Atom Transfer Radical Polymerization and Copolymerization of Vinyl Acetate Catalyzed by Copper Halide/Terpyridine

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Copper-mediated atom transfer radical polymerization (ATRP) is versatile for living polymerizations of a wide range of monomers, but ATRP of vinyl acetate (VAc) remains challenging due to the low homolytic cleavage activity of the carbon-halide bond of the dormant poly(vinyl acetate) (PVAc) chains and the high reactivity of growing PVAc radicals. Therefore, all the reported highly active copper-based catalysts are inactive in ATRP of VAc. Herein, we report the first copper-catalyst mediated ATRP of VAc using CuBr/2,2′:6′,2″-terpyridine (tPy) or CuCl/tPy as catalysts. The polymerization was a first order reaction with respect to the monomer concentration. The molecular weights of the resulting PVAc linearly increased with the VAc conversion. The living character was further proven by self-chain extension of PVAc. Using polystyrene (PS) as a macroinitiator, a well-defined diblock copolymer PS-b-PVAc was prepared. Hydrolysis of the PS-b-PVAc produced a PS-b-poly(vinyl alcohol) amphiphilic diblock copolymer. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 737–746, 2009
Keywords: catalysis, polymerization, reaction kinetics, atom transfer radical, polymerization, living radical polymerization

Introduction

Vinyl acetate (VAc) is an important monomer because poly(vinyl acetate) (PVAc) and its hydrolyzed product, poly(vinyl alcohol) (PVA), have numerous applications in coating, fiber, textile, adhesive, pharmaceutical and photographic industries. VAc can only undergo radical polymerization. Therefore, great efforts have been made to explore the living radical polymerization of VAc for making PVAc and PVA with controlled molecular weights and structures. Matyjaszewski and coworker [1]first reported the controlled radical polymerization of VAc initiated by Al(iBu)$_3$/TEMPO (TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy), but this system was found to be complicated and difficult to reproduce.[2] Later, this group synthesized PVAc with predictable molecular weight by radical telomerization using CCl_4 as an initiator in the presence of Fe(OAc)$_2$/ *N,N,N′,N″,N″*-pentamethyldiethylenetriamine.[3] Controlled/living polymerizations of VAc via RAFT process,[4–6] xanthate-mediated polymerization,[7–10] and degenerative iodine transfer[11–13] were then reported. Recently, cobalt-complexes,[14–21] organotellium[22] and organostibine[23,24] were found effective in the controlled/living radical polymerization of VAc.

Atom transfer radical polymerization (ATRP), a transition metal-mediated living radical polymerization, is very versatile for many vinyl monomers including (meth)acrylates, styrenic monomers, and acrylamides.[25,26] However, ATRP of VAc is still not very successful. The carbon-halogen bonds (C-Br or C-Cl) of the dormant PVAc chains are too strong to be homolytically activated by the reported ATRP catalysts,[27,28] resulting in an extremely low activation constant k_{act} and therefore a very low ATRP equilibrium constant K_{eq} ($=k_{act}/k_{deact}$) in VAc polymerization, as illustrated in Scheme 1 and Eq. 1.[25,26] Thus, even the highly active

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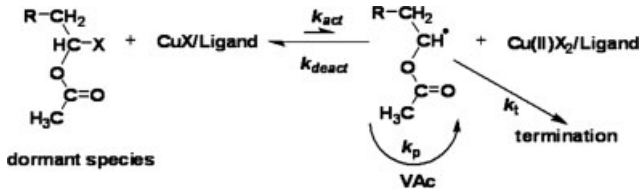


Scheme 1. The equilibrium in ATRP of VAc.

ATRP catalyst, CuBr/tris[2-(dimethylamino)ethyl]amine (Me_6TREN),[29] is too "mild" for VAc polymerization. In addition, the VAc propagating radical is not stabilized and thus is highly reactive and prone to chain transfer and termination reactions. Therefore, ATRP of VAc has been considered highly challenging. There is only one report of possible ATRP of VAc, in which dicarbonylcyclopentadienyliron dimer $[Fe(Cp)(CO)_2)]_2$ was used as catalyst in the presence of Al(O-*i*-Pr)$_3$ or Ti(O-*i*-Pr)$_4$ as additives with an iodide compound as initiator.[30] However, the iodine-degenerative transfer process could not be excluded during the polymerization because alkyl-iodides alone could mediate degenerative transfer polymerization of VAc.[11–13] The metal alkoxides played an important role in this polymerization. No polymerization occurred or the polymerization was extremely slow without this additive. Thus, the underlying mechanism of this system was still unclear.[30] All the attempts in ATRP of VAc using copper-based ATRP catalysts failed.

$$R_p = \frac{-dM}{dt} = \frac{k_p k_{act}[RX][M][CuX]}{k_{deact}[CuX_2]}$$
$$PDI = \frac{M_w}{M_n} = 1 + \left(\frac{k_p[RX]}{k_{deact}[CuX_2]}\right)\left(\frac{2}{p} - 1\right) \quad (1)$$

During our study on highly active catalysts, we found that copper halide/2,2′:6′,2″-terpyridine (CuBr/tPy or CuCl/tPy) could catalyze a very fast polymerization of acrylates even at room temperature. Further tests showed that the catalysts could catalyze a living radical polymerization of VAc. Herein, we report the first copper-mediated ATRP of VAc using CuBr/tPy or CuCl/tPy as catalyst and ethyl 2-bromoisobutyrate (EBiB) as an initiator. CuBr/tPy and CuCl/tPy catalyzed a living polymerization of VAc and block copolymerization using a polystyrene (PS) macroinitiator. Hydrolysis of the PS-b-PVAc produces the corresponding PS-b-PVA amphiphilic diblock copolymer. This amphiphilic copolymer formed micelles in water and had a lower critical solution temperature (LCST) phase behavior in mixed THF/water solution.

Experimental Section

Materials

1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA, 98%), methyl α-bromophenylacetate (MBPA), methyl 2-bromopropionate (MBP, 96%), ethyl 2-bromoisobutyrate (EBiB, 98%), 2,2′:4″,6″-terpyridine (tPy, 98%), 1,4,8,11,-tetraazacyclotetradecane (CYCLAM, 98%) were purchased from Aldrich and used as received. Styrene (St, 99%, Aldrich) and vinyl acetate (VAc, 99%, Aldrich) were washed with 5 wt% NaOH aqueous solution and vacuum distilled over CaH_2 twice. Copper (I) bromide (CuBr, 99%, Aldrich) and copper (I) chloride (CuCl, 99%, Aldrich) were purified according to literature.[31] Ligands tris[2-(dimethylamino)ethyl]amine (Me_6TREN), tris[(2-pyridyl)-methyl]-amine (TPMA), *N,N′, N″,N‴*-tetra[(methoxycarbonyl)ethyl]-1,4,8,11-tetraazacyclotetradecane ($Meco_4$CYCLAM), and *N,N,N′,N′*-tetra[(2-pyridal)methyl]-ethylenediamine (TPEN) were prepared according to the reported methods.[32–34]

