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Synthesis of Well-Defined Poly(vinyl acetate)-*b*-Polystyrene by Combination of ATRP and RAFT Polymerization

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ABSTRACT: The synthesis of well-defined poly(vinyl acetate)-*b*-polystyrene (PVAc-*b*-PSt) by combination of atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization was described. Two difunctional compounds, *S*-(2-chloropropionoxyethoxycarbonylmethyl) *O*-ethyl xanthate (**2**) and *S*-(2-bromo-2-methylpropionoxyethoxycarbonylmethyl) *O*-ethyl xanthate (**3**), with an activated halide group and a xanthate group in the molecule were synthesized. The activated halide group was used as an ATRP initiator to initiate polymerization of St, and the xanthate group was used as a RAFT agent to mediate polymerization of VAc. Thus, **2** was first used to mediate the radical polymerization of VAc, followed by ATRP of St, while **3** was used first to initiate the ATRP of St, followed by the RAFT polymerization of VAc. Both approaches indicate that either the radical polymerization of St or that of VAc is controlled, and well-defined PVAc-*b*-PSt is obtained as confirmed by gel permeation chromatography and NMR measurements.

Introduction

In recent years, controlled/living radical polymerization (CLRP) has been widely used to synthesize polymers with controlled molecular weights and low polydispersity index (PDI $= M_w/M_n$) or to synthesize polymers with complex architectures such as block, star, comb, and cyclic (co)polymers. Nitroxide-mediated radical polymerization (NMP),[1−3] atom transfer radical polymerization (ATRP),[4,5] and reversible addition-fragmentation chain transfer (RAFT)[6−8] polymerization are among the most widely used CLRP methods. Although these methods can control the polymerization of most vinyl monomers that can be radically polymerized such as styrene (St), (meth)acrylates, and so forth, the CLRP of vinyl acetate (VAc) is difficult. This is because the propagating radical of VAc is so active and the chain propagating rate is very fast. Until now, the following methods have been developed to control the radical polymerization of VAc: degenerative transfer (DT) polymerization with alkyl iodides,[9,10] RAFT polymerization using xanthates[11,12] or dithiocarbamates[13] as the chain transfer agents, iron-catalyzed,[14,15] cobalt-mediated radical polymerization (CMRP),[16−19] and an organotellurium- or organostibine-mediated process.[20,21] However, due to the large disparate reactivities of VAc and other vinyl monomers, it is still challenging to prepare well-defined block copolymers of VAc and other monomers, especially poly(vinyl acetate)-*b*-polystyrene (PVAc-*b*-PSt), through one mechanism. PVAc-*b*-PSt was synthesized by a photochemical binary initiation system using ethanolamine−benzophenone,[22] but both of the blocks were uncontrolled. The same block copolymer was synthesized by CMRP,[23] but the PSt block was uncontrolled. Combination of different methods has been tested for this purpose: synthesis of PVAc block first followed by block copolymerization with St,[24−26] or first synthesis of PSt block followed by block copolymerization with VAc.[27,28] These methods however have disadvantages; either PSt or PVAc is uncontrolled. Combination of CMRP and ATRP has been shown to be a good method to synthesize well-defined PVAc-*b*-PSt; however, transformation of the PVAc end groups to activated bromides is necessary.[29,30] Very recently, PVAc-*b*-PSt with well-defined blocks was synthesized by "click chemistry",[31] but this method needs a final purification procedure.

On the basis of the fact that radical polymerization of VAc can be well-controlled with xanthates, and well-defined PSt can be obtained by ATRP, we propose that well-defined PVAc-*b*-PSt can be synthesized through the design of compounds that can control the polymerization of VAc and St simultaneously. Here, we report the results based on this idea.

Experimental Section

Materials. Vinyl acetate (AR, Beijing Chemicals Co.) was dried over calcium hydride and distilled under nitrogen. Styrene (AR, Beijing Chemicals Co.) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) were dried over calcium hydride and distilled under reduced pressure. 2,2′-A) (AIBN, AR, Beijing Chemicals Co.) was recrystallized from methanol. Ethyl 2-bromoisobutyrate (EBiB, 98%), methyl 2-chloropropionate (MCP, 97%), (1-bromoethyl)benzene (97%), copper(I) bromide (CuBr, 99.999%), and copper(I) chloride (CuCl, 99.995+%) were from Aldrich and used as received. All other reagents, including dicyclohexyl carbodiimide (DCC, Fluka, 99%), 4-dimethylamino pyridine (DMAP, Acros, 99%), potassium *O*-ethyl xanthate (CP, Beijing Chemicals Co.), 2-chloropropionic acid (AR, Beijing Chemicals Co.), 2-bromoisobutyric acid (AR, Beijing Chemicals Co.), and bromoacetyl bromide (Alfa Aesar, 98%), were used as received. 1-Bromoethyl acetate[32] and *S*-methoxycarbonylmethyl *O*-ethyl xanthate (**1b**)[33] were prepared as described in the literature. All solvents were purified using common methods.

Characterization. Gel permeation chromatography (GPC) was carried out in tetrahydrofuran (THF) (flow rate: 1 mL/min) at 35 °C with a Waters 1525 binary HPLC pump equipped with a Waters 2414 refractive index detector and three Waters Styragel HR columns (1×10^4, 1×10^3, and 500 Å pore sizes). Monodisperse polystyrene standards were used for calibration. The NMR spectra were recorded in $CDCl_3$ on a Bruker ARX-400 spectrometer or a Varian Gemini 300 spectrometer.

***S*-1-Acetoxyethyl *O*-Ethyl Xanthate (1a).** In a 100 mL round-bottom flask, potassium *O*-ethylxanthate (8.5 g, 53 mmol) was dissolved in ethanol (50 mL) and 1-bromoethyl acetate (9.0 g, 50 mmol) was added, and the mixture was stirred for 12 h at room temperature. The precipitate was isolated by filtration and washed three times with CH_2Cl_2. The organic solution was combined, and the solvent was evaporated off. The product was purified by silica

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gel chromatography (eluent: petroleum ether/ethyl acetate = 20/1, v/v) and obtained as a pale yellow liquid in 30% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.39 (t, 3H, CH_3CH_2), 1.60 (d, 3H, $CH_3CH(OOCCH_3)$), 2.05 (s, 3H, CH_3CO), 4.60−4.64 (m, 2H, CH_3CH_2), 6.65 (q, 1H, CH_3CH). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.4 (CH_3CH_2), 19.7 (CH_3CH), 20.7 (CH_3CO), 69.8 (CH_3CH_2), 76.9 (CH_3CH), 169.1 (CH_3CO), 210.0 (OCS).

