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Synthesis of Poly(vinyl acetate)-*b*-polystyrene and Poly(vinyl alcohol)-*b*-polystyrene Copolymers by a Combination of Cobalt-Mediated Radical Polymerization and RAFT Polymerization

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ABSTRACT: Well-defined poly(vinyl acetate)-*block*-polystyrene (PVAc-*b*-PSt) block copolymers were successfully synthesized by a combination of cobalt-mediated radical polymerization (CMRP) and reversible addition−fragmentation chain transfer (RAFT) polymerization. PVAc and PVAc-*b*-PSt (with an average PSt repeating unit of 2 or 6) were first synthesized via CMRP with cobalt(II) acetylacetonate as a regulating agent. The cobalt complexes attached to their ω chain ends were modified into a phenyl dithioester group by reacting with bis(thiobenzoyl) disulfide, producing PVAc and PVAc-*b*-PSt macro-chain-transfer agents (PVAc-CTA and PVAc-PSt-CTA), respectively. The RAFT polymerization of styrene with PVAc-CTA or PVAc-PSt-CTA was conducted in *N,N*-dimethylformamide at 80 °C. PVAc-*b*-PSt block copolymers synthesized with PVAc-PSt6-CTA (with an average PSt repeating unit of 6) exhibited narrowest molecular weight distributions (M_w/M_n = 1.28−1.30) even at high conversions. The PVAc-*b*-PSt block copolymer ($M_{n(GPC)}$ = 21 000 g/mol, M_w/M_n = 1.28) was hydrolyzed to amphiphilic poly(vinyl alcohol)-*block*-PSt (PVA-*b*-PSt) block copolymer under basic conditions. The PVA-*b*-PSt micelles were spherical in shape with an average diameter of 44 ± 18 nm.

Introduction

Amphiphilic poly(vinyl alcohol) (PVA) block copolymers, which can be prepared by the hydrolysis of poly(vinyl acetate) (PVAc) block copolymers, have attracted attention due to their potential applications in coatings, adhesives, thin films, and dispersion systems.[1−3] However, the synthesis of well-defined PVAc block copolymers has been challenging because the controlled/living radical polymerization (CRP) of vinyl acetate (VAc) is difficult to control due to a high reactivity of its propagating radicals. The synthesis of PVAc block copolymers, such as PVAc-*block*-polystyrene (PVAc-*b*-PSt) and PVAc-*block*-poly(methyl methacrylate) (PVAc-*b*-PMMA), has been studied extensively by using consecutive telomerization and atom transfer radical polymerization (ATRP).[4−8] VAc telomers were first synthesized by the telomerization of VAc with carbon tetrachloride, followed by ATRP of styrene (St) or methyl methacrylate (MMA) with the VAc telomers as macroinitiators. However, the low molecular weight (MW) with broad MW distribution of the VAc telomers makes it difficult to produce well-defined, high-MW PVAc block copolymers through this method.

Recently, the CRP of VAc was achieved via reversible addition−fragmentation chain transfer (RAFT) polymerization[9−13] and cobalt-mediated radical polymerization (CMRP).[14−21] However, only a few PVAc block copolymers were synthesized by consecutive RAFT polymerization or CMRP because only a few monomers could be consecutively polymerized in a controlled manner with PVAc macroinitiators prepared by RAFT polymerization or CMRP of VAc. For example, the consecutive CMRP of PVAc-*b*-PSt block copolymers with PVAc macroinitiators was uncontrolled (M_w/M_n = 1.50−2.90).[19] Debuigne et al.[20] converted the cobalt complex attached to the ω chain end of the PVAc macroinitiators into an α-bromoester or an α-bromoketone in order to control the polymerization of the second block of PSt. The end-group-modified PVAc chains were used as macroinitiators for the ATRP of St to obtain well-defined PVAc-*b*-PSt block copolymers. On the other hand, Tong et al.[22] employed ATRP and RAFT polymerization techniques to synthesize well-defined PVAc-*b*-PSt block copolymers (M_w/M_n = 1.36−1.46). They used difunctional initiators for the ATRP of St and the RAFT polymerization of VAc. However, they could not hydrolyze the PVAc-*b*-PSt to get PVA-*b*-PSt due to the ester linkages in the starting difunctional initiators.

In the present study, well-defined PVAc-*b*-PSt block copolymers were successfully synthesized for the first time by a combination of CMRP and RAFT polymerization. PVAc and PVAc-*b*-PSt macroinitiators were first synthesized via CMRP, and then the cobalt complex attached to their ω chain ends was converted into a dithioester group for the RAFT polymerization of St. The synthesized PVAc-*b*-PSt block copolymer was hydrolyzed to amphiphilic PVA-*b*-PSt block copolymer, and its micellar characteristics in aqueous solution were investigated.

