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Polymerization of Vinyl Acetate Promoted by Iron Complexes

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ABSTRACT: Polymerization of vinyl acetate (VOAc) was carried out using CCl_4 as the initiator in the presence of the $Fe(OAc)_2$/PMDETA (PMDETA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) complex. Poly(vinyl acetate) with a wide range of molecular weights was synthesized in a predictable fashion in high yields (ca. 70%) by varying the ratio of the initial concentrations of monomer and initiator. The resulting poly(vinyl acetate) (M_n = 3600 and M_w/M_n = 1.81) was used as an efficient macroinitiator for the synthesis of block copolymers with *n*-butyl acrylate (M_n = 11 000 and M_w/M_n = 1.41) and styrene (M_n = 24 300 and M_w/M_n = 1.42) using typical atom transfer radical polymerization (ATRP) catalytic systems. However, more detailed kinetic studies revealed that the VOAc polymerization did not obey ATRP behavior but was a redox-initiated radical telomerization with CCl_4 acting as both the initiator and the main-chain transfer agent. Block copolymerization was due to the chain extension with the trichloromethyl end groups.

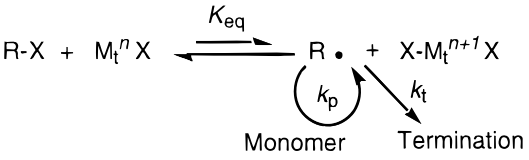
Introduction

Recent years have witnessed the rapid development of "living"/controlled radical polymerization.[1] Different approaches have been developed where a dynamic equilibrium is established between propagating radicals and dormant polymer chains. One such approach is transition-metal-catalyzed atom transfer radical polymerization (ATRP).[2] A variety of transition metals, such as copper,[3−6] ruthenium,[7,8] iron,[9,10] and nickel,[11,12] have been successfully employed in ATRP. In a typical ATRP, an organic halide is used as the initiator. In the presence of a transition-metal complex, initiating radicals are generated which react with the monomer to propagate. The growing polymer chains are rapidly deactivated by the transition-metal species in its higher oxidation state to form the polymeric halide dormant species and regenerate the reduced transition-metal complex. Repetition of the radical generation, addition to alkene, and deactivation process yields a well-defined polymer with controlled molecular weight and low polydispersity.

Although a variety of monomers have been successfully polymerized in a well-controlled manner, the "living"/controlled radical polymerization of vinyl acetate (VOAc) remains a challenging task. The importance of controlling VOAc polymerization arises not only from its industrial importance but also from the fact that VOAc has so far been polymerized only via a radical mechanism. The first example of "living" radical polymerization of VOAc was reported using $Al(iBu)_3$/2,2′-bipyridine/TEMPO (TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy) as the initiator.[13] A hexacoordinated aluminum persistent radical was proposed in the tentative mechanism. However, the polymerization was later found to be much more complicated and difficult to reproduce.[14] Two other accounts on controlled radical polymerization of VOAc have also been reported. They are based on degenerative transfer processes. Thus, poly(vinyl acetate) (pVOAc) of relatively low molecular weights were prepared with the use of azobis(isobutyronitrile) (AIBN) as the radical initiator in the presence of alkyl iodides.[15] In the other approach, reversible addition−fragmentation chemistry was applied for the controlled polymerization of VOAc.[16] As part of the effort to better understand limitations of ATRP for the controlled polymerization of a wide range of monomers, we report our studies of ATRP of VOAc with various initiating systems.

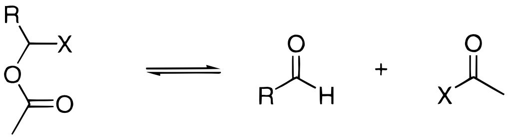
Results and Discussion

A series of polymerizations were carried out under standard ATRP conditions using methyl 2-bromopropionate as the initiator and CuBr complexed by either 2,2′-dipyridyl (bpy) or *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) as the catalyst at temperatures ranging from 50 to 110 °C; however, no formation of pVOAc was observed. The use of other common ATRP initiators or chlorine as the exchanging halogen afforded similar results (cf. Table 2). The difficulty encountered in the ATRP of VOAc may be attributed to the low equilibrium constant (K_{eq}) as defined in eq 1.