***S*-1-Phenylethyl *O*-Ethyl Xanthate (1c).** Following the synthetic procedure described for **1a**, (1-bromoethyl)benzene was used as the starting material. The product was filtered over basic alumina with diethyl ether and obtained as a pale yellow liquid in 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.39 (t, 3H, CH_3CH_2), 1.72 (d, 3H, CH_3CH), 4.62 (q, 2H, CH_3CH_2), 4.91 (q, 1H, CH_3CH), 7.27−7.40 (m, 5H, C_6H_5). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.6 (CH_3CH_2), 21.6 (CH_3CH), 49.1 (CH_3CH), 69.6 (CH_3CH_2), 127.3, 127.4, 128.4, 141.6 (C_6H_5), 213.1 (OCS).

2-Hydroxyethyl Bromoacetate. In a 100 mL round-bottom flask, ethylene glycol (40 mL, 0.72 mol) and pyridine (7.9 g, 0.1 mol) were added, bromoacetyl bromide (20.2 g, 0.1 mol) was finally added dropwise at 0 °C, and the solution was stirred at room temperature for 24 h. The solution was filtered over silica gel to remove the pyridinium salt and further purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 1/1, v/v). The product was obtained as a colorless liquid in 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 3.85−3.89 (m, 4H, $BrCH_2COOCH_2CH_2OH$), 4.30−4.33 (m, 2H, $BrCH_2COOCH_2CH_2OH$).

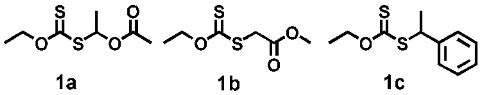
***S*-(2-Hydroxyethoxycarbonylmethyl) *O*-Ethyl Xanthate.** Following the synthetic procedure described for **1a**, 2-hydroxyethyl bromoacetate was used as the starting material, and the product was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 3/1, v/v) to get a pale yellow liquid in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.43 (t, 3H, CH_3CH_2), 3.85 (t, 2H, CH_2CH_2OH), 3.98 (s, 2H, SCH_2COO), 4.23−4.30 (m, 2H, CH_2CH_2OH), 4.66 (q, 2H, CH_3CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.6 (CH_3CH_2), 37.7 (SCH_2COO), 60.7 (CH_2CH_2OH), 67.2 (CH_2CH_2OH), 70.7 (CH_3CH_2), 168.1 ($COOCH_2CH_2OH$), 212.6 (OCS).

***S*-(2-Chloropropionoxyethoxycarbonylmethyl) *O*-Ethyl Xanthate (2).** The solution of DCC (6.3 g, 30 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a mixture of *S*-(2-hydroxyethoxycarbonylmethyl) *O*-ethylxanthate (2.2 g,10 mmol), 2-chloropropionic acid (3.24 g, 30 mmol), and DMAP (0.9 g, 7 mmol) dissolved in CH_2Cl_2 (20 mL) at 0 °C. After complete addition, the reaction was stirred at room temperature and monitored by thin-layer chromatography (TLC). The precipitate was isolated by filtration and washed three times with CH_2Cl_2. The combined organic solution was evaporated to dryness and purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 10/1, v/v) to get a pale yellow liquid in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.43 (t, 3H, CH_3CH_2), 1.70 (d, 3H, CH_3CH), 3.95 (s, 2H, SCH_2CO), 4.40−4.43 (m, 5H, CH_3CH, CH_2CH_2), 4.65 (q, 2H, CH_3CH_2).^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.6 (CH_3CH_2), 21.3 (CH_3CH), 37.5 (SCH_2CO), 52.1 (CH_3CH), 62.9, 63.1 (CH_2CH_2), 70.6 (CH_3CH_2), 167.6 (CH_2CO), 169.7 (OOCCH), 212.3 (OCS).

***S*-(2-Bromo-2-methylpropionoxyethoxycarbonylmethyl) *O*-Ethyl Xanthate (3).** Following the same synthetic procedure described for **2**, 2-bromoisobutyric acid was used as the starting material. The product was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate = 20/1, v/v) to get a pale yellow liquid in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 1.43 (t, 3H, CH_3CH_2), 1.95 (s, 6H, $C(CH_3)_2$), 3.96 (s, 2H, SCH_2COO), 4.40−4.43 (m, 4H, CH_2CH_2), 4.66 (q, 2H, CH_3CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.7 (CH_3CH_2), 30.6 ($C(CH_3)_2$), 37.6 (SCH_2COO), 55.3 ($C(CH_3)_2$), 62.9, 63.2 (CH_2CH_2), 70.7 (CH_3CH_2), 167.7 (CH_2COO), 171.4 ($OOCC(CH_3)_2$), 212.4 (OCS).

Typical Procedure for the RAFT Polymerization of VAc. A mixture of **2** (0.315 g, 1 mmol), AIBN (16.4 mg, 0.1 mmol), THF (5.3 mL), and vinyl acetate (8.6 g, 0.1 mol) was degassed by three freeze−pump−thaw cycles, sealed under nitrogen, and heated at 60 °C. Samples were taken periodically with a syringe to follow the kinetics of the polymerization process. VAc conversion was determined by weighing the collected polymer after removal of the monomer and solvent *in vacuo*.

Scheme 1



1a **1b** **1c**

Table 1. RAFT Polymerization of VAc at 60 °C Mediated with 1a−c[a]

RAFT agent	$M_{n,GPC}$[b]	$M_{n,theor}$[c]	M_{NMR}[d]	conv (%)[e]	M_w/M_n[b]	time (h)	inhibition time (h)
1a	6200	5400	5200	60	1.13	6.5	3.5
1b	6100	5400	5200	60	1.12	2.5	0.5
1c[f]	5700	4500	4100	50	1.12	72	48

[a] $[VAc]_0/[\mathbf{1}]_0/[AIBN]_0 = 100:1:0.1$, $[VAc]_0 = 10.85$ mol/L. [b] GPC data were based on polystyrene standard calibration. [c] $M_{n,theor} = M_{n,\mathbf{1}} + ([VAc]_0/[\mathbf{1}]_0) \times M_{VAc} \times$ conversion. [d] ^{1}H NMR in $CDCl_3$. [e] Measured by gravimetry. [f] $[\mathbf{1c}]_0/[AIBN]_0 = 5:1$. AIBN: 2,2′-azobis(isobutyronitrile).