Characterization

Monomer conversions were determined by ^{1}H NMR spectra. Both ^{1}H NMR and inverse-gated-decoupling ^{13}C NMR of PVAc spectra were recorded on a Bruker Advance DRX-400 spectrometer. Pulse program zgig30 (D1 = 30 s) was used to perform ^{13}C NMR measurements. Deuterated dimethylsulfoxide (DMSO-d_6) and chloroform ($CDCl_3$) were dried over molecular sieve overnight before use. Chemical shifts δ were given in ppm referenced to the internal standard tetramethylsilane (TMS, δ = 0 ppm). The molecular weights of polymers were determined by a Waters gel permeation chromatography (GPC) equipped with two 300 mm Waters solvent-saving Styrgel columns (molecular weight ranges: 5×10^2–3×10^4, 5×10^3–6×10^5) and a Waters 2414 refractive index detector. The eluent was THF at a flow rate of 0.3 mL/min and the column temperature was 30°C. A series of polystyrene standards with molecular weights ranging from 1450 to 450,000 were used to generate the universal calibration curve of PVAc. Dynamic laser light scattering study was carried out on a Malvern Nano ZS (scattering angle 173°) to measure the hydrodynamic radius of the PS-b-PVA micelles in aqueous solution at 25°C. The equipment is quipped with a 40 mW He-Ne laser operating at 633 nm and calibrated with 60 nm latex standard. The cloud points of the PS-b-PVA block polymer in THF/water mixture were determined by monitoring the optical density at 500 nm of stirred polymer solutions with increasing temperature using an Agilent 8453 UV-Vis Spectrophotometer. Infrared spectra (IR) were recorded on a Perkin Elmer Spectrum 2000 FTIR spectrometer (NaCl) with a scanning range from 600 cm^{-1} to 3800 cm^{-1}. Thermo gravimetric analysis (TGA) was carried out with a Perkin Elmer TGA 7 thermogravimetric analyzer under nitrogen flow (30 mL/min) at a heating rate of 20°C/min from 50°C to 500°C. Differential scanning calorimetry (DSC) was performed under a nitrogen flow (40 mL/min) at a heating rate of 20°C/min with a DSC QP10 from TA Instruments.

ATRP of vinyl acetate

A typical polymerization procedure of VAc is as follows. CuBr (28.7 mg, 0.20 mmol), tPy (46.5 mg, 0.20 mmol) and a stirring bar were charged into a Schlenk flask and the flask was tightly sealed with a rubber septum. Oxygen was removed from the flask by applying high vacuum and backfilling with argon (5 cycles). VAc (2.8 mL, 30.0 mmol) purged with argon for 30 min was then added using a gastight syringe under protection of argon. After the reaction flask was equilibrated to 70°C in an oil bath, degassed initiator EBiB (30 μL, 0.20 mmol) was added via a gastight

syringe. At timed intervals, samples were withdrawn via degassed gastight syringes, placed in hermetic vials, and stored in a freezer for NMR and GPC measurements.

Chain extension of PVAc

A polymerization of VAc using above procedure with VAc/EBiB/CuBr/tPy ratio of 75:1:1:1 was stopped at 43% conversion to prepare low molecular weight PVAc for chain extension. The PVAc was precipitated in ether and redissolved in THF. The THF solution was quickly precipitated with ice-cold water to remove the copper salts. The precipitate was dried and dissolved in THF again before it was filtered through a column of neutral alumina. The filtrate was dried and the purified PVAc was collected. This PVAc macroinitiator had a M_n of 4500 and a PDI of 1.48.

PVAc macroinitiator (0.9 g, 0.20 mmol), CuBr (28.7 mg, 0.20 mmol) and tPy (46.5 mg, 0.20 mmol) were charged into a Schlenk flask. The flask was tightly sealed with a rubber septum and then degassed (5 cycles) to remove the air in the flask. Degassed VAc (1.9 mL, 20.0 mmol) was added via a degassed gastight syringe and the mixture was heated at 70°C in an oil bath. After 10 h, the polymerization reached about 64% conversion determined by NMR. The polymerization was stopped and the solution was precipitated in cold water. The precipitate was collected and dried under vacuum.

Synthesis of PS-b-PVAc block copolymer

The PS-b-PVAc block copolymer was prepared by ATRP of VAc using a PS macroinitiator (PS-Br) with narrow molecular weight distribution (M_n = 4200, PDI = 1.12). It was synthesized by ATRP of styrene using CuBr/HMTETA as catalyst and EBiB as initiator. The polymerization was conducted at 90°C using St/EBiB/CuBr/HMTETA of 40:1:1 and stopped at ~87% monomer conversion. The purification of PS-Br macroinitiator is the same as the purification of PVAc macroinitiator.

PS-Br (0.84 g, 0.20 mmol), CuBr (28.7 mg, 0.20 mmol) and tPy (46.5 mg, 0.20 mmol) were added into a Schlenk flask. The flask was tightly sealed with a rubber septum and then degassed (5 cycles). Degassed VAc (1.4 mL, 15.0 mmol) was added using a degassed gastight syringe and the mixture was heated at 70°C in an oil bath. After 6 h, the polymerization reached about 35% conversion by NMR. It was stopped and the solution was precipitated in cold methanol. The precipitate was collected and dried under vacuum.

Synthesis of PS-b-PVA amphiphilic block copolymer

The PS-b-PVA block copolymer was prepared by hydrolysis of the corresponding PS-b-PVAc copolymer. PS-b-PVAc (PS M_n = 4200, PVAcM_n = 2700) (0.55 g) was dissolved in 25 mL of THF. NaOH aqueous solution (1.5 N, 5 mL) was mixed with the THF solution and the mixture was stirred at 50°C for 24 h. An excess of methanol was then added to precipitate the produced PS(4200)-b-PVA(1380) block copolymer. The product was collected and dried in vacuum.

Preparation of micelle formed from PS-b-PVA block copolymer in water

The above PS-b-PVA (0.05 g) was dissolved in 1 mL of THF and this solution was added dropwise in 10 mL of distilled water with vigorous stirring. THF was then removed by dialysis against distilled water and a clear transparent micelle solution was obtained for size measurement. Another 0.1 g block PS-b-PVA was dissolved in 5 mL of THF. This solution was added dropwise into 5 mL of distilled water. The water/THF mixture was vigorously agitated for 12 h. The light absorbance at 500 nm of the mixture was measured using a UV-Vis spectrometer to determine its phase transition temperature.

Results and Discussion

ATRP of VAc

Highly active ATRP catalysts reported in literature[35] were first tested for ATRP of VAc. For example, CuBr/HMTETA was found to polymerize methacrylates at 1 mol % catalyst relative to initiator.[36] Matyjaszewski et al reported that activator generated by electron transfer (AGET) ATRP polymerized styrene and methyl methacrylates at 1 mol % CuBr/Me_6TREN or CuBr/TPMA relative to initiator in a well controlled manner.[37] We recently found that 1 mol % CuBr/TPEN relative to initiator was sufficient to mediate well-controlled polymerizations of methacrylates, acrylates and styrenic monomers.[38,39] With these catalysts the polymerizations, however, either could not proceed or stopped at very low conversions (<10%) (Table 1). The low activities of these catalysts suggest that their equilibrium constants K_{eq} ($K_{eq} = k_{act}/k_{deact}$) are still insufficiently high for ATRP of VAc (Scheme 1), as discussed in the Introduction. CuBr complexed with cyclic ligand $Meco_4$CYCLAM was reported to exhibit very high activity for acrylate, acryamide and styrene monomers.[40,41] The VAc polymerization catalyzed by CuBr/$Meco_4$CYCLAM reached ~58% conversion in 12 h, but the molecular weights of the resulting PVAc did not increase with the monomer conversion, suggesting a conventional free radical polymerization.

During our study on highly active ATRP catalysts, we found that CuBr/tPy had a high activity. A 5 mol % CuBr/tPy relative to EBiB could polymerize methyl acrylate to 80% conversion in 10 min at room temperature, producing poly(methyl acrylate) with relative high polydispersity (PDI = ~1.7). The polymerization was highly exothermic and even caused the monomer solution boiling in an insulated tube. Its high activity motivated us to use it for ATRP of VAc. With methyl 2-bromopropionate (MBP) as initiator, CuBr/tPy slowly polymerized VAc to 43% conversion in 15 h (Table 1). The polymerization initiated by more reactive methyl α-bromophenylacetate (MBPA) produced a large amount of precipitates (Cu(II) complex) immediately after the addition of MBPA, indicating that the initiation was too fast and the irreversible radical terminations occurred, producing an excess Cu(II)/tPy species. Consequently, the polymerization was slow (<25% in 11 h). EBiB seems the best initiator for this system, producing PVAc with controlled molecular weights with high conversions (Table 1, entry 7 and 8).