(1)

Other factors include possible side reactions such as the decomposition of the dormant species. For example, decomposition pathway as shown in eq 2 has been suggested.[17]



(2)

It is also likely that the growing radicals may be oxidized through an outer-sphere electron transfer process to generate the corresponding carbocation as displayed in eq 3.[18] Similar oxidation of the propagating

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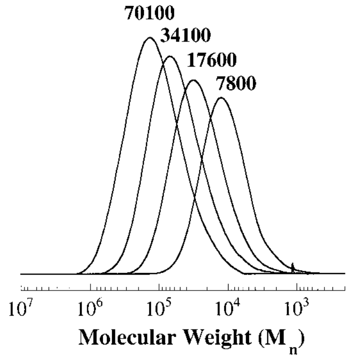


Figure 1. SEC chromatograms of pVOAc prepared using CCl_4 as the initiator in the presence of $Fe(OAc)_2$/PMDETA complex. Conditions: 50 °C; $[VOAc]_0 = 10.8$ M (bulk); $[CCl_4]_0/[Fe(OAc)_2]_0/[PMDETA]_0 = 1/1/1$; $[VOAc]_0/[CCl_4]_0 = 117$ (conversion = 63%, $M_{n,SEC} = 7800$), 233 (conversion = 66%, $M_{n,SEC} = 17\,600$), 467 (conversion = 74%, $M_{n,SEC} = 34\,100$), and 1167 (conversion = 81%, $M_{n,SEC} = 70\,100$).

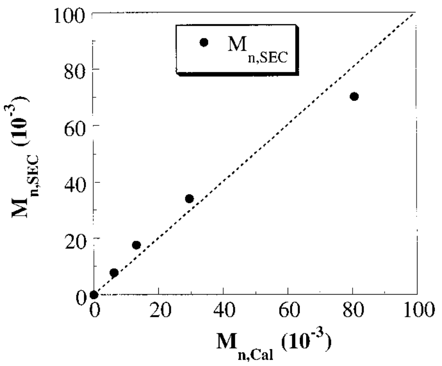
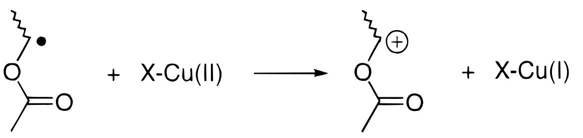


Figure 2. Dependence of $M_{n,SEC}$ vs $M_{n,Cal}$ for the polymerizations of VOAc initiated by $CCl_4/Fe(OAc)_2$/PMDETA. See Figure 1 for conditions.

radicals has been proposed to account for the slow termination reaction in copper-mediated ATRP of styrene.[19]



(3)

Interestingly, polymers were obtained when $Fe(OAc)_2$ complexed by PMDETA was employed as a catalyst with CCl_4 as the initiator. Representative size exclusion chromatography (SEC) traces (Figure 1) showed progressive shift toward higher molecular weights with decreasing amount of CCl_4 used. Moreover, an almost linear relationship between the experimental molecular weights ($M_{n,SEC}$) and the theoretical values ($M_{n,Cal}$) was obtained (Figure 2). The theoretical values were calculated on the basis of ratios of consumed monomer to initiator assuming quantitative initiation from CCl_4 according to eq 4.

$$M_{n,Cal} = ([VOAc]_0/[CCl_4]_0) \times 86.09 \times \text{conversion} + 154 \quad (4)$$

In addition, pVOAc made with the $CCl_4/Fe(OAc)_2$/PMDETA initiating system ($M_n = 3600$ and $M_w/M_n = 1.81$) was used as an efficient macroinitiator for the synthesis of block copolymers with *n*-butyl acrylate (*n*BA) ($M_n = 11\,000$ and $M_w/M_n = 1.41$) and styrene (Sty) ($M_n = 24\,300$ and $M_w/M_n = 1.42$) using typical ATRP catalytic systems (Figure 3). The SEC traces of the block copolymers shifted cleanly to higher molecular weights, and polydispersities were reduced. Thus, it appeared from single-point experiments that polymerization of VOAc with the $CCl_4/Fe(OAc)_2$/PMDETA initiating system was controlled.