Typical Procedure for the ATRP of St. CuBr (96 mg, 0.67 mmol) was added to a mixture of St (7 g, 67 mmol), **3** (251 mg, 0.67 mmol), and PMDETA (116 mg, 0.67 mmol) degassed by three freeze−pump−thaw cycles. The mixture was sealed under nitrogen and heated at 60 °C. Samples were taken periodically with a syringe to follow the kinetics of the polymerization process. All the St conversions unless otherwise specified were determined by ^{1}H NMR spectroscopy with anisole as the internal reference by comparing the integration corresponding to $CH_2{=}CH(C_6H_5)$ (5.23, 5.73 ppm) to that corresponding to $CH_3OC_6H_5$ (3.80 ppm).

Synthesis of Bromine-Terminated PSt by ATRP. CuBr (138 mg, 0.96 mmol) was added to a mixture of St (10 g, 96 mmol), EBiB (188 mg, 0.96 mmol), and PMDETA (166 mg, 0.67 mmol) degassed by three freeze−pump−thaw cycles. The mixture was sealed under nitrogen and heated at 60 °C. After 25 h, the solution was diluted with THF and filtered over neutral alumina. The obtained solution was concentrated and precipitated in methanol five times to obtain bromine-terminated PSt ($M_{n,GPC} = 8400$, PDI = 1.11, 65% conversion).

Typical Procedure for the Synthesis of PVAc-*b*-PSt Using PVAc-Cl as Initiator. CuCl (25 mg, 0.25 mmol) was added to a mixture of St (5.3 g, 51 mmol), PVAc-Cl (0.4 g, 0.12 mmol, $M_{NMR} = 3300$, PDI = 1.10), and PMDETA (43 mg, 0.25 mmol). The mixture was degassed by three freeze−pump−thaw cycles, sealed under nitrogen, and heated at 80 °C. Samples were taken periodically with a syringe to follow the kinetics of the polymerization process.

Typical Procedure for the Synthesis of PSt-*b*-PVAc Using Pst-RAFT. A mixture of PSt-RAFT (0.8 g, 0.18 mmol, $M_{n,GPC} = 4400$, PDI = 1.11), AIBN (16 mg, 0.1 mmol), and vinyl acetate (12 g, 0.14 mol) was degassed by three freeze−pump−thaw cycles, sealed under nitrogen, and heated at 60 °C. Samples were taken periodically with a syringe to follow the kinetics of the polymerization process.

Results and Discussion

RAFT Polymerization of VAc. Xanthates are good transfer agents to mediate the radical polymerization of VAc.[11] Stenzel et al.[12] investigated a series of xanthates with different Z-groups and found that *O*-ethyl xanthate was the best one. Therefore, xanthates **1a**−**c** were synthesized (Scheme 1) and used to mediate the radical polymerization of VAc. Typical results are summarized in Table 1. Both **1a** and **1b** could successfully mediate the radical polymerization of VAc. Low polydispersity PVAc was obtained after 6.5 or 2.5 h with similar molecular weights, but the inhibition time when **1a** was used is longer than that in the case of **1b**. When **1c** was used, PVAc with low

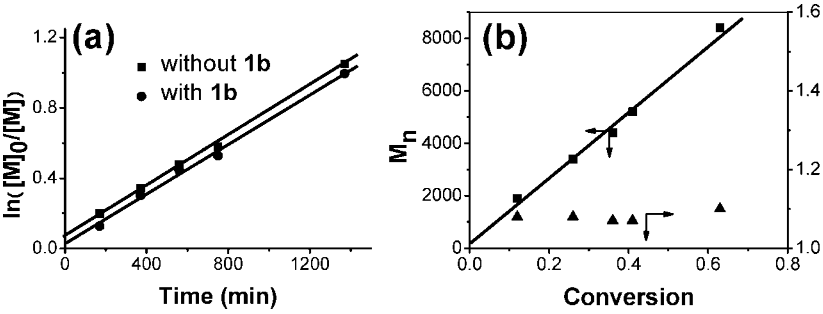


Figure 1. (a) Time dependence of ln([*M*]$_0$/[*M*]) for the bulk ATRP of St at 60 °C and (b) number average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) versus monomer conversion in the presence of **1b**. [St]$_0$/[EBiB]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 100:1:1:1, [St]$_0$ = 8.74 mol/L, [**1b**]$_0$/[EBiB]$_0$ = 1:1. [*M*]$_0$ and [*M*] are the St concentration at time 0 and *t*, respectively. EBiB, ethyl 2-bromoisobutyrate; PMDETA, *N,N,N′,N″,N″*-pentamethyldiethylenetriamine.

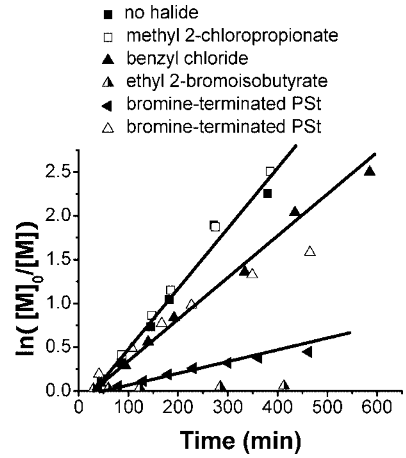
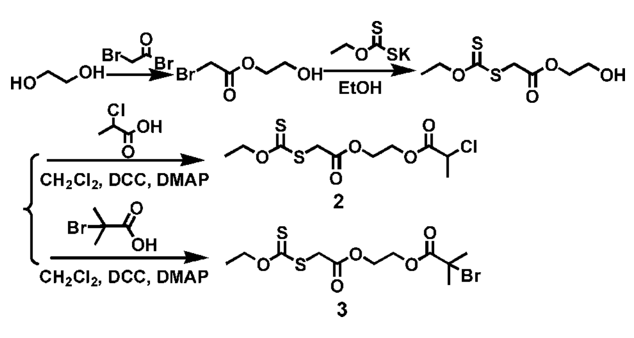