Experimental Section

Materials. VAc (Aldrich, > 99%) and St (Tokyo Kasei, 98%) were passed through a column filled with neutral alumina, dried over CaH_2, distilled under reduced pressure, and then degassed with several freeze−thawing cycles. *N,N*-Dimethylformamide (DMF, Duksan, 99.5%) was dried over CaH_2, distilled under reduced pressure, and then degassed with several freeze−pump−thaw cycles. 2,2′-Azobis(isobutyronitrile) (AIBN, Tokyo Kasei, 98%) was recrystallized from methanol. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako, 96%), cobalt(II) acetylacetonate [$Co(acac)_2$, Aldrich, 97%], dimethyl sulfoxide (DMSO, Aldrich, ≥99.7%), tetrahydrofuran (THF, Duksan, 99.5%), *N,N*-dimethylformamide (DMF, Aldrich, ≥99.8%), potassium hydroxide (KOH, Duksan, 85%), and methanol (Duksan, 99.5%) were used as received. BTBD was synthesized in 85% yield according to the procedure reported in

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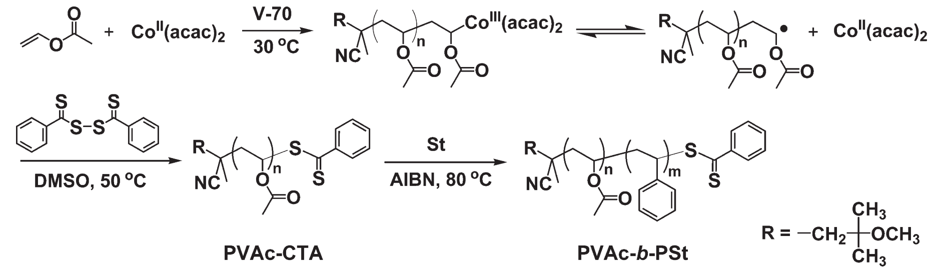
Scheme 1. Synthesis Procedure of PVAc-CTA and PVAc-*b*-PSt[a]



[a] Co^{II}(acac)$_2$, cobalt(II) acetylacetonate; V-70, 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile); DMSO, dimethyl sulfoxide; AIBN, 2,2′-azobis-(isobutyronitrile); PVAc-CTA, poly(vinyl acetate) macro-chain-transfer agent; PVAc-*b*-PSt, poly(vinyl acetate)-*block*-polystyrene.

the literature.[23] ^{1}H NMR (400 MHz, CDCl$_3$) spectrum, δ (ppm): 7.92 (d, 4H, *o*-Ar*H*), 7.52 (m, 2H, *p*-Ar*H*), 7.37 (dd, 4H, *m*-Ar*H*).

CMRP of VAc. The CMRP of VAc was performed in the presence of Co(acac)$_2$ with V-70 at 30 °C. The CMRP of VAc at a ratio of $[VAc]_0/[V\text{-}70]_0/[Co]_0 = 150/3/1$ was carried out as follows: Co(acac)$_2$ (0.186 g, 0.723 mmol), V-70 (0.669 g, 2.17 mmol), and degassed VAc (10.0 mL, 109 mmol) were added to a 50 mL reaction flask equipped with a magnetic stir bar under a nitrogen atmosphere. The reaction mixture was degassed by bubbling with nitrogen for 30 min and then stirred at 30 °C for 5 days. The monomer conversion was determined by weighing the polymer after removing the residual monomers under vacuum at room temperature. The product yield was 5.2 g (conversion = 55.7%). The PVAc chains were end-capped by a Co(acac)$_2$ complex (PVAc-Co(acac)$_2$). The pink PVAc-Co(acac)$_2$ was stored under inert atmosphere. $M_{n(GPC)} = 11\,000$ g/mol, $M_w/M_n = 1.20$.

Synthesis of PVAc Macro-Chain-Transfer Agent (PVAc-CTA). BTBD (0.556 g, 1.82 mmol), PVAc-Co(acac)$_2$ (2.0 g, 0.18 mmol), and DMSO (15 mL) were charged into a 50 mL reaction flask equipped with a magnetic stir bar. The reaction mixture was degassed by bubbling with nitrogen for 30 min and then stirred at 50 °C for 24 h. The separated cobalt complexes were completely removed by filtration using aluminum oxide. The residual BTBD and other impurities were removed by dialysis (MWCO 3500 Da) against acetone for 3 days. The purified polymer was then analyzed by ^{1}H NMR (400 MHz, CDCl$_3$) spectrum, δ (ppm): 7.92 (d, 2H, *o*-Ar*H*), 7.52 (m, 1H, *p*-Ar*H*), 7.37 (dd, 2H, *m*-Ar*H*), 4.8 (1H, $-CH-OCOCH_3$ of PVAc), 2.0 (3H, $-OCOCH_3$ of PVAc), 1.75 (2H, $-CH_2-CH-OCOCH_3$ of PVAc).

