA$_1$-PS$_{500}$	0.986	40, 115
	5,390		970	–		PVA$_1$-PS$_{970}$	0.541	47
	5,850		1,520	–		PVA$_1$-PS$_{1520}$	0.196	–
	7,090		2,260	–		PVA$_1$-PS$_{2260}$	0.125	68
Poly(VAc/VPi-*b*-St)	6,110	1,670	1,040	1,480	56.1	PVA$_2$-PS$_{1040}$	1.07	77
	7,030		1,520	–		PVA$_2$-PS$_{1520}$	0.977	94
Poly(VPi-*b*-St)	5,990	1,580	1,030	–	59.1	PVA$_3$-PS$_{1030}$	4.47	49
	6,430		1,470	1,700	59.6	PVA$_3$-PS$_{1470}$	4.07	57

$M_{n,\mathrm{th}}$ [St]$_0$/[Macroinitiator]$_0$×104×Conversion (%)
PVA$_1$ PVA derived from PVAc
PVA$_2$ PVA derived from Poly(VPi-*co*-VAc)
PVA$_3$ PVA derived from PVPi

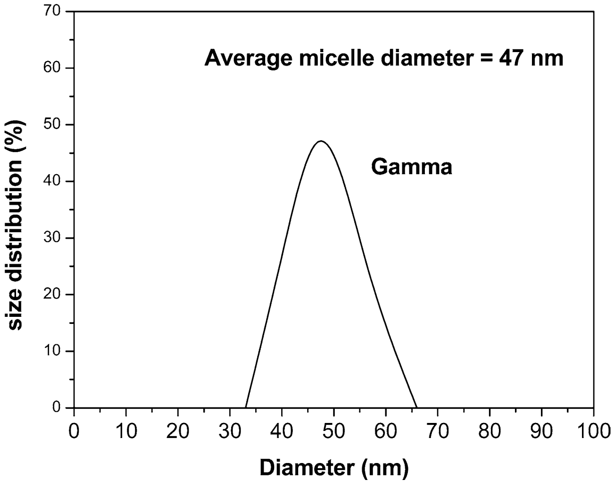


Fig. 5 Size distribution profiles of PVA_1-PS_{970} copolymeric micelles measured by DLS

because it produces distinct excimer fluorescence under conditions of sufficiently high concentration and mobility [42]. In Fig. 7, the fluorescence emission spectra of pyrene are shown at various concentrations of PVA_1-PS_{970} containing 6×10^{-7} M of pyrene. The two noteworthy features of these spectra are that the intensity decreases with decreasing polymer concentration and that there are obvious changes in the intensity ratio of the band (I_1) to the band (I_3), I_1/I_3. The I_1/I_3 ratio depends on the polarity of the pyrene surroundings, which can be used to determine the CMC values [13, 41]. Figure 8 shows the intensity ratios (I_1/I_3) of pyrene monomer emission spectra versus the logarithm of concentrations of PVA_1-PS_{500}, PVA_1-PS_{970}, PVA_1-PS_{1520}, and PVA_1-PS_{2260} block copolymers. A negligible change of intensity ratios was observed at a low concentration range, but above a certain concentration the intensity ratios show a sharp decrease, which indicates the incorporation of pyrene into the hydrophobic core region of the micelles. Therefore, the CMC was determined from the graphical intersecting point at the low concentration range in Fig. 8 and listed in Table 2. As can be seen in Table 2, the CMC values of the block copolymers are extremely low and have an inverse correlation with the molecular weight of the PS block, and increase with increase in the syndiotacticity of the PVA block. The former is ascribed to the decreased solubility as the molecular weight of PS block increased, while the latter may be ascribed to more dense arrangement or the formation of multi-layer at the interface as PVA blocks have higher syndiotacticity [44]. It is known that PVA homopolymer with high syndiotacticity has stronger intermolecular forces (hydrogen bonding) and poor solubility in water [30, 33].

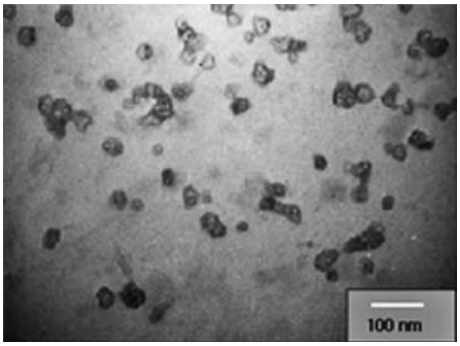


Fig. 6 Transmission electron micrograph image of the micelles prepared by PVA_3-PS_{1030} copolymer

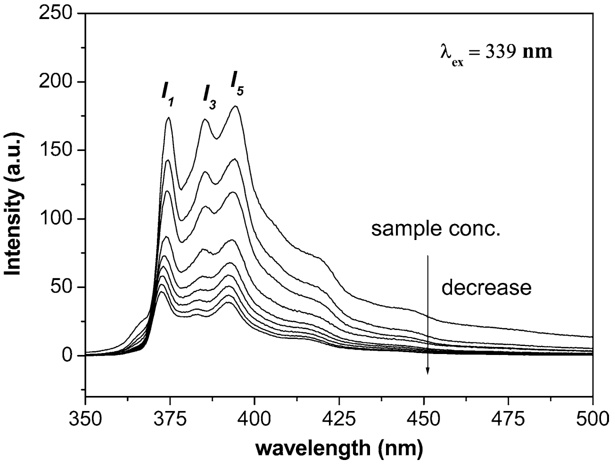


Fig. 7 Fluorescence emission spectra of pyrene (6×10^{-7} M) in the presence of decreasing concentrations of PVA_1-PS_{970} copolymer