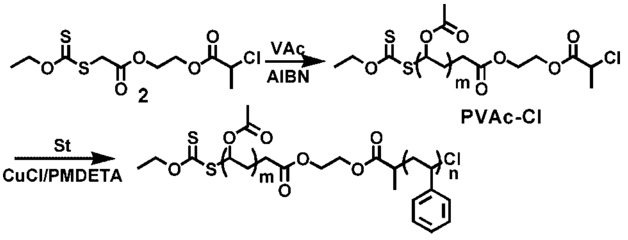
Figure 2. Time dependence of ln([*M*]$_0$/[*M*]) for the solution radical polymerization of vinyl acetate (VAc) mediated by **1b** at 60 °C. [VAc]$_0$/[**1b**]$_0$/[AIBN]$_0$ = 100:1:0.1; [**1b**]$_0$/[halide]$_0$ = 1:1 for small molecular halides; [VAc]$_0$/[**1b**]$_0$/[PSt]$_0$/[AIBN]$_0$ = 100:1:0.1:0.1 for bromine-terminated PSt (solid left triangle); [VAc]$_0$/[**1b**]$_0$/[PSt]$_0$/[AIBN]$_0$ = 100:1:0.1:0.4 for bromine-terminated PSt (open triangle). PSt: $M_{n,GPC}$ = 8400, M_w/M_n = 1.11). Solvent: tetrahydrofuran. [VAc]$_0$ = 7.1 mol/L; [M]$_0$ and [M] are the VAc concentration at time 0 and *t*, respectively. AIBN, 2,2′-azobis(isobutyronitrile); GPC, gel permeation chromatography.

Scheme 2. Synthesis of Two Difunctional Compounds with an Activated Halide Group and a Xanthate Group in the Molecule[a]



[a] DCC, dicyclohexyl carbodiimide; DMAP, 4-dimethylamino pyridine.

Scheme 3. General Strategy for the Preparation of Well-Defined PVAc-*b*-PSt by RAFT Polymerization of VAc, Followed by ATRP of St[a]



[a] PMDETA, *N,N,N′,N″,N″*-pentamethyldiethylenetriamine; AIBN, 2,2′-azobis(isobutyronitrile).

PDI could also be obtained after 72 h, but a very long inhibition time (48 h) was observed. This may be caused by the poor reactivity of the formed 1-phenyl ethyl radical to initiate the radical polymerization of VAc.[34,35] The results with **1b** are consistent with the report by Stenzel et al.[12] Therefore, **1b** and compounds with a similar structure were chosen to mediate the radical polymerization of VAc.

ATRP of St in the Presence of 1b. Xanthates are reportedly not good mediators for the radical polymerization of St.[33] Our results also confirmed this. For example, when St was polymerized under the conditions: [St]$_0$/[AIBN]$_0$ = 1000:1, [AIBN]$_0$/[**1b**]$_0$ = 1:1, 5.5 h, 60 °C, the molecular weight of the PSt obtained was much higher than the theoretical molecular weight ($M_{n,theor} = M_{n,\mathbf{1b}} + ([St]_0/[\mathbf{1b}]_0) \times M_{St} \times$ conversion), and the PDI of PSt was 1.7. We then conducted the ATRP of St with or without **1b** under the following conditions: [St]$_0$/[EBiB]$_0$/[PMDETA]$_0$/[CuBr]$_0$ = 100:1:1:1, [**1b**]$_0$/ [EBiB]$_0$ = 1:1, 60 °C. The results are shown in Figure 1. Both of the kinetics are first-order as evidenced by the linear time dependence of ln([*M*]$_0$/[*M*]), indicating that the concentration of radicals is constant during the polymerization (Figure 1a). The similar slopes of the plots imply that **1b** has little effect on the ATRP of St. This was further confirmed by the constant concentration of **1b** with increasing St conversion (Figure S-1 in the Supporting Information), the linear increase of the molecular weights with conversion, and the low PDIs (<1.1) of PSt (Figure 1b). If the temperature was raised to 80 or 100 °C or if **1b** was added with the molar ratio of [**1b**]$_0$/[EBiB]$_0$ = 5:1, similar results can be obtained. We then examined the ^{1}H NMR spectrum of PSt (data not shown), and no signals from $CH_3CH_2OCS_2-$ (at 4.6 ppm) and $-CH_2CH(C_6H_5)S_2COC_2H_5$ (at 4.9 ppm by comparing with **1c**) were observed. This indicates that very few PSt propagating radicals have transferred to **1b**. This is because the chain transfer constants of xanthates for St polymerizations are 0.6−2;[36] these values are almost 3 orders of magnitude lower than those of the dithioesters agents, which are effective RAFT agents for the radical polymerization of St. Furthermore, PSt obtained in the presence of **1b** was used as a macroinitiator for chain extension under ATRP conditions, a complete chain extension with no residual macroinitiator was observed, and PSt with high molecular weight and low PDI was obtained (Figure S-2 in the Supporting Information). All these results confirm that **1b,** when used at an equal molar ratio

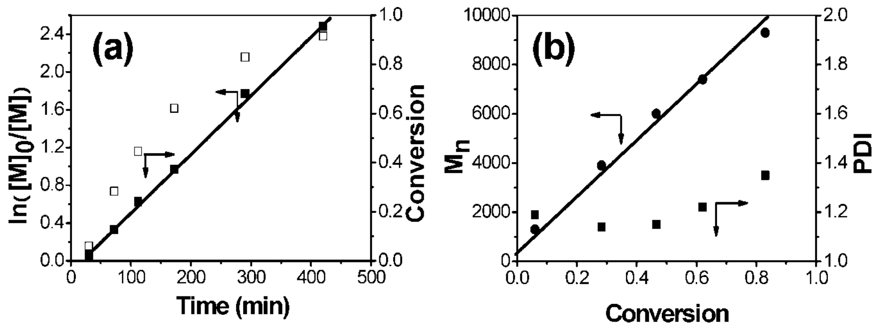


Figure 3. (a) Time dependence of ln($[M]_0$/$[M]$) and monomer conversion for the solution radical polymerization of VAc mediated by **2** at 60 °C and (b) number average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) versus monomer conversion. $[VAc]_0/[\mathbf{2}]_0/[AIBN]_0 = 100:1:0.1$, $[VAc]_0 = 7.1$ mol/L. Solvent: tetrahydrofuran. $[M]_0$ and $[M]$ are the vinyl acetate concentration at time 0 and t, respectively. AIBN: 2,2′-azobis(isobutyronitrile).