Table 1. ATRPs of VAc at 70°C*

Entry	Initiator	Catalyst	Time (h)	Conv (%)	$M_{n,theo}$	$M_{n,GPC}$	PDI
1	EBiB	CuBr/HMTETA	10	No polymer	–	–	–
2	EBiB	CuBr/Me6TREN	10	8	1032	1500	1.85
3	EBiB	CuBr/TPEN	8	6	774	1700	2.10
4	EBiB	CuBr/Meco4CYCLAM	12	52	6708	7700	1.82
5	MBPA	CuBr/tPy	11	21	2709	45,000	1.62
6	MBP	CuBr/tPy	15	43	5547	7100	1.57
7	EBiB	CuBr/tPy	10	70	9030	11,600	1.74
8	EBiB	CuCl/tPy	10	80	10,320	13,300	1.69

*[VAc] = 10.8 M, [initiator] = 72 mM, VAc/initiator/catalyst = 150:1:1.

Figure 1 shows the kinetic plots of the polymerization of VAc at 70°C initiated by EBiB. The polymerizations by CuBr/tPy and CuCl/tPy proceeded smoothly and reached 70% and 80% conversions in 10 h. Obviously, the polymerization was faster than the reported $[Fe(Cp)(CO)_2)]_2$ catalyst (~60% conversion in 60 h at 60°C).[30] The CuBr/tPy-catalyzed polymerization was faster than that by CuCl/tPy at the initial period but slowed slightly later. Both $\ln([M]_0/[M])$ ~t plots were linear, indicating that the concentrations of growing radicals remained constant in both polymerizations.

The number-average molecular weights of the resulting PVAc did increase linearly with the monomer conversion (Figure 2), indicating that the copper-based catalysts indeed mediated a living radical polymerization of VAc. This also indicates that the polymerization was not a redox-initiated radical telomerization, whose M_n vs. monomer conversion relationship is of a typical free radical polymerization.[42] The measured molecular weights of PVAc were higher than their theoretical values with an initiation efficiency of about 0.75. The molecular weight distribution of the obtained PVAc was unimodal and the polydispersity was relatively narrow at low conversions (M_w/M_n ~1.4 at 16% conversion) and slightly broadened at high conversion (M_w/M_n = ~1.7, 80%). One reason for the relatively high polydispersity is the high propagation constant (k_p) of VAc as illustrated in Eq. 1 (k_p = 3700 L/mol·s for VAc, 176 L/mol·s for St and 367 L/mol·s for MMA at 60°C). This polydispersity is, however, lower than that of PVAc prepared with $[Fe(Cp)(CO)_2)]_2$ (M_w/M_n = ~2.0 at 55% conversion with Bu_2NH or *i*-Bu_3Al as an additive).[30]

These results indicate that CuBr/tPy or CuCl/tPy was sufficiently active for ATRP of VAc. Matyjaszewski et al. reported that copper halides complexed with 4,4′,4″-tri-tert-butyl-2,2′:6′,2″-terpyridine (TBtPy) had a fast activation but a slow deactivation.[43] CuBr/TBtPy at 1/1 ratio of catalyst/initiator polymerized MA in 3 h at 50°C. However, we found that a 5 mol % CuBr/tPy relative to the initiator EBiB could polymerize MA in 10 min at room temperature. Thus, copper halides complexed with the unsubstituted tPy may have even higher activation constant than CuX/TBtPy and thereby CuX/tPy could effectively abstract the Br or Cl from the dormant PVAc chains (Scheme 1). In contrast to the uncontrolled polymerization of St with the catalysis of CuBr/tPy,[44] the polymerization of VAc with CuX/tPy was controlled/living as evidenced by the linear increase in PVAc molecular weights with conversion (Figure 2). This also indicates that CuX_2/tPy could deactivate the propagating PVAc radicals to establish the ATRP equilibrium (Scheme 1).

The reason that CuX/tPy can mediate ATRP of VAc may be the just right activity and solubility of resulting CuX_2/tPy.

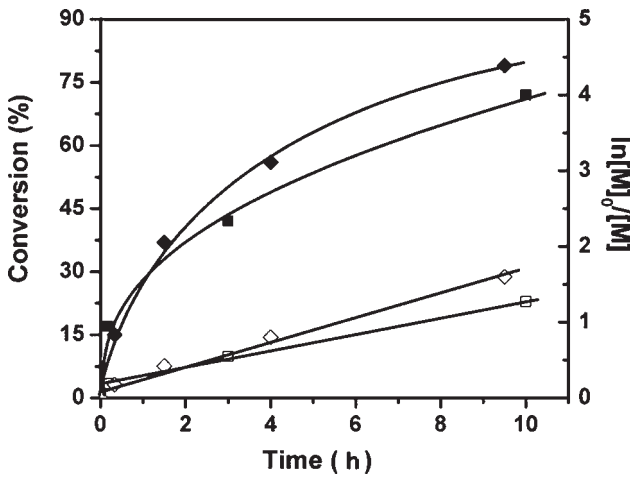


Figure 1. Kinetics of ATRP of VAc at 70 °C using EBiB as initiator and CuBr/tPy (■,□) or CuCl/tPy (◆,◇) as catalyst.

Conditions: [VAc] = 10.8 M, [EBiB] = [CuBr/tPy] = [CuCl/tPy] = 72 mM.

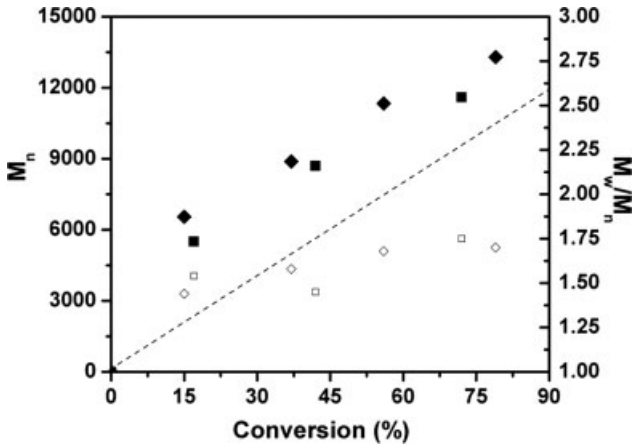


Figure 2. The molecular weight and polydispersity of PVAc as a function of the monomer conversion for the ATRP of VAc using CuBr/tPy (■,□) and CuCl/tPy (◆,◇) as catalysts.

The dotted line represents the theoretical molecular weights. See Figure 1 for conditions.