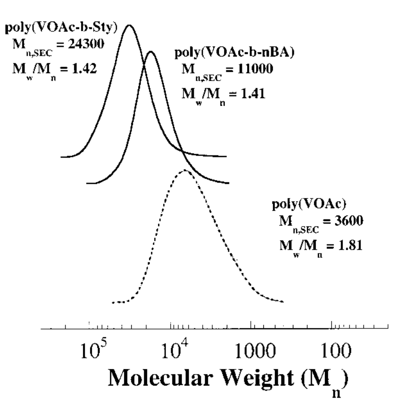


Figure 3. SEC chromatograms of pVOAc prepared using $CCl_4/Fe(OAc)_2$/PMDETA and its subsequent block copolymerizations. Conditions for the synthesis of pVOAc: 50 °C; $[VOAc]_0 = 5.4$ M (50 vol % EtOAc); $[VOAc]_0/[CCl_4]_0 = 40$; $[CCl_4]_0/[Fe(OAc)_2]_0/[PMDETA]_0 = 1/0.2/0.2$; time = 10 h; conversion = 45%; $M_{n,SEC} = 3600$; $M_w/M_n = 1.81$. Conditions for the synthesis of poly(VOAc-*b*-Sty): 90 °C; $[styrene]_0 = 8.7$ M (bulk); $[styrene]_0/[p(VOAc)\text{-}CCl_3]_0 = 628$; $[p(VOAc)\text{-}CCl_3]_0/[CuBr]_0/[dNbpy]_0 = 1/2.5/5.0$; time = 15 h; conversion = 46%. Conditions for the synthesis of poly(VOAc-*b*-*n*BA): 90 °C; $[nBA]_0 = 7.0$ M (bulk); $[nBA]_0/[p(VOAc)\text{-}CCl_3]_0 = 502$; $[p(VOAc)\text{-}CCl_3]_0/[CuBr]_0/[dNbpy]_0 = 1/2.5/5.0$; time = 11 h; conversion = 15%.

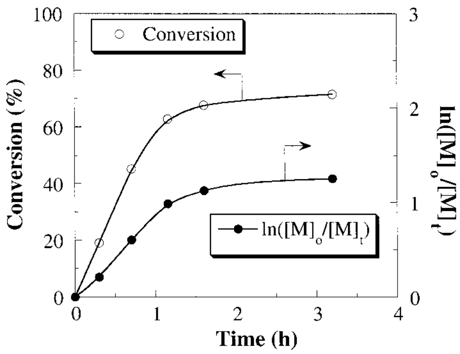


Figure 4. Kinetic plot for the polymerization of VOAc promoted by $Fe(OAc)_2$/PMDETA using CCl_4 as the initiator. Conditions: 50 °C; $[VOAc]_0 = 5.4$ M (50 vol % EtOAc); $[VOAc]_0/[CCl_4]_0 = 233$; $[CCl_4]_0/[Fe(OAc)_2]_0/[PMDETA]_0 = 1/1/1$.

Further detailed kinetic studies were carried out to gain better insight into the polymerization. Figure 4 shows the semilogarithmic kinetic plot of the polymerization of VOAc which was initiated by CCl_4 and promoted by the $Fe(OAc)_2$/PMDETA complex. The concentration of the propagating species was approximately constant until the polymerization reached ca. 60% monomer conversion, and then the polymerization rate dropped abruptly. The molecular weight vs conversion plot shows that polymers with high molecular weights were formed at the early stage of the polymerization and that the experimental molecular weight remained relatively constant throughout the reaction (Figure 5). In addition, polymers with relatively high polydispersities ($M_w/M_n \sim 1.8-2.0$) were obtained, independent of conversion.

Different initiators were also examined, and the results are shown in Table 1. With CCl_4 as the initiator,

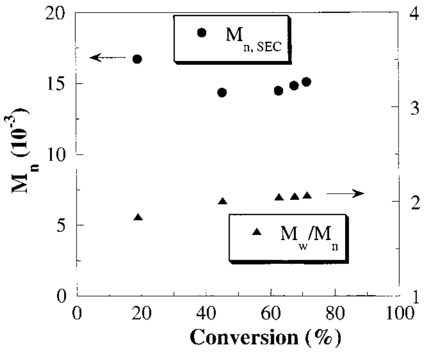


Figure 5. Dependence of molecular weight ($M_{n,SEC}$) and polydispersity (M_w/M_n) on monomer conversion. See Figure 4 for conditions.