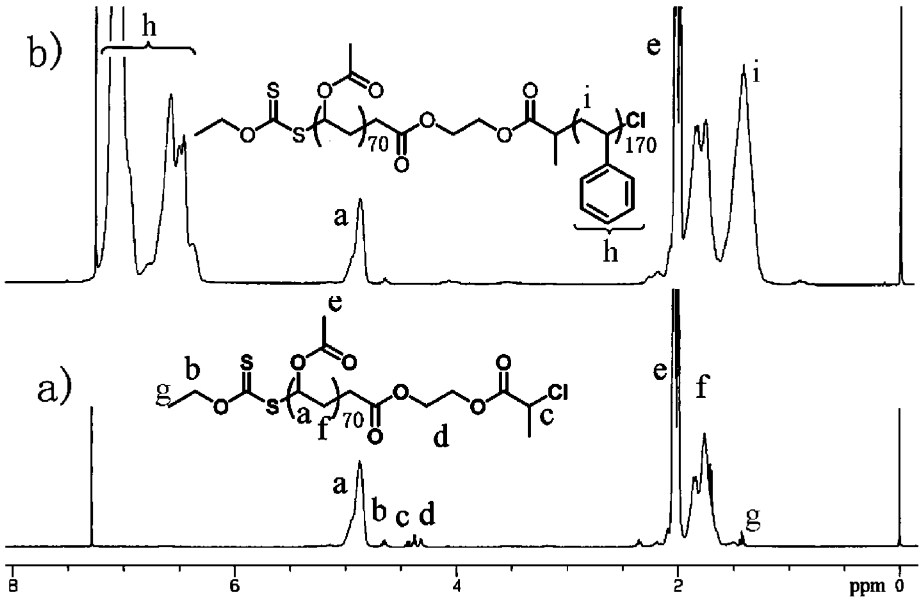


Figure 4. ^{1}H NMR spectra of (a) the poly(vinyl acetate) macroinitiator (PVAc-Cl, $M_{n,GPC} = 8600$, $M_w/M_n = 1.21$) and (b) the obtained poly(vinyl acetate)-*b*-polystyrene in $CDCl_3$. GPC: gel permeation chromatography.

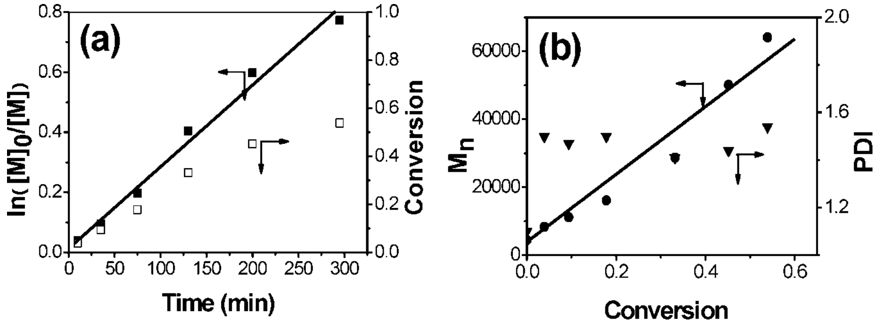


Figure 5. (a) Time dependence of ln($[M]_0$/$[M]$) and monomer conversion for the bulk ATRP of St using poly(vinyl acetate) macroinitiator (PVAc-Cl, $M_{NMR} = 3300$, $M_w/M_n = 1.10$) at 80 °C and (b) number average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) versus monomer conversion. $[St]_0/[PVAc\text{-}Cl]_0/[CuCl]_0/[PMDETA]_0 = 420:1:2:2$, $[St]_0 = 8.74$ mol/L. $[M]_0$ and $[M]$ are the styrene concentration at time 0 and t, respectively. PMDETA: *N,N,N′,N″,N″*-pentamethyldiethylenetriamine.

to the ATRP initiator, has very little effect on the ATRP of St. The same results were observed when **1a** was used instead of **1b**.

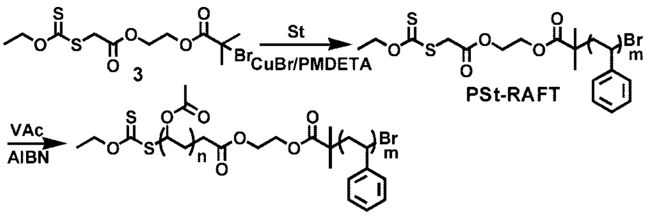
RAFT Polymerization of VAc in the Presence of Common ATRP Initiators. The PVAc propagating radical is very active, and chain transfer reactions occur easily. Halides are common ATRP initiators which have large transfer constants for active radicals. Therefore, the influence of different ATRP initiators, MCP, EBiB, benzyl chloride, and bromine-terminated PSt ($M_{n,GPC} = 8400$, PDI = 1.11), on the solution RAFT polymerization of VAc was investigated. The kinetic results are shown in Figure 2. It can be seen that when MCP was added in an equal molar ratio to **1b**, a linear relationship of ln($[M]_0$/$[M]$) versus time (up to 70% conversion) and an inhibition time of about 0.5 h are observed. PVAc with lower PDI (<1.4) were obtained, and the molecular weights increased linearly with VAc conversion (Figure S-3b in the Supporting Information). These results are the same as those in the absence of MCP, indicating

Table 2. Synthesis of Block Copolymers with Various Molecular Weights Using Poly(vinyl acetate) As Macroinitiators (PVAc-Cl) or Using Polystyrene As Macromolecular Chain Transfer Agents (PSt-RAFT)[a]

first block		PSt-*b*-PVAc				
M_{NMR}[b] (10^3)	M_w/M_n	conv[c] (%)	$M_{n,theor}$ (10^3)	$M_{n,GPC}$[f] (10^3)	M_{NMR}[b] (10^3)	M_w/M_n[f]
PVAc-Cl, 5.1[g]	1.10	15	12.9[d]	19.1	12.7	1.46
		32	21.1[d]	30.4	17.6	1.42
		70	40.8[d]	58.0	25.3	1.42
PVAc-Cl, 9.8[h]	1.28	5	14.7[d]	21.3	20.3	1.39
		22	30.9[d]	49.2	30.7	1.36
PSt-RAFT, 7.3[i]	1.10	7	15.3[e]	20.7	17.7	1.41
		47	58.4[e]	56.7	51.6	1.43
		84	99.0[e]	96.1	72.5	1.45
PSt-RAFT, 12.9[j]	1.11	4	20.6[e]	25.5	25.8	1.43
		29	68.4[e]	66.1	57.8	1.46