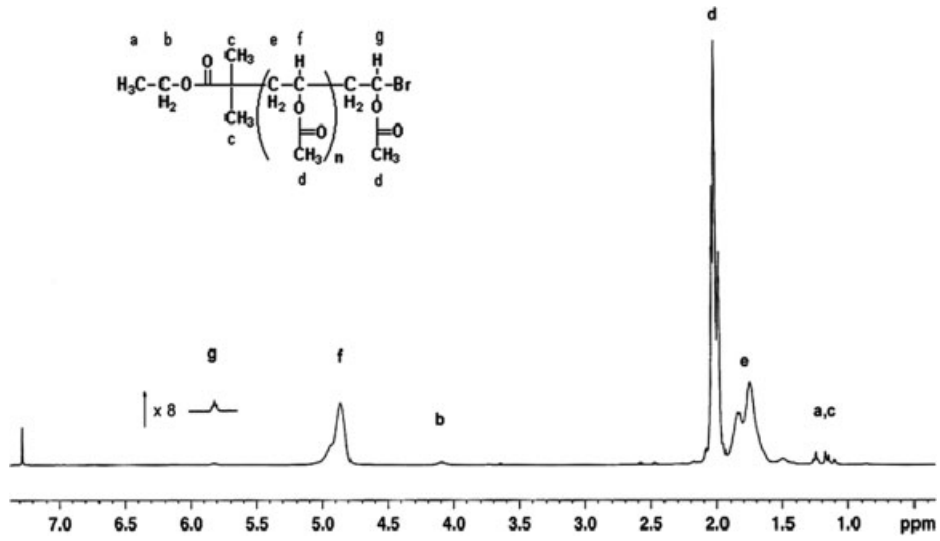
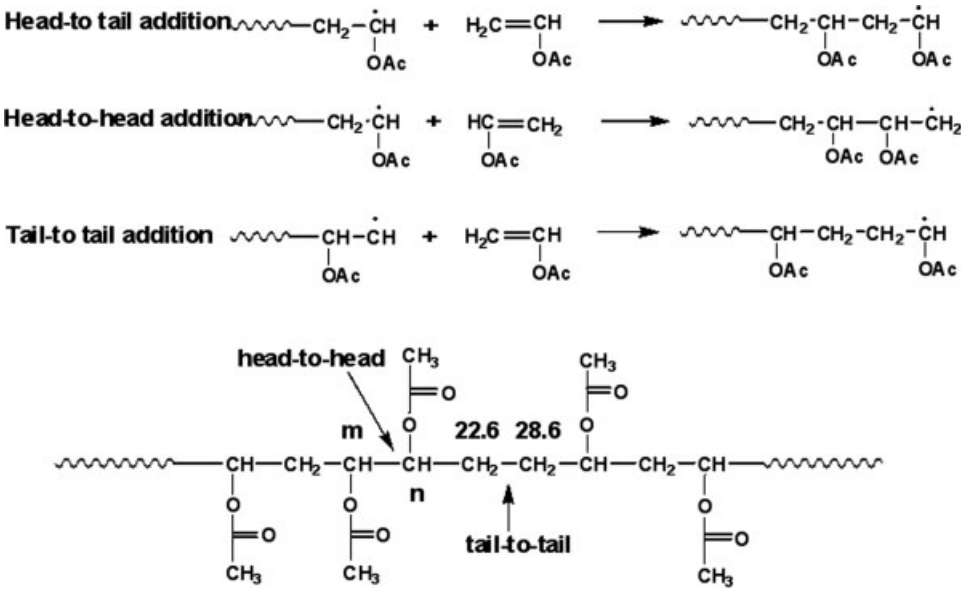


Figure 3. ^{1}H NMR spectrum of PVAc prepared with CuBr/tPy as catalyst and EBiB as initiator.

The PVAc radical is highly active, about three orders more active than a PS radical. Thus, CuX_2-deactivators having a right activity for radicals from styrene and (meth)acrylates, such as the CuX_2-complexes of Me_6TREN, TPEN and TPMA, are too active for a VAc radical. VAc radicals would be immediately deactivated by these highly active deactivators and have no chance to propagate VAc monomers. The polymerization of MA by CuBr/tPy is uncontrolled, suggesting that $CuBr_2$/tPy has a very low activity and cannot efficiently deactivate MA radicals. This low activity of $CuBr_2$/tPy, however, is just right for the highly active VAc radicals. The solubility of the $CuBr_2$/tPy is also important. For example, if a small amount of a polar solvent (e.g., γ-butyrolactone) was added to the VAc polymerization solution catalyzed by CuBr/tPy, the polymerization could not proceed or very slow. This was because the increase of the $CuBr_2$/tPy concentration greatly increased the deactivation rate.

End group analysis

The terminal group of the prepared PVAc was analyzed by ^{1}H NMR (Figure 3). Besides the strong peaks (peak f, d and e) from the repeat unit of VAc, small peaks (a, b, c) from initiator EBiB were also observed. The ω-terminal methine proton (g) with a C-Br bond appeared at $\sim$5.8 ppm, indicating the preservation of end group in VAc polymerization. Based on the integration ratio of peak g and peak b, 89% of terminal bromide was found to be preserved. The number average molecular weight of PVAc was estimated to be 4230 from the integration of peak f and peak b, which is very close to the value (4500) measured by GPC.



Scheme 2. Microstructure of PVAc prepared with CuBr/tPy catalyst and EBiB initiator.

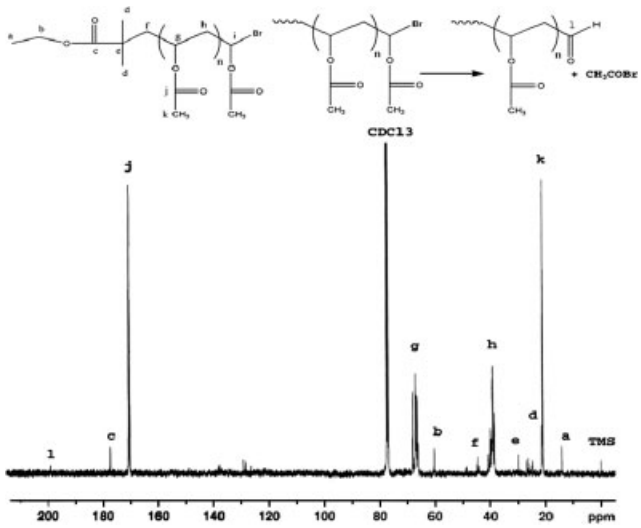


Figure 4. ^{13}C NMR spectrum of PVAc prepared with CuBr/tPy as catalyst and EBiB as initiator.

attributed to the tail-to-tail structure (Scheme 2), which was about 5.7% of the total repeating units. The signal of the head-to-head structure (carbon m, n) at about 75–77 ppm and the ω-terminal methine carbon with a C-Br bond (carbon i, ~76 ppm) were unfortunately overlapped in the solvent $CDCl_3$ peaks. The very weak peaks between 120 and 140 ppm were from the residual ligand tPy in PVAc. The weak peak at 198.9 ppm was from the aldehyde end group (carbon l),[51] indicating that some bromo-terminated PVAc, 14% of the total end group (at conversion of 43%) estimated from the peak integrations, decomposed to the aldehyde group during the polymerization or purification. Thus, the decomposition of the active chain ends to the dead aldehyde ends may be another cause of the relatively broad molecular distribution of PVAc (PDI: 1.4–1.7). The decomposition of the bromo-terminated PVAc, however, is much less significant than that in alkyl iodides-mediated degenerative transfer polymerization of VAc. For example, at 37% VAc conversion, about 26% of the end groups of the PVAc decomposed to the aldehyde-end groups.[12,51]

^{13}C NMR study on the microstructure of PVAc

During radical polymerization, VAc predominantly undergoes head-to-tail addition with some head-to head and tail-to-tail additions (Scheme 2). Figure 4 shows the ^{13}C NMR spectrum of a prepared PVAc. The four major peaks at 20.9 ppm, 39.5 ppm, 66.9 ppm, and 170.4 ppm were assigned to methyl, methylene, methine and carbonyl carbon atoms respectively.[45,46] The splitting and overlapping of methylene and methine peaks at 20.9 ppm and 39.5 ppm were caused by the chain stereo-regularity, i.e., chain confirmation and tactic sequence.[47,48] The minor peaks at 14.1ppm, 21.1ppm, 30.0ppm, 60.3ppm, 177.3 ppm from initiator EBiB were also well resolved in the spectrum. Based on Levy and Nelson' method[49,50] the minor peaks at 24.6 ppm and 27.1 ppm were

Chain extension (self-blocking) of PVAc

Self-blocking polymerization of VAc was conducted using PVAc macroinitiator and CuBr/tPy as catalyst to further prove the livingness of the polymerization. Figure 5 shows the GPC curves of the PVAc macroinitiator and the resulting "block" copolymer. The elution peak of the macroinitiator with M_n of 4500 and polydispersity of 1.48 clearly shifted to a high molecular weight (M_n = 10,500, PDI = 1.64). The small shoulder peak was from the PVAc macroinitiator due to the termination during the initiation and the dead chains with aldehyde end groups. Nevertheless, this experiment proves the living character of ATRP of VAc catalyzed by CuBr/tPy. It also suggests a relatively high preservation of the end functionalities of the PVAc macroinitiator.