Table 1. Use of Various Initiators in the Polymerization of VOAc Promoted by $Fe(OAc)_2$/PMDETA Complex

entry[a]	initiator	time (h)	conv (%)	$M_{n,Cal}$[b]	$M_{n,SEC}$	M_w/M_n
1	CCl_4	0.4	63	6300	7800	1.8
2	$CHCl_2CO_2CH_3$	0.2	46	4600	4300	2.4
3	$CH_3CHClCO_2CH_3$	12.0	14	1400	117700	2.2
4	CBr_4	16.2	<5	<500	oligomers	
5	$CHBr_3$	16.2	22	2200	2100	2.6
6	$CH_3CHBrCO_2CH_3$	12.0	35	3500	217800	1.9
7	CHI_3	0.4	<5	<500	oligomers	

[a] Conditions: 50 °C; $[VOAc]_0 = 10.8$ M (bulk); $[VOAc]_0/[initiator]_0 = 117$; $[initiator]_0/[Fe(OAc)_2]_0/[PMDETA]_0 = 1/1/1$. [b] Calculated according to eq 4.

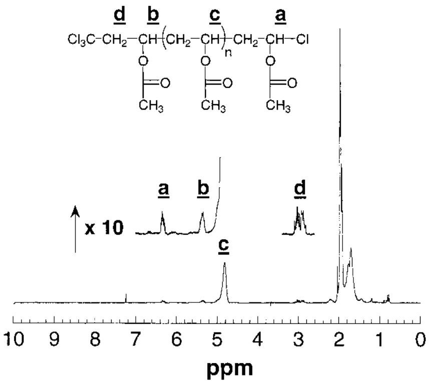
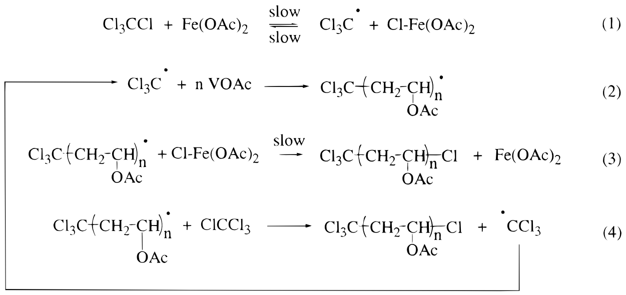


Figure 6. ^1H NMR spectrum of pVOAc prepared using CCl_4 as the initiator in the presence of $Fe(OAc)_2$/PMDETA complex. Conditions: 50 °C; $[VOAc]_0 = 5.4$ M (50 vol % EtOAc); $[CCl_4]_0/[Fe(OAc)_2]_0/[PMDETA]_0 = 2/0.25/0.25$; $[VOAc]_0/[CCl_4]_0 = 25$ (conversion = 41%; $M_{n,SEC} = 2070$; $M_w/M_n = 1.79$)

Scheme 1. Telomerization of VOAc Using CCl_4/$Fe(OAc)_2$/PMDETA



the formed pVOAc had experimental molecular weight ($M_{n,SEC} = 7800$) close to the theoretical value ($M_{n,Cal} = 6300$), which was calculated according to eq 4. A similar result was obtained using methyl 2,2-dichloroacetate (entry 2) or bromoform (entry 5) as the initiator. However, other initiators either led to pVOAc with too high molecular weight or resulted in the formation of oligomers. For example, methyl 2-chloropropionate or methyl 2-bromopropionate yielded polymers with $M_{n,SEC} > 100\,000$ and $M_w/M_n \sim 2.0$, whereas carbon tetrabromide and iodoform only afforded oligomers.

Polymerizations of VOAc promoted by various copper complexes were also carried out. As shown in Table 2, low conversions (5−10%) and oligomers ($M_{n,SEC} = 400-1200$) were obtained in all cases. Unsuccessful polymer formation can be attributed to the low equilibrium constant for VOAc in ATRP and possible side reactions as discussed previously. Apparently, $Fe(OAc)_2$ complexed by PMDETA is a less efficient deactivator than the copper complexes, enabling higher polymer yields.