[a] PMDETA, *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine; AIBN, 2,2′-azobis(isobutyronitrile). [b] ^{1}H NMR in $CDCl_3$. [c] Measured by gravimetry. [d] $M_{n,theor} = M_{n,PVAc\text{-}Cl} + ([St]_0/[PVAc\text{-}Cl]_0) \times M_{St} \times$ conversion. [e] $M_{n,theor} = M_{n,PSt\text{-}RAFTl} + ([VAc]_0/[PSt\text{-}RAFT]_0) \times M_{VAc} \times$ conversion. [f] GPC data were based on polystyrene standard calibration. [g] $[St]_0/[PVAc\text{-}Cl]_0/[CuCl]_0/[PMDETA]_0 = 490{:}1{:}1{:}1$, bulk, 80 °C. [h] $[St]_0/[PVAc\text{-}Cl]_0/[CuCl]_0/[PMDETA]_0 = 940{:}1{:}2{:}2$, bulk, 80 °C. [i] $[VAc]_0/[PSt\text{-}RAFT]_0/[AIBN]_0 = 1300{:}1{:}0.6$, bulk, 60 °C. [j] $[VAc]_0/[PSt\text{-}RAFT]_0/[AIBN]_0 = 2200{:}1{:}0.7$, bulk, 60 °C.

Scheme 4. General Strategy for the Preparation of Well-Defined PVAc-*b*-PSt by ATRP of St, Followed by RAFT Polymerization of VAc[a]



[a] PMDETA, *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine; AIBN, 2,2′-azobis(isobutyronitrile).

that MCP has little influence on the polymerization rate. When benzyl chloride was added, controlled radical polymerization of VAc could still be achieved but with a lower polymerization rate. However, the effect of EBiB is very much obvious: the polymerization became very slow, only 5% conversion was obtained after 7 h, and the obtained PVAc gradually changed to a brown color when dried in air. These results are reasonable if we consider the different chain transfer constants of halides for radicals, which correlate with the carbon−halogen bond dissociation enthalpies (BDEs). The BDE of EBiB is the smallest and that of MCP is the largest among the three halides.[37] The chain transfer of the PVAc propagating radical to EBiB will generate a bromine-terminated PVAc, which is unstable and hydrolyzed easily in air. The hydrolysis will lead to the formation of a conjugated unsaturated aldehyde which is responsible for the brown color of PVAc.[10,24] This has been confirmed by ^{1}H NMR measurement of the PVAc (data not shown).

Since the idea of the paper is to synthesize PSt-*b*-PVAc via combination of ATRP of St and RAFT polymerization of VAc, the effect of bromine-terminated PSt on the RAFT polymerization of VAc was investigated. We conducted two polymerizations with different concentrations of AIBN. As can be seen from Figure 2, the polymerization of VAc can be controlled to a certain conversion but with lower polymerization rates, especially when a lower concentration of AIBN was used. GPC traces of the reaction mixture at different VAc conversions (Figure S-4 in the Supporting Information) suggest that no change of the peak corresponding to bromine-terminated PSt was observed. An increase of PVAc molecular weights with VAc conversion can still be achieved. This indicates that bromine-terminated PSt does influence the RAFT polymerization of VAc at higher VAc conversion through the chain transfer reaction of the PVAc propagating radicals to the bromine of PSt. As a result, PSt radicals will form, but they are difficult to add to VAc monomers or transfer to xanthates; they have to be terminated, resulting in lower radical concentration. A higher concentration of AIBN will result in faster polymerization of VAc to suppress the chain transfer reaction even at a higher VAc conversion.

Synthesis of PVAc-*b*-PSt. On the basis of the above results, compounds **2** and **3** which both had a xanthate group and an ATRP initiator group were synthesized (Scheme 2). We hope to use them to synthesize PVAc-*b*-PSt by combination of RAFT polymerization (control of the radical polymerization of VAc) and ATRP (control of the radical polymerization of St). The copolymer could be synthesized via two different sequences, first RAFT polymerization of VAc and then ATRP of St, or in the opposite sequence.

A. First RAFT Polymerization of VAc, Followed by ATRP of St. As the 2-chloropropionate group has little influence on the RAFT polymerization of VAc, **2** was used to synthesize a PVAc-Cl macroinitiator first, and then it was used to initiate the ATRP of St and get PVAc-*b*-PSt (Scheme 3).

Figure 3 shows the kinetics results of the RAFT polymerization of VAc using **2** as a chain transfer agent. Solution polymerization was chosen to get a good kinetic result because of the high viscosity of the bulk polymerization solution at high monomer conversion. As illustrated in Figure 3a, the linear relationship between $\ln([M]_0/[M])$ versus time indicates that the polymerization is first-order until 80% conversion. An inhibition time of less than 0.5 h is observed. The controlled nature was further confirmed by the linear increase of the molecular weights with conversion and the low PDIs (<1.4) of PVAc (Figure 3b). The bulk RAFT polymerization of VAc in the presence of **2** was also conducted (Figure S-5 in the Supporting Information). The linear increase of molecular weights with monomer conversion and low polymer PDIs (<1.3) were observed, indicating that the bulk polymerization was well-controlled. As the rate of bulk polymerization is faster than that of solution polymerization, PVAc-Cl was prepared by bulk polymerization and analyzed by ^{1}H NMR (Figure 4a); typical signals of the end groups (b, c, d, g) are clearly observed besides the signals of the PVAc chain (a, e, f). The degree of polymerization of PVAc (DP = 70, M_n = 6300) can be calculated by comparison of the integration corresponding to $-CH_2\mathit{CH}(OCOCH_3)-$ (a) of PVAc to that corresponding to $CH_3\mathit{CH_2}OCS_2-$ (b). It is less than the molecular weight determined by GPC (M_n = 8600), which may be caused by GPC calibration with PSt standards. The above results show that the RAFT polymerization of VAc in the presence of **2** was very successful.