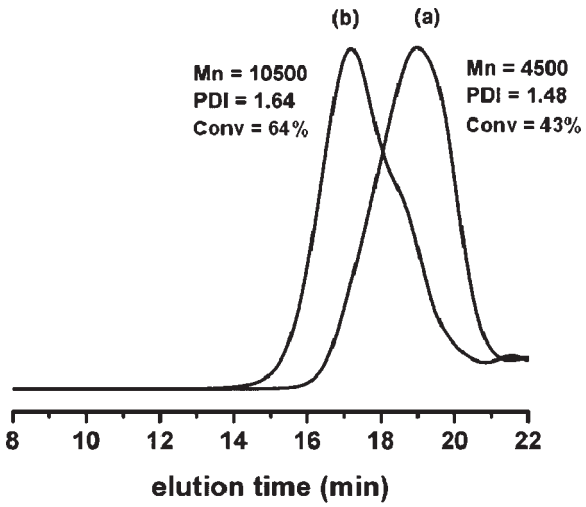


Figure 5. GPC curves of the PVAc macroinitiator (a) and the chain-extended PVAc (b).

Experimental conditions: 70°C, [VAc] = 10.8 M, [CuBr] = [tPy] = $[PVAc_{macroini}]$ = 0.11 M.

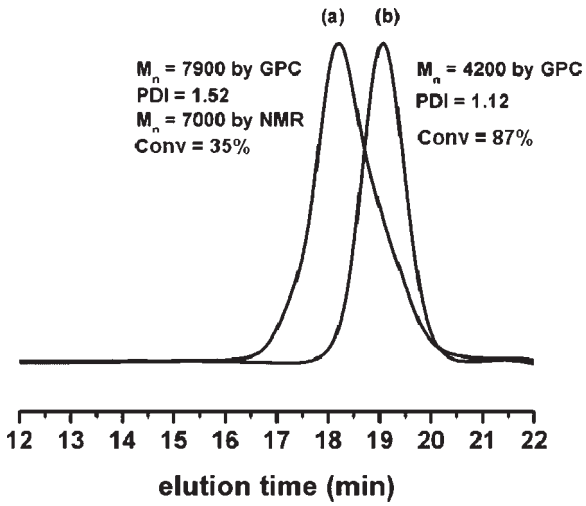


Figure 6. GPC curves of block copolymer PS-b-PVAc (a) and the corresponding PS macroinitiator (b).

Conditions: 70°C, [VAc] = 10.8 M, [CuBr] = [tPy] = $[PS_{macroini}]$ = 0.14 M.

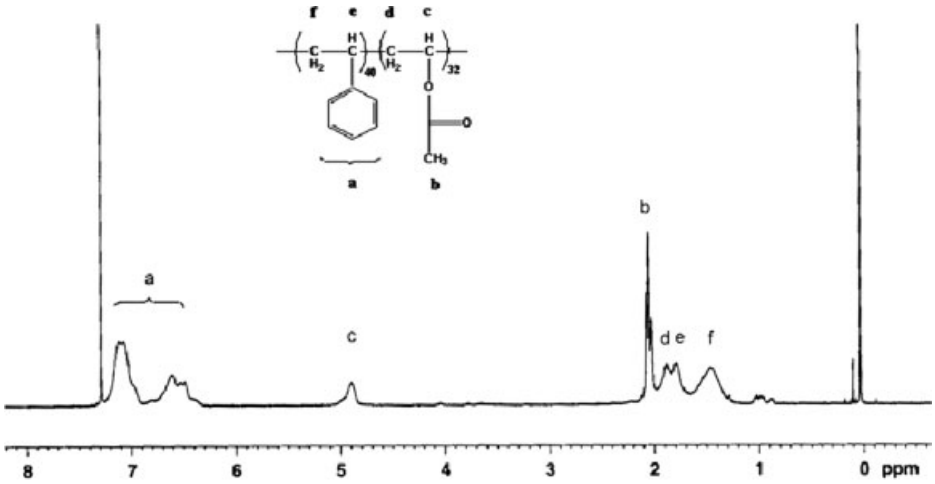


Figure 7. ^{1}H NMR spectrum of the PS(M_n = 4200)-b-PVAc(M_n = 2700) copolymer.

Synthesis and characterization of PS-b-PVAc block copolymer

Because of the difficulty in controlled radical polymerization of VAc, PS-block-PVAc copolymers were generally prepared by a combination of conventional radical polymerization and controlled radical polymerization. For example, VAc was firstly polymerized by conventional radical polymerization (telomerization with chloroform or initiation by halogenated azo-initiators)[42,52] to synthesize halogen-ended PVAc macroinitiators. This ill-defined PVAc macroinitiators were used to initiate the ATRP of styrene to prepare PVAc-b-PS. In the cobalt complex-mediated living radical polymerization of VAc, the prepared PVAc could not directly initiate living polymerization of the second monomer because the PVAc chains were end-capped with the cobalt complex. They had to react with α-bromoester or α-bromoketone-containing nitroxide to remove the cobalt complex and convert themselves into active bromide-containing macroinitiator for ATRP of the second monomer such as styrene.[20] In another report, the cobalt complex end-capped PVAc was directly used to initiate styrene radical polymerization at 30°C. The polymerization of styrene, however, was not controlled, resulting in a broad molecular weight distribution of PVAc-b-PS (PDI 1.6–3.4).[53]

A facile synthesis of PS-b-PVAc by direct initiation of VAc with PS macroinitiator was achieved using CuBr/tPy as the catalyst. PS macroinitiator (M_n = 4200, PDI = 1.12) was synthesized by ATRP of styrene using CuBr/HMTETA as catalyst and EBiB as initiator. This macroinitiator initiated VAc in the presence of CuBr/tPy, producing PS-b-PVAc with slightly higher polydispersity (Figure 6). The elution peak of the macroinitiator clearly shifts to a high molecular weight region (short elution time) without unreacted PS macroinitiators, indicating a nearly complete formation of PS-b-PVAc. Thus, compared to the PVAc macroinitiator method employing Co-mediated polymerization of VAc,[20] this one-step method produces pure block copolymers. Reversing the order of the block copolymerization, i.e., using PVAc macroinitiator to initiate styrene polymerization, resulted in a polymer with a broad molecular weight distribution. This is due to the slow initiation in styrene polymerization because the initiator with the PVAc end group structure is not good for styrene polymerization.[25,54]

The actual molecular weight of prepared PS-b-PVAc block copolymer was determined by ^{1}H NMR spectrum (Figure 7). Typical signals from the PVAc segment (b, c) and the PS segment (a, f) were clearly observed. From their intensities and the M_n of the PS block (4200), the actual molecular weight of the PVAc block was determined to be 2700. The copolymer had 38% PVAc as calculated from its NMR spectrum. The DSC curve (Figure 8) of the copolymer had one glass transition at about 43°C corresponding to the T_g (temperature of glass transition) of pure PVAc, and one at about 88°C corresponding to the T_g of short PS chains. The TGA result (Figure 9) shows a two-step weight loss. The copolymer first lost about 40% weight at 358°C (the temperature at the maximum weight loss rate) corresponding to the PVAc thermal degradation temperature and then totally degraded at about 444°C corresponding to the PS degradation temperature.[55] The TGA result also shows that the block copolymer