Synthesis of PVAc-*b*-PSt Macro-Chain-Transfer Agent (PVAc-PSt-CTA). The average block length of the St units was controlled by polymerizing St at different molar ratios of $[PVAc\text{-}Co(acac)_2]_0/[St]_0$. The CMRP of St at a ratio of $[PVAc\text{-}Co(acac)_2]_0/[St]_0 = 10/1$ was carried out as follows: PVAc-Co-(acac)$_2$ (2.0 g, 0.18 mmol), St (0.20 mL, 1.82 mmol), and DMSO (5 mL) were charged into a 50 mL reaction flask equipped with a magnetic stir bar. The reaction mixture was degassed by bubbling with nitrogen for 30 min and then stirred at 50 °C for 3 h. A BTBD (0.556 g, 1.82 mmol) solution in degassed DMSO (10 mL) was then added to the reaction mixture and stirred at 50 °C for 24 h. After that, the mixture was dialyzed (MWCO 3500 Da) against acetone for 3 days to remove the residual St, BTBD, and other impurities. The purified polymer was then analyzed by ^{1}H NMR (400 MHz, CDCl$_3$) spectrum, δ (ppm): 7.92 (d, 2H, *o*-Ar*H*), 7.52 (m, 1H, *p*-Ar*H*), 7.37 (dd, 2H, *m*-Ar*H*), 7.35−6.3 (5H, $-CH_2-CH-ArH$ of PSt), 1.53 (2H, $-CH_2-CH-ArH$ of PSt), 4.8 (1H, $-CH-OCOCH_3$ of PVAc), 2.0 (3H, $-OCOCH_3$ of PVAc), 1.75 (2H, $-CH_2-CH-OCOCH_3$ of PVAc).

RAFT Polymerization of St with PVAc-CTA or PVAc-PSt-CTA. PVAc-CTA or PVAc-PSt-CTA (0.05 mmol), AIBN (3.7 mg, 0.022 mmol), St (1.30 mL, 11.36 mmol), and DMF (1.4 mL) were charged into a 50 mL reaction flask equipped with a magnetic stir bar under a nitrogen atmosphere. The mixture was then placed in a preheated oil bath at 80 °C for 24 h. The resulting PVAc-*b*-PSt was precipitated in an excess of methanol and dried under vacuum at 50 °C. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum, δ (ppm): 7.35−6.3 (5H, $-CH_2-CH-ArH$ of PSt), 4.8 (1H, $-CH-OCOCH_3$ of PVAc), 2.0 (3H, $-OCOCH_3$ of PVAc), 1.75 (2H, $-CH_2-CH-OCOCH_3$ of PVAc), 1.53 (2H, $-CH_2-CH-ArH$ of PSt).

Hydrolysis of PVAc-*b*-PSt. A 1 N KOH aqueous solution (1 mL) was added to a PVAc-*b*-PSt solution (3 mg/mL) in a mixed solvent of THF/methanol (v/v 15/2). After being stirred at room temperature for 12 h, the reaction mixture was precipitated into an excess of methanol, and then the precipitate was washed several times with methanol. The purified polymer was then analyzed by ^{1}H NMR (400 MHz, DMSO-d_6) spectrum, δ (ppm): 7.35−6.3 (5H, $-CH_2-CH-ArH$ of PSt), 4.1−4.7 (1H, $-CH_2-CH-OH$ of PVA), 3.85 (1H, $-CH_2-CH-OH$ of PVA), 1.2−1.7 (2H, $-CH_2-CH-ArH$ of PSt).

Preparation of the PVA-*b*-PSt Micelles. PVA-*b*-PSt (5 mg) was dissolved in 2 mL of a mixed solvent of THF/DMSO (1/1 v/v), and then 10 mL of deionized water was added to the polymer solution with vigorous stirring for micellization. The micelle solution was dialyzed (MWCO 3500 Da) against 2 L of water for 48 h. The final concentration of the block copolymer was 0.28 mg/mL.

Characterization. The MW and polydispersity of the resulting polymers were determined by a gel permeation chromatography (GPC) system (Young Lin SP930D solvent delivery pump) coupled with an RI detector (RI 750F) and three columns [PLGel 20 μm Mixed-A (300 × 7.7 mm, exclusion range: 2000−40 000 000 g/mol) and PLGel 10 μm 10^4 Å; Agilent technologies, and GPC KF-806 (300 × 8 mm, 10 μm, exclusion range: < 20 000 000 g/mol); Shodex]. The eluent used was THF at 40 °C with a flow rate of 1.0 mL/min. PSt standards were used for calibration. ^{1}H nuclear magnetic resonance (NMR) spectroscopy was performed using a Varian VXR-Unity NMR spectrometer (400 MHz) with CDCl$_3$ and DMSO-d_6 as solvents. The transmission electron microscopy (TEM) images were obtained with a JEM-2100F transmission electron microscope operating at an accelerating voltage of 120 kV. For the TEM analysis, a drop of micelle solution in water (0.28 mg/mL) was deposited onto a 200 mesh carbon-coated copper grid.