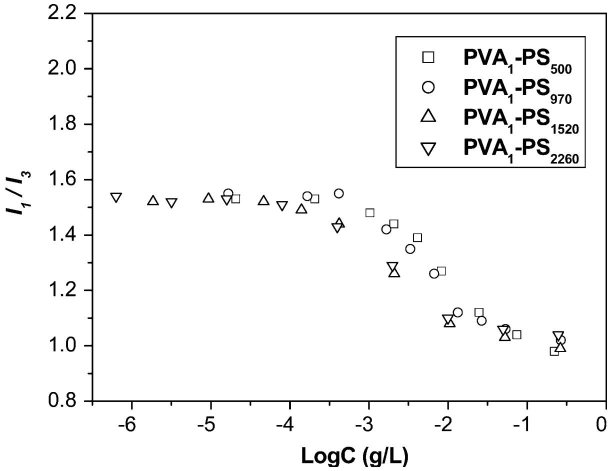


Fig. 8 Plot of the fluorescence intensity ratio I_1/I_3 (from pyrene emission spectra) versus log C for poly(VA-*b*-St) block copolymers

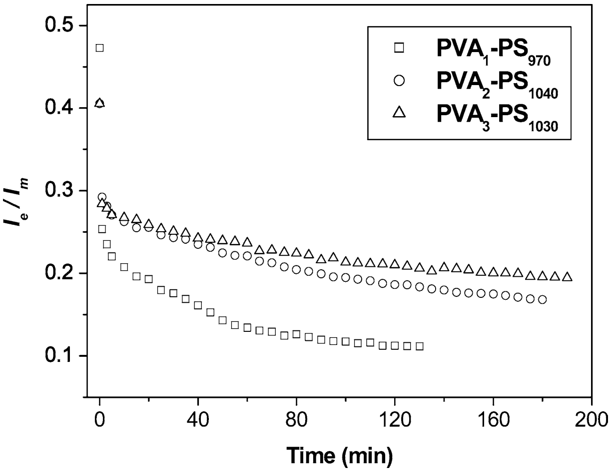


Fig. 9 I_e/I_m ratio as a function of time after mixing pyrene-loaded micelle with pyrene-free micelles

Kinetic stability of micelles

Fluorescence methods can also be used to study the kinetics of exchange of molecules solubilized in block copolymer micelles between micelles and intermicellar solution. Cao et al. [42] have investigated the solubilization of pyrene in PMMA-*b*-PS-*b*-PMMA triblock copolymers in water. Micelles with pyrene were mixed with micelles without pyrene, and the time dependence of the ratio of excimer intensity, I_e (at 469 nm) to monomer fluorescence intensity, I_m (at 374.5 nm) was measured. In this study, a micellar solution containing 4.6×10^{-5} M of pyrene was selected to carry out an exchange experiment of pyrene solubilized in block copolymer micelles. When copolymer micelles containing pyrene are mixed with micelles without pyrene, the pyrene molecules are exchanged between micelles and I_e decreases leading to the I_e/I_m ratio decrease with time as shown in Fig. 9. The time scale of this ratio change reflects the rate at which this exchange occurs, because the rate-determining step is not the rate of micelle–micelle collision, but pyrene diffusion within the PS core [42]. There is a relatively rapid change in I_e/I_m at the beginning, specially in the case of low syndiotacticity, followed by a very slow equilibration as the PVA block has higher syndiotacticity. These indicate that the rate of release and exchange decreases and the equilibration time increases with the syndiotacticity of the PVA block after mixing, namely the kinetic stability of the micelles is enhanced by the higher syndiotacticity. The reason may be related to the fact that the higher syndiotacticity of PVA block forms a stronger intermolecular hydrogen bonding [30, 33], so that the hydrophilic PVA block forms a tighter outshell around the micellar core, and therefore the diffusion of the pyrene from the PS micelle core toward the surface is retarded.

Conclusions

Well-defined amphiphilic diblock copolymers, poly(VA-*b*-St)s with different syndiotacticity of the PVA block and varying composition were synthesized via consecutive telomerization of vinyl esters, ATRP with styrene, and saponification, and then the amphiphilic block copolymeric micelles were prepared by dialysis against water. DLS and TEM measurements confirmed the formation of micelles, and the size of the micelle formed was less than 100 nm and their size increases with the chain length of the PS block. The block copolymers in the water showed CMC in the range of 0.125–4.47 mg/l. The CMC values increase with decrease in the molecular weight of the PS block and with increase in the syndiotacticity of the PVA block. In addition, as the block copolymers contain higher syndiotacticity of PVA block, the rate of release and exchange of pyrene molecules become very slow at long time, that is, the kinetic stability of the micelles was obviously enhanced. Therefore, the poly(VA-*b*-St) copolymeric micelles with higher syndiotactic PVA block have a good potential for applications such as drug delivery systems.

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