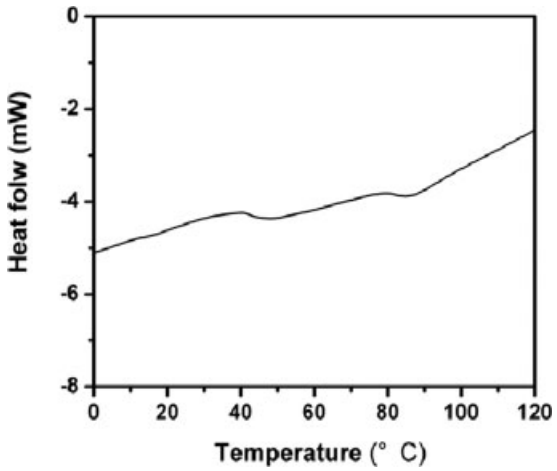


Figure 8. DSC trace of PS(M_n = 4200)-b-PVAc(M_n = 2700) block copolymer.

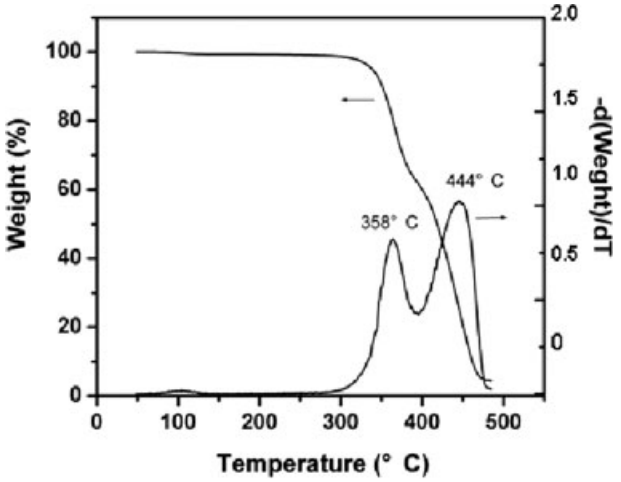


Figure 9. Thermogravimetric analysis of the PS(M_n = 4200)-b-PVAc(M_n = 2700) block copolymer.

was consisted of about 40 wt % of PVAc and 60 wt % of PS, which was consistent with the NMR result. All these data confirmed that the PS-b-PVAc prepared by this one-step method was pure.

Synthesis and characterization of PS-b-PVA block copolymer

The hydrolysis of PS(M_n = 4200)-b-PVAc(M_n = 2700) produced an amphiphilic polystyrene (M_n = 4200)-b-poly(vinyl alcohol) (M_n = 1380) diblock copolymer (PS-b-PVA). The FTIR spectrum of the PS-b-PVA (Figure 10) show that the typical carbonyl (C=O) absorption of PVAc at about 1738 cm^{-1} disappeared after hydrolysis while a strong and broad absorption at 3377 cm^{-1} from hydroxyl (—OH) groups appeared, indicating a complete removal of the acetate groups. This amphiphilic PS-b-PVA formed micelles in water at room temperature with an average diameter of 120 nm and low particle size distribution (Figure 11). No large

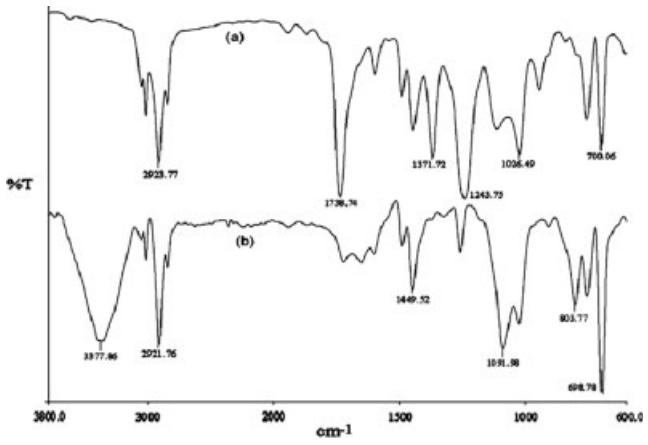


Figure 10. FTIR spectra of PS(M_n = 4200)-b-PVAc(M_n = 2700) (a), and PS(M_n = 4200)-b-PVA(M_n = 1380) block copolymer (b).

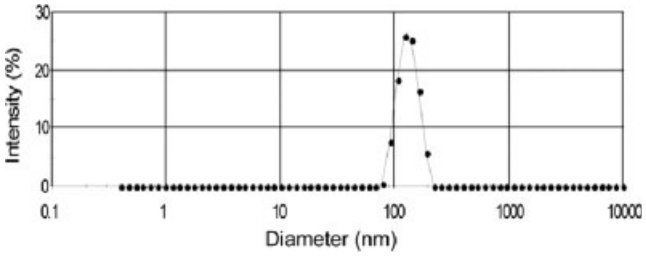


Figure 11. Size distribution of the micelle formed at room temperature from amphiphilic PS(M_n = 4200)-b-PVA(M_n = 1380) block copolymer in water at 0.5 wt %.

vesicles were found in THF/water mixture that was reported by Jerome et al.[20]

The amphiphilic PS(M_n = 4200)-b-PVA(M_n = 1380) block copolymer has an interesting temperature-dependent

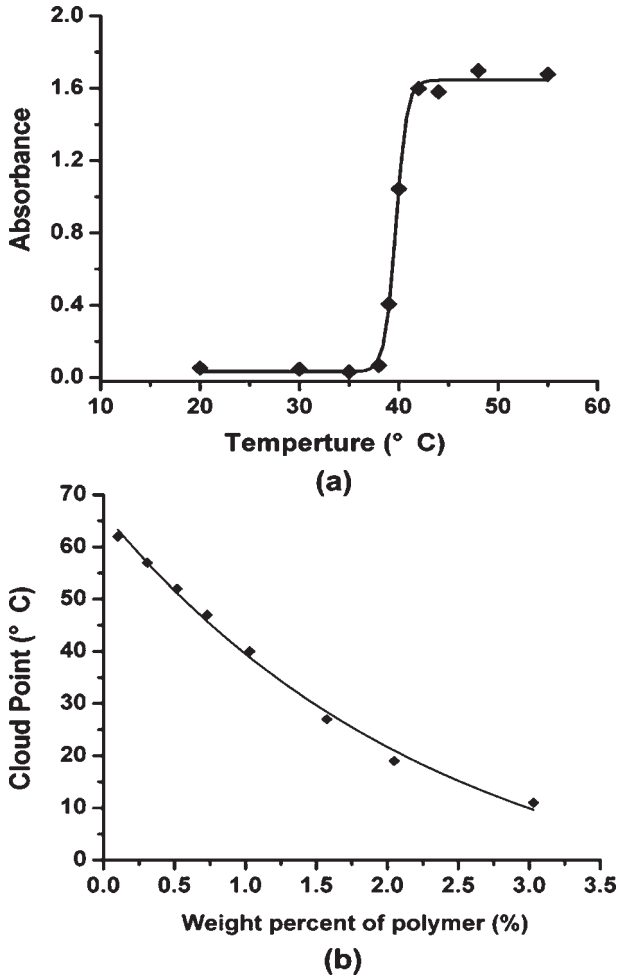


Figure 12. (a) Light absorbance at 500 nm of the block PS(M_n = 4200)-b-PVA(M_n =1380) copolymer in 1/1 (v/v) THF/water mixture (1 wt %) as a function of temperature; (b) The cloud temperature of PS(M_n = 4200)-b-PVA(M_n = 1380) block polymer in 1/1 (v/v) THF/water mixture as a function of polymer concentration.