Results and Discussion

Scheme 1 shows the synthesis route for PVAc-CTA. PVAc-Co(acac)$_2$ was first synthesized via the CMRP of VAc at 30 °C for 5 days with V-70 as an initiator and Co(acac)$_2$ as a regulating agent.[14] PVAc-Co(acac)$_2$ polymers with different MWs were synthesized by employing different molar ratios of $[VAc]_0/[V\text{-}70]_0/[Co]_0$. When the molar ratios of $[VAc]_0/[V\text{-}70]_0/[Co]_0$ were 100/3/1 and 150/3/1, the number-average MWs (M_n) of the resulting PVAc-Co(acac)$_2$ polymers, as determined by GPC analysis, were 7500 and 11 000 g/mol, respectively.

A wide range of phenyl dithioester CTAs have been successfully used for the RAFT polymerization of St.[24] In the present study, the ω chain end of the PVAc-Co(acac)$_2$ was modified into a phenyl dithioester group for the RAFT polymerization of St. The carbon−cobalt (C−Co) bonds in the PVAc-Co(acac)$_2$ chains were homolytically cleaved at 50 °C in DMSO to yield PVAc macroradicals, which underwent radical reactions to BTBD. 2-(2-Cyanopropyl) dithiobenzoate and 4-cyanopentanoic acid dithiobenzoate, well-known RAFT agents, were similarly synthesized using BTBD.[24] DMSO was used as the reaction solvent to increase the generation efficiency of the PVAc macroradicals. It was reported that the homolytic cleavage of the C−Co bonds in PVAc-Co(acac)$_2$ chains could be dramatically increased by adding a small amount of an electron-donating compound, such as pyridine, water, or DMSO.[25−27] The coordination of these electron-donating compounds to the free sites of the cobalt complex in PVAc-Co(acac)$_2$ weakened the strength of the C−Co bonds and allowed much easier generation of PVAc macroradicals. The PVAc-Co(acac)$_2$ chains had a violet color due to the cobalt complex, whereas PVAc-CTA had a reddish-brown color due to the phenyl dithioester group. Figure 1 shows the ^{1}H NMR spectrum of PVAc-CTA ($M_{n(NMR)}$ = 10 800 g/mol). The peaks of the ω end phenyl group protons (**e**, **f**, and **g**) are clearly observed. The modification efficiency of the ω end groups was determined to be >95% by comparing the integration ratio of the $-OCHH_3$ protons (**a**) to the ω end phenyl group protons (**e**, **f**, and **g**).

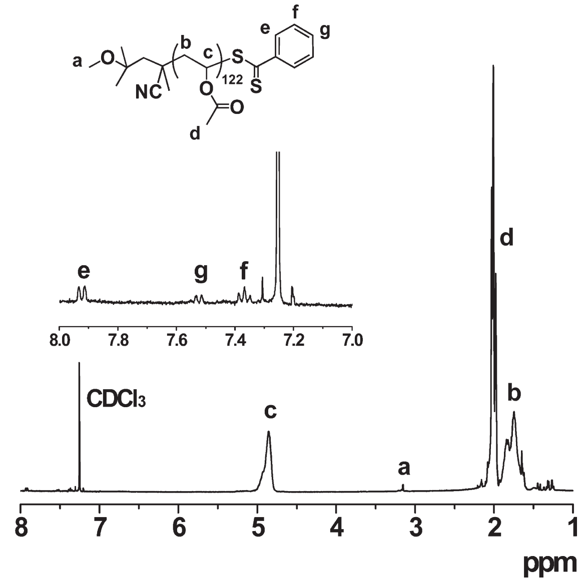


Figure 1. ^{1}H NMR spectrum of poly(vinyl acetate) macro-chain-transfer agent (PVAc-CTA, $M_{n(NMR)}$ = 10 800 g/mol) in CDCl$_3$.