PVAc-Cl (M_{NMR}=3300, PDI=1.10) was then used as a macroinitiator to initiate the bulk ATRP of St under the following conditions: $[St]_0/[PVAc\text{-}Cl]_0/[CuCl]_0/[PMDETA]_0 = 420{:}1{:}2{:}2$, 80 °C. The results are shown in Figure 5. The controlled nature was again confirmed by the linear relationship of $\ln([M]_0/[M])$ versus time and the linear increase of molecular weights with conversion (up to 50% conversion), but the PDIs of the copolymer are around 1.5. The broad PDI of the copolymer can be explained as follows. MCP is a poor initiator for the ATRP of St due to the lower initiating rate than the chain propagating rate of St.[38] Therefore, the PVAc-Cl macroinitiator was consumed slowly and would coexist with the block copolymers for some time. This was confirmed by the bimodal GPC trace with a clear residual of the PVAc-Cl macroinitiator at the early stage of the polymerization (Figure

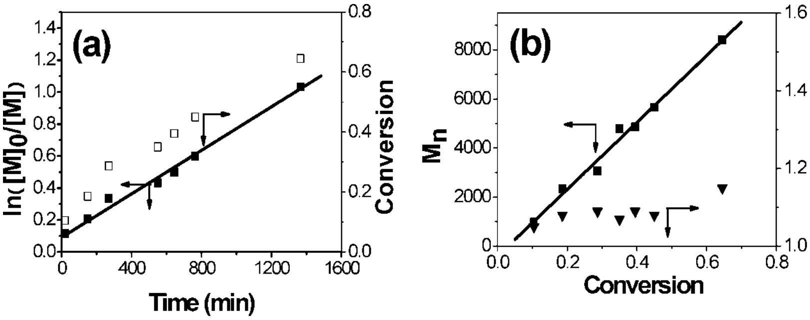


Figure 6. (a) Time dependence of ln([*M*]$_0$/[*M*]) and monomer conversion for the bulk ATRP of St at 60 °C and (b) number average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) versus monomer conversion. $[St]_0/[\mathbf{3}]_0/[CuBr]_0/[PMDETA]_0 = 100{:}1{:}1{:}1$, $[St]_0 = 8.74$ mol/L. $[M]_0$ and $[M]$ are the styrene concentration at time 0 and *t*, respectively. PMDETA: *N,N,N′,N″,N″*-pentamethyldiethylenetriamine.

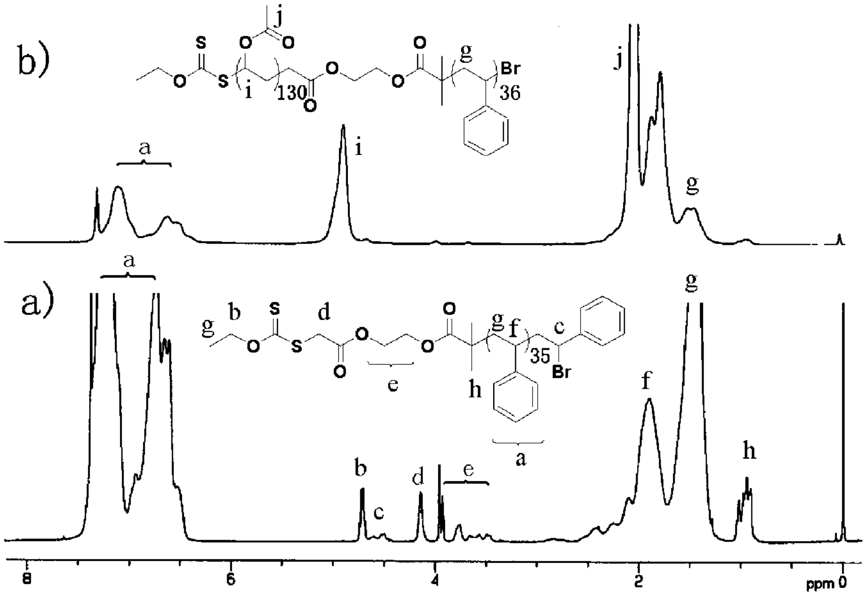


Figure 7. ^{1}H NMR spectra of (a) the polystyrene macromolecular chain transfer agent (PSt-RAFT, $M_{n,GPC} = 3300$, $M_w/M_n = 1.10$) and (b) the obtained polystyrene-*b*-poly(vinyl acetate) in $CDCl_3$. GPC: gel permeation chromatography.

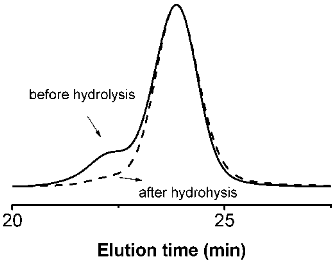
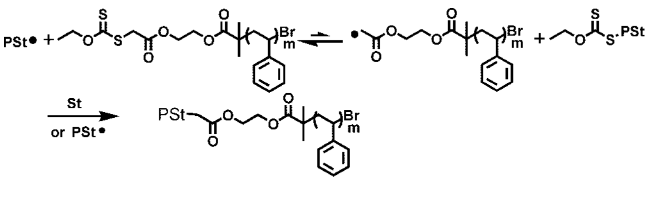


Figure 8. GPC traces of polystyrene macromolecular chain transfer agent (PSt-RAFT, $M_{n,GPC} = 5600$, $M_w/M_n = 1.13$) before and after ($M_{n,GPC} = 5200$, $M_w/M_n = 1.05$) hydrolysis.

Scheme 5. Proposed Mechanism for the Generation of High Molecular Weight PSt When Compound 3 Was Used to Initiate the ATRP of St



S-6 in the Supporting Information). One PVAc-*b*-PSt sample ($PVAc_{70}$-*b*-PSt_{170}) was analyzed by ^{1}H NMR (Figure 4b); it can be seen that, in addition to the characteristic signals of the PVAc block (a, e), typical signals of the PSt block (i, h) are clearly observed. The degree of polymerization of PSt can be calculated from the integration ratio of $-CH_2CH(C_6H_5)-$ (h) of the PSt block to $-CH_2CH(OOCCH_3)-$ (a) of the PVAc block. It must be noted that, to get well-defined block copolymers, the polymerization should be stopped after a suitable conversion. This is because the PVAc-Cl macroinitiator cannot be completely consumed after a certain amount of St conversion (about 10%) (Figure S-6 in the Supporting Information). Various block copolymers with high molecular weights of PSt blocks were synthesized by using different PVAc-Cl macroinitiators and controlling the St conversions. They are summarized in Table 2.

B. First ATRP of St, Followed by RAFT Polymerization of VAc. Since EBiB has a large influence on the RAFT polymerization of VAc, **3** was used as an ATRP initiator to synthesize PSt-RAFT, and then it was used to mediate the RAFT polymerization of VAc to get PSt-*b*-PVAc (Scheme 4).