The redox-initiated radical telomerization has been well studied.[20] Typically, CCl_4 or $RCCl_3$ is used as the telogen, and salts of transition metals, such as iron or copper, are used as the catalysts. Results from Figures 4 and 5 and Table 1 suggest that polymerization of VOAc with CCl_4 as the initiator in the presence of the $Fe(OAc)_2$/PMDETA complex is a redox-initiated radical telomerization (Scheme 1).

Thus, the telomerization was initiated by halogen abstraction from CCl_4 by $Fe(OAc)_2$/PMDETA. However, different from typical ATRP or conventional redox-initiated radical telomerization where the chain transfer constant to the transition-metal salt (e.g., $CuCl_2$ or $FeCl_3$) is much greater than that to the telogen/initiator, the major chain transfer pathway in the CCl_4/$Fe(OAc)_2$/PMDETA system was likely transfer to initiator. Under such conditions, molecular weight was controlled by CCl_4, which acted as both the initiator and the main-chain transfer agent (INIFER)[21] (Scheme 1, steps 1 and 4). Since the chain transfer constant to CCl_4 in the polymerization of VOAc is about 1 under the reaction conditions,[22] the ratio of consumed monomer to CCl_4 remained approximately constant throughout the polymerization. As a result, polymers with fairly constant molecular weights were obtained (Figure 5). Once growing polymer radicals were terminated by Cl transfer from CCl_4 to form the C−Cl bond, both end groups, i.e., CCl_3CH_2-[23] and $-CH(OAc)Cl$, had much lower reactivities than CCl_4 itself. This led to inactive polymer chains, and the polymerization stopped around ca. 70% monomer conversion when all the initiator was consumed and no more radicals could be generated (Figure 4). The employment of an initiator with a transfer constant either too low (e.g., methyl 2-chloropropionate) or too high (e.g., CBr_4) yielded polymers with very high molecular weights or oligomers, respectively (Table 1). In addition, when the polymerization was carried out in the presence of an additive with a much higher chain transfer constant than CCl_4, such as $FeCl_3$, CBr_4, or CHI_3, only the formation of oligomers was observed. In contrast, additives with low chain transfer constants, such as $IC(CH_3)_3$ and nBu$_4$NBr, did not significantly affect the polymerization (Table 3).

The structure of pVOAc prepared with CCl_4 and the $Fe(OAc)_2$/PMDETA complex was analyzed by ^1H NMR spectroscopy (Figure 6). The signals at 3.00 and 5.35 ppm correspond to the methylene and methine protons adjacent to the trichloromethyl group at the α-end, respectively. A similar assignment of ^1H NMR signals has been made for the telomerization of VOAc initiated by a peroxide and $CHCl_3$.[24] The resonance at 6.35 ppm corresponds to the methine proton adjacent to terminal

Table 2. Polymerizations of VOAc Promoted by Copper Complexes

entry[a]	initiator	CuX	ligand	conv (%)	$M_{n,Cal}$[b]	$M_{n,SEC}$	M_w/M_n
1	$CH_3CHBrCO_2CH_3$	CuBr	dNbpy	5	500	1250	24.8[c]
2	$CH_3CHBrCO_2CH_3$	CuBr	PMDETA	13	1300	690	1.9
3	$CH_3CHClCO_2CH_3$	CuCl	PMDETA	14	1400	650	1.6
4	CCl_4	CuCl	PMDETA	17	1700	480	1.4
5	CCl_4	CuOAc	PMDETA	18	1800	420	4.2

[a] Conditions: 90 °C; $[VOAc]_0 = 10.8$ M (bulk); $[VOAc]_0/[initiator]_0 = 117$; $[initiator]_0/[CuX]_0/[ligand]_0 = 1/1/1$; time = 15 h. [b] Calculated according to eq 4. [c] Bimodal distribution.