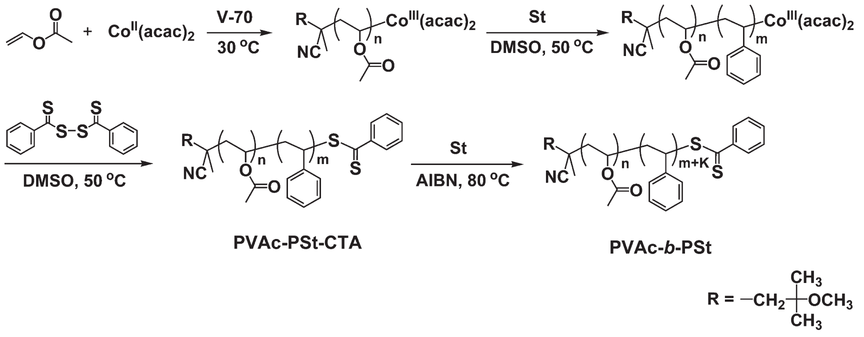
Table 1 lists the results of the RAFT polymerization of St with PVAc-CTA. The M_n of PVAc-CTA was also determined by comparing the integration ratio of the $-OCHH_3$ protons (**a**) to the $-CH_2CH(OCOCH_3)$ proton (**c**) (Figure 1). The polymerizations were carried out at 80 °C at a molar ratio of $[St]_0/[CTA]_0/[AIBN]_0$ = 568/2.5/1. Although the RAFT polymerization of St was possible, the PVAc-*b*-PSt block copolymers exhibited relatively high polydispersity values. This poor control may be caused by the high reactivity of PVAc macroradicals (reinitiating R group). Therefore, in order to control the RAFT polymerization of St, the reactivity of PVAc macroradicals was adjusted by introducing several St units into PVAc-CTA. As shown in Scheme 2, the CMRP of St with PVAc-Co(acac)$_2$ was first carried out at 50 °C for 3 h through the reversible termination mechanism. The average block length of PSt was controlled by changing the molar ratio of $[PVAc\text{-}Co(acac)_2]_0/[St]_0$. When the

Table 1. RAFT Polymerization Results of St at 80 °C for 24 h[a]

				PVAc-*b*-PSt[b]			
macro-CTAs	$M_{n(NMR)}$ (g/mol)[c]	$M_{n(GPC)}$ (g/mol)[d]	M_w/M_n[d]	conv (%)[e]	$M_{n(theor)}$ (g/mol)[f]	$M_{n(GPC)}$ (g/mol)[d]	M_w/M_n[d]
PVAc-CTA	7 800	8 100	1.18	13	10 900	15 500	1.47
	10 800	11 800	1.20	15	14 300	17 000	1.52
PVAc-PSt2-CTA	8 000	8 400	1.19	20	12 700	16 300	1.37
	11 000	12 100	1.21	15	14 600	18 700	1.45
PVAc-PSt6-CTA	8 400	9 500	1.21	48	19 700	21 000	1.28
	11 400	12 300	1.23	45	22 000	25 500	1.30

[a] $[St]_0/[Macro\text{-}CTA]_0/[AIBN]_0$ = 568/2.5/1, $[St]_0$ = 1.3 mL. [b] Poly(vinyl acetate)-*block*-polystyrene (PVAc-*b*-PSt) was recovered by precipitation in an excess of methanol. [c] Calculated by ^{1}H NMR in CDCl$_3$. [d] Determined by gel permeation chromatography using polystyrene standard in THF. [e] Determined by a gravimetric method. [f] The theoretical molecular weight ($M_{n(theor)}$) = 104.15 (M_{St}) × ($[St]_0/[PVAc\text{-}CTA \text{ or } PVAc\text{-}PSt\text{-}CTA]_0$) × conversion + $M_{n(NMR)}$ of PVAc-CTA or PVAc-PSt-CTA. PVAc-CTA, poly(vinyl acetate) macro-chain-transfer agent; PVAc-*b*-PSt, poly(vinyl acetate)-*block*-polystyrene; PVAc-PSt2-CTA, PVAc-*b*-PSt macro-chain-transfer agent with an average PSt repeating unit of 2; PVAc-PSt6-CTA, PVAc-*b*-PSt macro-chain-transfer agent with an average PSt repeating unit of 6.

Scheme 2. Synthesis Procedure of PVAc-PSt-CTA and PVAc-*b*-PSt[a]



[a] Co^{II}(acac)$_2$, cobalt(II) acetylacetonate; DMSO, dimethyl sulfoxide; AIBN, 2,2′-azobis(isobutyronitrile); PVAc-*b*-PSt, poly(vinyl acetate)-*block*-polystyrene; PVAc-PSt-CTA, poly(vinyl acetate)-*block*-polystyrene macro-chain-transfer agent.

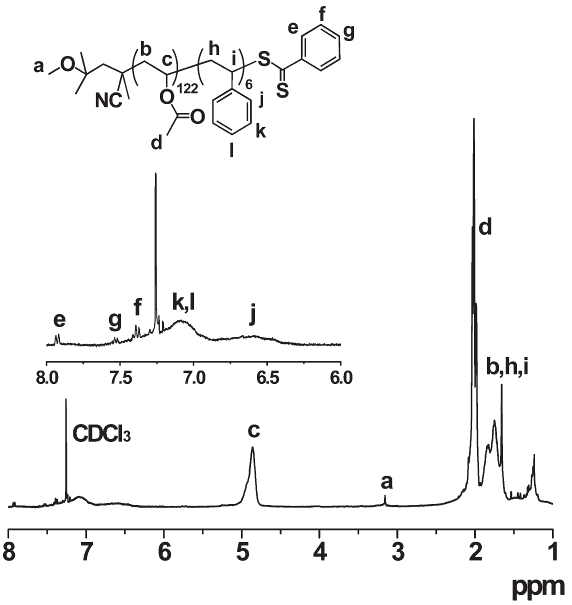


Figure 2. ^{1}H NMR spectrum of poly(vinyl acetate)-*block*-polystyrene macro-chain-transfer agent with an average PSt repeating unit of 6 (PVAc-PSt6-CTA, $M_{n(NMR)}$ = 11 400 g/mol) in $CDCl_3$.