phase separation in 1/1 (v/v) THF/water mixture. Figure 12 (a) shows the light absorbance at 500 nm of the PS-b-PVA in 1/1 (v/v) THF/water mixture (1 wt %) as a function of temperature. A distinct and rapid rise in light absorbance occurred at 40.2°C, indicating that the block polymer precipitated from the THF/water solution at the temperature higher than 40.2°C. This temperature, denoted as the cloud-point temperature, of PS-b-PVA in THF/water (1/1 v/v) was strongly dependent on its concentration (Figure 12b). The cloud-point rapidly decreased with the increase of polymer concentration in the range of 0 ~3 wt %. Obviously, this block copolymer solution showed a typical lower critical solution temperature (LCST) phase behavior. These results again confirmed that the PS(M_n = 4200)-b-PVA(M_n = 1380), as well as its precursor PS(M_n = 4200)-b-PVAc(M_n = 2700), was indeed a block copolymer rather than a two homopolymer mixture.

Conclusion

In summary, the first copper-based catalyst CuX/2,2′:6′,2″-terpyridine (CuX/tPy, X = Br or Cl) for the controlled/living polymerization of VAc is reported. The living characters of the polymerization were confirmed by a linear increase in the molecular weights of prepared PVAc with the monomer conversion, self-chain extension and block copolymerization. A facile synthesis of PS-b-PVAc block copolymer was developed by using PS macroinitiator and CuBr/tPy as catalyst. Hydrolysis of the PS-b-PVAc produced the corresponding PS-b-PVA block copolymer, which formed micelles in water solution, and exhibited lower critical solution temperature (LCST) phase behavior in mixed THF/water solution.

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Literature Cited

1. Mardare D, Matyjaszewski K. "Living" radical polymerization of vinyl acetate. *Macromolecules*. 1994;27:645–649.
2. Granel C, Jerome R, Teyssie P, Jasieczek CB, Shooter AJ, Haddleton DM, Hastings JJ, Gigmes D, Grimaldi S, Tordo P, Greszta D, Matyjaszewski K. Investigation of methyl methacrylate and vinyl acetate polymerization promoted by Al(iBu)$_3$/2,2′-bipyridine and Al(iBu)$_3$/2,2′-bipyridine/TEMPO complexes. *Macromolecules*. 1998; 31:7133–7141.
3. Xia J, Paik H-J, Matyjaszewski K. Polymerization of vinyl acetate promoted by iron complexes. *Macromolecules*. 1999;32:8310–8314.
4. Boschmann D, Vana P. Poly(vinyl acetate) and poly(vinyl propionate) star polymers via reversible addition fragmentation chain transfer (RAFT) polymerization. *Polym Bull*. 2005;53:231–242.
5. Stenzel MH, Davis TP, Barner-Kowollik C. Poly(vinyl alcohol) star polymers prepared via MADIX/RAFT polymerization. *Chem Commun*.2004:1546–1547.
6. Russum JP, Barbre ND, Jones CW, Schork FJ. Miniemulsion reversible addition fragmentation chain transfer polymerization of vinyl acetate. *J Polym Sci Part A: Polym Chem*. 2005;43:2188–2193.
7. Stenzel MH, Cummins L, Roberts GE, Davis TP, Vana P, Barner-Kowollik C. Xanthate mediated living polymerization of vinyl acetate: a systematic variation in MADIX/RAFT agent structure. *Macromol Chem Phys*. 2003;204:1160–1168.
8. Theis A, Davis TP, Stenzel MH, Barner-Kowollik C. Probing the reaction kinetics of vinyl acetate free radical polymerization via living free radical polymerization (MADIX). *Polymer*. 2006;47:999–1010.
9. Simms RW, Davis TP, Cunningham MF. Xanthate-mediated living radical polymerization of vinyl acetate in miniemulsion. *Macromol Rapid Commun*. 2005;26:592–596.
10. Bernard J, Favier A, Zhang L, Nilasaroya A, Davis TP, Barner-Kowollik C, Stenzel MH. Poly(vinyl ester) star polymers via xanthate-mediated living radical polymerization: from poly(vinyl alcohol) to glycopolymer stars. *Macromolecules*. 2005;38:5475–5484.
11. Iovu MC, Matyjaszewski K. Controlled/living radical polymerization of vinyl acetate by degenerative transfer with alkyl iodides. *Macromolecules*. 2003;36:9346–9354.
12. Koumura K, Satoh K, Kamigaito MYO. Iodine transfer radical polymerization of vinyl acetate in fluoroalcohols for simultaneous control of molecular weight, stereospecificity, and regiospecificity. *Macromolecules*. 2006;39:4054–4061.
13. Borkar S, Sen A. Controlled copolymerization of vinyl acetate with 1-alkenes and their fluoro derivatives by degenerative transfer. *J Polym Sci Part A: Polym Chem*. 2005;43:3728–3736.
14. Peng C-H, Scricco J, Li S, Fryd M. Wayland B B Organo-cobalt mediated living radical polymerization of vinyl acetate *Macromolecules*. 2008;41:2368–2373.
15. Maria B, Kaneyoshi H, Matyjaszewski K, Poli R. Effect of electron donors on the radical polymerization of vinyl acetate mediated by [Co(acac)$_2$]: degenerative transfer versus reversible homolytic cleavage of an organocobalt(III) complex. *Chem Eur J*. 2007;13:2480–2492.
16. Kaneyoshi H, Matyjaszewski K. Radical (co)polymerization of vinyl chloroacetate and N-vinylpyrrolidone mediated by bis(acetylacetonate)cobalt derivatives. *Macromolecules*. 2006;39:2757–2763.
17. Detrembleur C, Debuigne A, Bryaskova R, Charleux B, Jerome R. Cobalt-mediated radical polymerization of vinyl acetate in miniemulsion: very fast formation of stable poly(vinyl acetate) latexes at low temperature. *Macromol Rapid Commun*. 2006;27:37–41.
18. Debuigne A, Caille J-R, Detrembleur C, Jerome R. Effective cobalt mediation of the radical polymerization of vinyl acetate in suspension. *Angew Chem Int Ed*. 2005;44:3439–3442.
19. Debuigne A, Caille J-R, Jerome R. Highly efficient cobalt-mediated radical polymerization of vinyl acetate. *Angew Chem Int Ed*. 2005;44:1101–1104.
20. Debuigne A, Caille J-R, Willet N, Jerome R. Synthesis of poly(vinyl acetate) and poly(vinyl alcohol) containing block copolymers by combination of cobalt-mediated radical polymerization and ATRP. *Macromolecules*. 2005;38:9488–9496.
21. Kaneyoshi H, Matyjaszewski K. Synthesis of poly(vinyl acetate)-graft-polystyrene by a combination of cobalt-mediated radical polymerization and atom transfer radical polymerization. *J Polym Sci Part A: Polym Chem*. 2007;45:447–459.
22. Yamago S. Development of organotellurium-mediated and organostibine-mediated living radical polymerization reactions. *J Polym Sci Part A: Polym Chem*. 2006;44:1–12.
23. Yamago S, Ray B, Iida K, Yoshida J, Tada T, Yoshizawa K, Kwak Y, Goto A, Fukuda T. Highly versatile organostibine mediators for living radical polymerization. *J Am Chem Soc*. 2004;126:13908–13909.
24. Srivastava AK, Chaurasia AK, Sharma S, Mishra G. Kinetics and mechanism of polymerization of vinyl acetate using triphenyl stibonium 1, 2, 3, 4-tetraphenyl- cyclopentadiene ylide. *J Sci Ind Res*. 2006;65:514–517.
25. Matyjaszewski K, Xia J. Atom transfer radical polymerization. *Chem Rev*. 2001;101:2921–2990.
26. Kamigaito M, Ando T, Sawamoto M. Metal-catalyzed living radical polymerization. *Chem Rev*. 2001;101:3689–3746.
27. Gillies M B, Matyjaszewski K, Norrby P-O, Pintauer T, Poli R, Richard P. A DFT study of R-X bond dissociation enthalpies of relevance to the initiation process of atom transfer radical polymerization. *Macromolecules*. 2003;36:8551–8559.
28. Matyjaszewski K, Poli R. Comparison of bond dissociation energies of dormant species relevant to degenerative transfer and atom transfer radical polymerization. *Macromolecules* 2005;38:8093–8100
29. Xia J, Matyjaszewski K. Controlled/"living" radical polymerization. Atom transfer radical polymerization of acrylates at ambient temperature. *Macromolecules*. 1998;31:5958–5959.