3 was used as the initiator for the ATRP of St under the following conditions: $[St]_0/[\mathbf{3}]_0/[CuBr]_0/[PMDETA]_0 = 100{:}1{:}1{:}1$, 60 °C. The kinetics results are shown in Figure 6. As can be seen in Figure 6a, the kinetics of ATRP of St in the presence of **3** is first-order. The controlled nature was further confirmed by the low PDIs (<1.2) of PSt and the linear increase of the molecular weights with St conversion (Figure 6b). However, in the GPC trace, a shoulder of the high molecular weight appeared at high conversion, the molecular weight of which

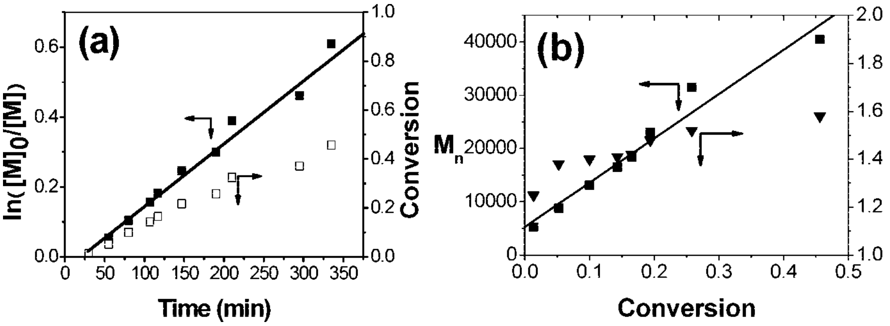


Figure 9. (a) Time dependence of ln([M]$_0$/[M]) and monomer conversion for the bulk radical polymerization of vinyl acetate (VAc) using polystyrene macromolecular chain transfer agent (PSt-RAFT, $M_{n,GPC}$ = 4400, M_w/M_n = 1.11) at 60 °C and (b) number average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) versus monomer conversion. [VAc]$_0$/[PSt-RAFT]$_0$/[AIBN]$_0$ = 770:1:0.56, [VAc]$_0$ = 10.85 mol/L. [M]$_0$ and [M] are the VAc concentration at time 0 and *t*, respectively. GPC, gel permeation chromatography; AIBN, 2,2′-azobis(isobutyronitrile).

was twice of that of the PSt main peak, and the content increased with conversion (Figure S-7 in the Supporting Information). The obtained PSt was analyzed by ^{1}H NMR (Figure 7a); in addition to the major characteristic signals of the PSt chain (a, f), the typical signals of the end groups (b, c, d, e, h) are clearly observed. The degree of polymerization of PSt (DP = 36, M_n = 4000) can be calculated by comparison of the integration ratio of $-CH_2CH(C_6H_5)-$ (a) to $-CH_3CH_2OC(S)S-$ (b).

To get further information of the high molecular weight product, one PSt sample thus obtained was hydrolyzed by sodium hydroxide in THF/methanol (1/1, v/v) at room temperature. GPC measurement shows that the shoulder from the high molecular weight PSt disappears, with no change of the main peak (Figure 8). Therefore, it cannot be formed by coupling of the PSt radicals. The appearance of the high molecular weight shoulder in the GPC trace can tentatively be explained as follows. If the PSt propagating radicals had transferred to the xanthate groups, a polymer chain with two propagation points at both ends would be produced, which would generate the PSt with twice the molecular weight and an ester bond in the middle of PSt backbone (Scheme 5). With polymerization progressing, the chain transfer reaction of the PSt propagating radical to xanthate is much more pronounced than it is in the early stage of polymerization. Therefore, the intensity of the shoulder increased with monomer conversion. The reason why this chain transfer reaction did not occur when the ATRP of St was carried out in the presence of **1b** is not clear now. According to a recent report, this kind of chain transfer reaction can be suppressed by changing the ligand for the ATRP of MMA.[39] It also implies that the chain transfer of the PSt propagating radicals to the xanthate groups of PVAc-Cl is little with symmetrical GPC traces even at high conversion (Figure S-6 in the Supporting Information).

One PSt-RAFT sample ($M_{n,GPC}$ = 4400, PDI = 1.11) was then used as the chain transfer agent to mediate the RAFT polymerization of VAc under the following conditions: [VAc]$_0$/[PSt-RAFT]$_0$/[AIBN]$_0$ = 770:1:0.56, 60 °C. A high ratio of [AIBN]$_0$ to [PSt-RAFT]$_0$ was used to get a fast polymerization and to suppress the chain transfer reaction of PVAc propagating radicals to the bromine-terminated PSt. The results are shown in Figure 9. A linear relationship between ln([M]$_0$/[M]) versus time was observed, indicating the first-order kinetics of the polymerization with respect to the concentration of VAc (Figure 9a). The molecular weights of the block copolymers increased linearly with VAc conversion, but the PDI of the copolymer was about 1.6 at high conversion (46%) (Figure 9b). The high PDI may be attributed to the observed residual PSt-RAFT (Figure S-8 in the Supporting Information), the chain transfer reaction of the PVAc propagating radical to the bromine-terminated PSt-RAFT (as discussed above), and the high ratio of [AIBN]$_0$ to [PSt-RAFT]$_0$ (less control of radical polymerization of VAc). This residual dead polymer was due to the chain transfer reaction of the PSt propagating radical to the xanthate group when preparing PSt-RAFT. This transfer reaction would result in the formation of a PSt with the end group of a similar structure to that of **1c,** which is inactive when used for the RAFT polymerization of VAc. The obtained PSt-*b*-PVAc (PSt$_{36}$-*b*-PVAc$_{130}$) was analyzed by ^{1}H NMR (Figure 7b); the typical signals of the PVAc block (i) are clearly observed besides the signals of the PSt block (a, g), and the degree of polymerization can be calculated from the integration ratio of $-CH_2CH(OOCCH_3)-$ (i) to $-CH_2CH(C_6H_5)-$ (a). Block copolymers with various molecular weights could also be synthesized by this method and are summarized in Table 2.

Conclusions

Difunctional compounds **2** and **3** were successfully used to synthesize PVAc-*b*-PSt with controlled molecular weights by combination of ATRP and RAFT. Although the control of both blocks is confirmed for both approaches, the PDIs of the obtained PVAc-*b*-PSt are a little bit higher. The method with **2,** RAFT polymerization of VAc first followed by ATRP of St, is better. Both blocks can be well-controlled to a high monomer conversion and well-defined PVAc-*b*-PSt can be obtained. When **3** was used, both the ATRP of St and the RAFT polymerization of VAc occurred with some side reactions. It should be pointed out that the obtained PVAc-*b*-PSt may not be hydrolyzed to get PVA-*b*-PSt due to the inherent ester bonds in the starting compounds, but this can be overcome by designing other difunctional molecules.

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Supporting Information Available: ^{1}H NMR spectra and gel permeation chromatography (GPC) traces of the polymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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