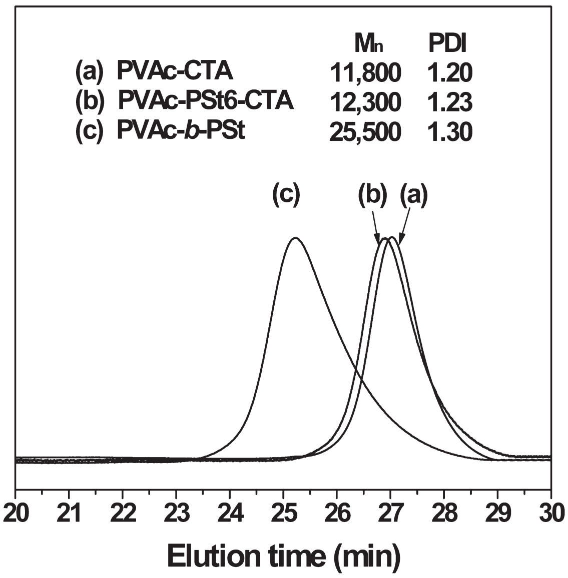


Figure 3. GPC curves of poly(vinyl acetate) macro-chain-transfer agent (PVAc-CTA), poly(vinyl acetate)-*block*-polystyrene macro-chain-transfer agent with an average PSt repeating unit of 6 (PVAc-PSt6-CTA), and poly(vinyl acetate)-*block*-polystyrene (PVAc-*b*-PSt). PVAc-*b*-PSt was prepared by RAFT polymerization of St with PVAc-PSt6-CTA in DMF at 80 °C for 24 h at a molar ratio of $[St]_0/[PVAc\text{-}PSt6\text{-}CTA]_0/[AIBN]_0$ = 568/2.5/1.

molar ratios of $[PVAc\text{-}Co(acac)_2]_0/[St]_0$ were 1/5 and 1/10, the average block lengths of PSt determined by ^{1}H NMR spectroscopy were 2 and 6, respectively. The ω chain end of the resulting PVAc-*block*-PSt-Co(acac)$_2$ (PVAc-PSt-Co(acac)$_2$) was consecutively modified into a phenyl dithioester group by reacting with BTBD. PVAc-PSt-CTA, with an average PSt repeating unit of 6, is referred to as PVAc-PSt6-CTA.

Figure 2 shows the ^{1}H NMR spectrum of PVAc-PSt6-CTA ($M_{n(NMR)}$ = 11 400 g/mol). The modification efficiencies of the ω end groups of PVAc-PSt2-Co(acac)$_2$ and PVAc-PSt6-Co(acac)$_2$ determined by ^{1}H NMR spectroscopy were ~82 and ~78%, respectively. Bryaskova et al.[19] reported that the CMRP of St with PVAc-Co(acac)$_2$ macroinitiator was uncontrolled due to the low efficiency of Co(acac)$_2$ to deactivate the PSt chains. Therefore, it is postulated that part of the PVAc-PSt-Co(acac)$_2$ chains was not converted into PVAc-PSt-CTA due to the separation of the cobalt complex. PVAc-PSt2 and PVAc-PSt6 generated from the separation of the cobalt complex remained during the RAFT polymerization of St. Fortunately, these polymeric impurities were completely removed during the recovery process after the RAFT polymerization of St. The resulting PVAc-*b*-PSt was precipitated in an excess of methanol, whereas the polymeric impurities were dissolved in the methanol.