30. Wakioka M, Baek KY, Ando T, Kamigaito M, Sawamoto M. Possibility of living radical polymerization of vinyl acetate catalyzed by iron(I) complex. *Macromolcules*. 2002;35:330–333.
31. Queffelec J, Gaynor SG, Matyjaszewski K. Optimization of atom transfer radical polymerization using Cu(I)/tris(2-(dimethylamino) ethyl)amine as a catalyst. *Macromolecules*. 2000;33: 8629–8639.
32. Ciampolini M, Nardi N. Five-coordinated high-spin complexes of bivalent cobalt, nickel, and copper with tris(2-dimethylaminoethyl)-amine. *Inorg Chem*. 1966;5:41–44.
33. Tyeklar Z, Jacobson RR, Wei N, Murthy NN, Zubieta J, Karlin KD. Reversible reaction of dioxygen (and carbon monoxide) with a copper(I) complex. X-ray structures of relevant mononuclear Cu(I) precursor adducts and the trans-(.mu.-1,2-peroxo)dicopper(II) product. *J Am Chem Soc*. 1993;115:2677–2689.
34. Bulach V, Mandon D, Fischer J, Weiss R. The high yield synthesis of *N*-tetrapropionic methyl ester, acid and carboxylate derivatives of 1,4,8,11-tetraazacyclotetradecane, and molecular structure of the tetramethylpropionate ester dication. *Inorg Chim Acta*. 1993;210:7–9.
35. Tang W, Matyjaszewski K. Effect of ligand structure on activation rate constants in ATRP. *Macromolecules*. 2006;39:4953–4959.
36. Faucher S, Zhu S. Heterogeneous atom transfer radical polymerization of methyl methacrylate at low metal salt concentrations. *Ind Eng Chem Res*. 2005;44:677–685.
37. Matyjaszewski K, Jakubowski W, Min K, Tang W, Huang J, Braunecker WA, Tsarevsky NV. Diminishing catalyst concentration in atom transfer radical polymerization with reducing agents. *Proc Natl Acad Sci USA*. 2006;103:15309–15314.
38. Tang H, Arulsamy N, Radosz M, Shen Y, Tsarevsky NV, Braunecker WA, Tang W, Matyjaszewski K. Highly active copper-based catalyst for atom transfer radical polymerization. *J Am Chem Soc*. 2006;128:16277–85.
39. Tang H, Radosz M, Shen Y. $CuBr_2$/N,N,N′,N′-tetra[(2-pyridyl)-methyl] ethylenediamine/tertiary amine as a highly active and versatile catalyst for atom-transfer radical polymerization via activator generated by electron transfer. *Macromol Rapid Commun*. 2006;27:1127–1131.
40. Teodorescu M, Matyjaszewski K. Atom transfer radical polymerization of (meth)acrylamides. *Macromolecules*. 1999;32:4826–4831.
41. Gromada J, Matyjaszewski K. Measurement of initial degree of polymerization without reactivation as a new method to estimate rate constants of deactivation in ATRP. *Macromolecules*. 2002;35:6167–6173.
42. Paik H-J, Teodorescu M, Xia J, Matyjaszewski K. Block copolymerizations of vinyl acetate by combination of conventional and atom transfer radical polymerization. *Macromolecules*. 1999;32:7023–7031.
43. Matyjaszewski K, Goebelt B, Paik H-j, Horwitz CP. Tridentate nitrogen-based ligands in Cu-based ATRP: a structure-activity study. *Macromolecules*. 2001;34:430–440.
44. Kickelbick G, Matyjaszewski K. 4,4′,4′′-tris(5-nonyl)-2,2′:6′,2′′-terpyridine as ligand in atom transfer radical polymerization (ATRP). *Macromol Rapid Commun*. 1999;20:341–346.
45. Katsuraya K, Hatanaka K, Matsuzaki K, Yamaura K. Assignment of finely resolved ^{13}C-NMR spectra of poly(vinyl acetate). *Macromol Rapid Commun*. 2000;21:697–700.
46. Moritani T, Fujiwara Y. ^{13}C- and ^{1}H-NMR investigations of sequence distribution in vinyl alcohol-vinyl acetate copolymers. *Macromolecules*. 1977;10:532–535.
47. Ibrahim B, Katritzky AR, Smith A, Weiss DE. Carbon-13 nuclear magnetic resonance spectroscopy of polymers. I. High resolution carbon-13 nuclear magnetic resonance spectroscopy. Tacticity studies on poly(vinyl acetate) and monomer distribution analysis in ethylene-vinyl acetate copolymers. *J Chem Soc Perkin Trans 2: Phys Org Chem*. 1974;13:1537–1542.
48. Amiya S, Uetsuki M. Microstructures in poly(vinyl alcohol-co-crotonic acid) studied by proton-NMR and carbon-13-NMR. *Macromolecules*. 1982;15:166–170.
49. Levy GC, Nelson GL. ^{13}C Nuclear Magnetic Resonance for Organic Chemists; Wiley-Interscience: New York, 1972.
50. Vercauteren FK, Donners WAB. A ^{13}C-nuclear magnetic resonance study of the microstructure of poly(vinyl alcohol). *Polymer*. 1986; 27:993–998.
51. Iovu MC, Simplaceanu V, Gil RR, Matyjaszewski K. ^{13}C DEPT NMR study of poly(vinyl acetate) synthesized by degenerative transfer polymerization with alkyl iodides. *Polym Prepr*. 2004;45:988–989.
52. Destarac M, Pees B, Boutevin B. Radical telomerization of vinyl acetate with chloroform. Application to the synthesis of poly(vinyl acetate)-block-polystyrene copolymers by consecutive telomerization and atom transfer radical polymerization. *Macromol Chem Phys*. 2000;201:1189–1199.
53. Bryaskova R, Willet N, Debuigne A, Jerome R, Detrembleur C. Synthesis of poly(vinyl acetate)-*b*-polystyrene and poly(vinyl alcohol)-b-polystyrene copolymers by cobalt-mediated radical polymerization. *J Polym Sci Part A: Polym Chem*. 2007;45:81–89.
54. Shipp DA, Wang J-L, Matyjaszewski K. Synthesis of acrylate and methacrylate block copolymers using atom transfer radical polymerization. *Macromolecules*. 1998;31:8005–8008.
55. Eroglu MS, Hazer B, Guven O, Baysal BM. Preparation and thermal characterization of block copolymers by macroazonitriles having glycidyl azide and epichlorohydrin moieties. *J Appl Polym Sci*. 1996;60:2141–2147.

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