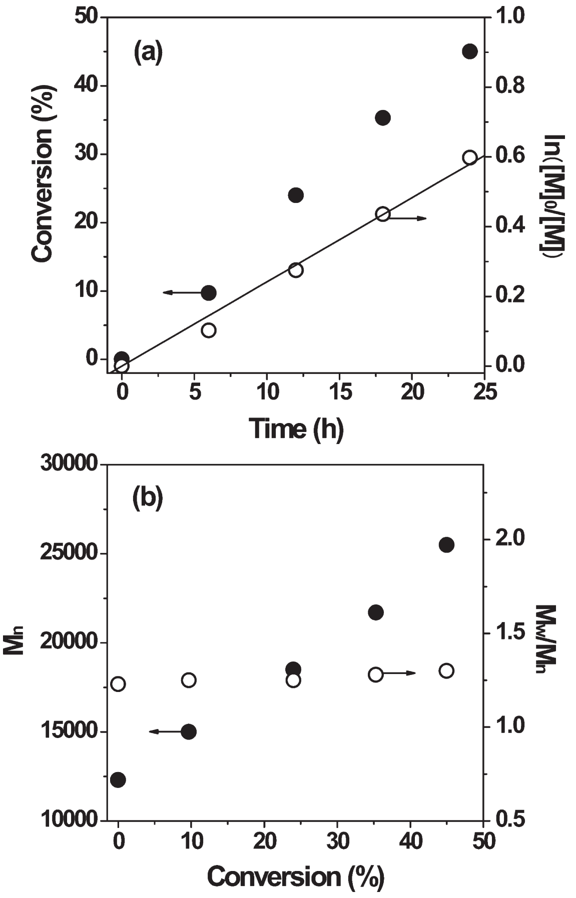


Figure 4. (a) Time dependence of $\ln([M]_0/[M])$ and monomer conversion for the RAFT polymerization of St using poly(vinyl acetate)-*block*-polystyrene macro-chain-transfer agent with an average PSt repeating unit of 6 (PVAc-PSt6-CTA, $M_{n(NMR)}$ = 11 400 g/mol) at 80 °C and (b) M_n and M_w/M_n vs monomer conversion. $[M]_0$ and $[M]$ are the St concentrations at time 0 and *t*, respectively. PVAc-*b*-PSt was recovered by precipitation in an excess of methanol.

The results of the RAFT polymerization of St with PVAc-PSt2-CTA and PVAc-PSt6-CTA are listed in Table 1. The MW distributions of PVAc-*b*-PSt prepared with PVAc-PSt2-CTA were broad, whereas those of PVAc-*b*-PSt prepared with PVAc-PSt6-CTA were much narrower even at high conversions. Figure 3 shows the GPC traces of the PVAc-CTA ($M_{n(GPC)}$ = 11 800 g/mol), PVAc-PSt6-CTA ($M_{n(GPC)}$ = 12 300 g/mol), and PVAc-*b*-PSt ($M_{n(GPC)}$ = 25 500 g/mol) prepared with the PVAc-PSt6-CTA. The GPC trace of the PVAc-*b*-PSt was monomodal, indicating that the initiation efficiency of PVAc-PSt6-CTA was very high, and most of PVAc-PSt6 (polymeric impurities) was removed during the recovery process. The clean and clear shift of the PVAc-PSt6-CTA peak toward the higher molar mass region also implied the successful synthesis of PVAc-*b*-PSt.

Figure 4 shows the kinetics investigations of the RAFT polymerization of St using PVAc-PSt6-CTA ($M_{n(NMR)}$=11 400 g/mol).

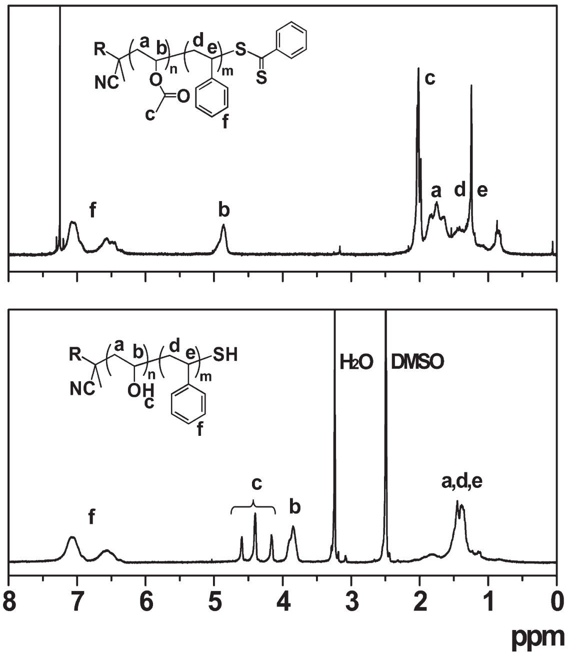


Figure 5. ^{1}H NMR spectra of poly(vinyl acetate)-*block*-polystyrene (PVAc-*b*-PSt, $M_{n(GPC)}$ = 21 000 g/mol, M_w/M_n = 1.28) in $CDCl_3$ and the hydrolyzed poly(vinyl alcohol)-*block*-polystyrene (PVA-*b*-PSt) in DMSO-d_6.

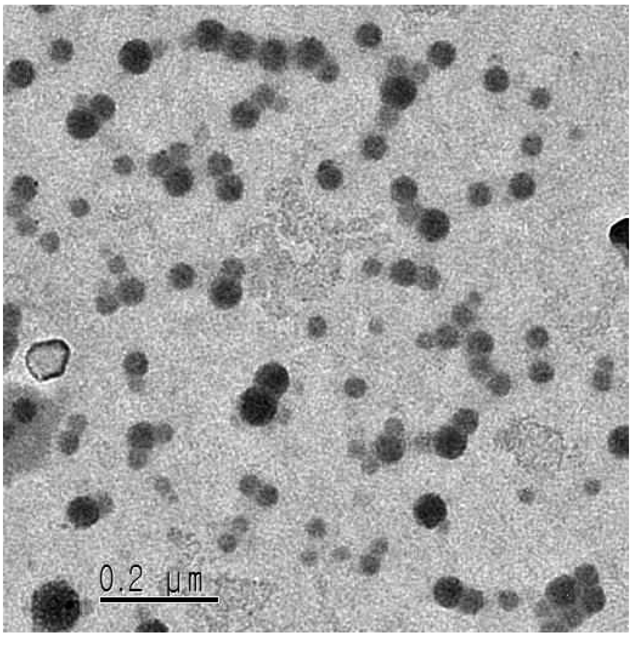


Figure 6. TEM image of poly(vinyl alcohol)-*block*-polystyrene (PVA-*b*-PSt) micelles. The PVA-*b*-PSt was prepared by hydrolysis of poly(vinyl acetate)-*block*-polystyrene (PVAc-*b*-PSt, $M_{n(GPC)}$ = 21 000 g/mol, M_w/M_n = 1.28).

As illustrated in Figure 4a, the linear relationship between ln([M]$_0$/[M]) vs time indicates that the polymerization is first-order until 45% conversion. The controlled nature was further confirmed by the linear increase of the MWs with conversion and the low polydispersity values of PVAc-*b*-PSt (M_w/M_n = 1.23−1.30) (Figure 4b).

PVAc-*b*-PSt block copolymers were directly hydrolyzed under basic conditions and obtained as a light yellow powder. Figure 5 shows the ^{1}H NMR spectra of the PVAc-*b*-PSt ($M_{n(GPC)}$ = 21 000 g/mol, M_w/M_n = 1.28) and the hydrolyzed PVA-*b*-PSt. The ^{1}H NMR spectrum of the PVA-*b*-PSt was obtained in DMSO-d_6 at 40 °C. The complete hydrolysis of the PVAc was confirmed by the total disappearance of the peak corresponding to the acetate group (2.0−2.2 ppm) and the shifting of the peak corresponding to the $-CH_2-CH-$ proton in the PVAc backbone. The resulting hydroxyl proton peaks were clearly observed at 4.2−4.7 ppm. Interestingly, it was reported that the thiocarbonylthio group of RAFT-synthesized polymers could be removed by hydrolysis to yield thiol-terminated polymeric chains using a strong base such as sodium hydroxide.[28] Therefore, it is believed that that the phenyl dithioester groups in the PVAc-*b*-PSt block copolymers were also hydrolyzed to the thiol group.

The micellar characteristics of PVA-*b*-PSt in aqueous solution were investigated using TEM. The PVP-*b*-PSt was prepared by hydrolysis of PVAc-*b*-PSt ($M_{n(GPC)}$ = 21 000 g/mol, M_w/M_n = 1.28). The micelle solution of the PVA-*b*-PSt was prepared by adding deionized water dropwise to the PVA-*b*-PSt solution in a mixed solvent of THF/DMSO (1/1 v/v). With increasing water content, the solubility of the mixed solvent continually became worse for the hydrophobic PSt block, which triggered the aggregation of the dissolved polymer chains. Figure 6 shows a TEM image of the PVA-*b*-PSt micelles. Spherical PVA-*b*-PSt micelles were successfully formed with an average diameter of 44 ± 18 nm.

Conclusions

Well-defined PVAc-*b*-PSt block copolymers were successfully synthesized by a combination of CMRP and RAFT polymerization. PVAc-CTA was prepared by modifying the ω chain end of the PVAc-Co(acac)$_2$ into a phenyl dithioester group by reacting with BTBD. The RAFT polymerization of St with PVAc-CTA was successful, but the resulting PVAc-*b*-PSt block copolymers exhibited relatively high polydispersity values. In order to control the RAFT polymerization of St, the reactivity of PVAc macroradicals was adjusted by introducing several St units into PVAc-CTA. PVAc-*b*-PSt prepared with PVAc-PSt6-CTA showed much narrower MW distributions than those of PVAc-*b*-PSt prepared with PVAc-CTA. PVAc-*b*-PSt block copolymer ($M_{n(GPC)}$ = 21 000 g/mol, M_w/M_n = 1.28) was directly hydrolyzed under basic conditions. The micelle solution of the resulting PVA-*b*-PSt was prepared by adding deionized water dropwise to the PVA-*b*-PSt solution in a mixed solvent of THF/DMSO (1/1 v/v). The PVA-*b*-PSt micelles were spherical in shape with an average diameter of 44 ± 18 nm.

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