Table 3. Effect of Additives in the Polymerization of VOAc Promoted by $Fe(OAc)_2$/PMDETA Complex

entry[a]	additive	time (h)	conv (%)	$M_{n,SEC}$	M_w/M_n
1		0.15	69	8400	1.9
2[b]	$FeCl_3$	5.0	< 5	oligomers	
3[c]	CBr_4	23.5	16	oligomers	
4[d]	CHI_3	23.5	10	oligomers	
5[c]	$C(CH)_3I$	16.0	33	3700	1.8
6[d]	*n*-Bu_4NBr	0.5	46	8000	2.1

[a] Conditions: 70 °C; $[VOAc]_0 = 10.8$ M (bulk); $[VOAc]_0/[CCl_4]_0 = 117$; $[CCl_4]_0/[Fe(OAc)_2]_0/[PMDETA]_0 = 1/0.5/0.5$. [b] $[CCl_4]_0/[Fe(OAc)_2]_0/[FeCl_3]_0/[[PMDETA]_0 = 1/0.5/0.1/0.6$. [c] $[CCl_4]_0/[Fe(OAc)_2]_0/[additive]_0/[[PMDETA]_0 = 1/0.5/1/0.5$, temp = 50 °C. [d] $[CCl_4]_0/[Fe(OAc)_2]_0/[additive]_0/[[PMDETA]_0 = 1/0.5/0.5/0.5$.

chlorine at the ω-end. The peak integration ratio of methine proton at the ω-end to the protons at the α-end is $a/b/d = 0.9/1/2$, indicating the presence of both trichloromethyl and chlorine end groups on a polymer chain and in good agreement with previous electrospray ionization mass spectroscopy (ESI MS) studies.[25] Using the ratio of the area of the two peaks (d/c or b/c), the number-average molecular weight by ^1H NMR ($M_{n,NMR}$) was determined to be 2250, which is close to the value from size exclusion chromatography calibrated against standard polystyrene samples ($M_{n,SEC} = 2070$).

Several factors in the polymerization of VOAc initiated by the $CCl_4/Fe(OAc)_2$/PMDETA system merit further discussion. First, deactivation or chain transfer of growing radicals by $Cl-Fe(OAc)_2$ is probably slow (Scheme 1, steps 1 and 3) to achieve polymers with high molecular weights ($M_{n,SEC}$ approaching 100 000) in high yields (ca. 70%). Second, abstraction of Cl from CCl_4 by $Fe(OAc)_2$ is likely also slow (Scheme 1, step 1). This results in the slow generation of primary radicals through the redox initiation and leads to high yield of polymer. Third, the significantly higher chain transfer constant of CCl_4 than Cl_3CC- additionally helps to preserve the trichloromethyl end group for a high efficiency of block copolymer formation with a variety of other monomers that are readily polymerizable by ATRP (Figure 3).

Similar block copolymers have been prepared previously using ATRP in conjunction with trichloromethyl-terminated pVOAc. The latter was synthesized using $CHCl_3$ as a transfer agent and benzoyl peroxide (BPO) as the initiator.[26] However, transfer coefficient for $CHCl_3$ is low ($C_{tr} = 0.01$), and it is difficult to prepare polymers with high molecular weights with good functionality without contamination of the end group originating from the BPO initiator. In contrast, application of CCl_4 as both the initiator and the main transfer agent gives better control of end groups over a wider range of molecular weights. Additionally, with a transfer coefficient $C_{tr} \sim 1$, CCl_4 can provide polymers with relatively low polydispersities and predictable molecular weights.

Conclusions

In summary, polymerization of VOAc using CCl_4 as the initiator in the presence of $Fe(OAc)_2$/PMDETA provided polymers with degrees of polymerization approximately predetermined by the ratio of the initial concentrations of monomer and initiator. Moreover, the synthesized pVOAc was successfully used for subsequent block copolymer formation by ATRP with styrene and *n*-butyl acrylate.

However, the polymerization did not proceed by ATRP with frequent activation/deactivation cycles but was a redox-initiated radical telomerization. The obtained polymers had $M_w/M_n \sim 1.8-2.0$. The major chain transfer pathway was likely transfer to initiator with a transfer constant of $C_{tr} \sim 1$ under the reaction conditions. This allowed for the facile synthesis of pVOAc with a wide range of molecular weights in high yields with good end group functionality.

Experimental Section

Materials. Vinyl acetate, styrene, and *n*-butyl acrylate from Aldrich were distilled over CaH_2 and stored under argon atmosphere at −15 °C. CuBr (98%) and CuCl (98+%) were purchased from Aldrich and purified according to the published procedure.[27] $FeCl_3$ (97%, Aldrich), CuOAc (99%, Strem Chemicals), and $Fe(OAc)_2$ (97%, Strem Chemicals) were used as received. CCl_4 (99.9+%), CBr_4 (99%), $CHBr_3$ (99+%), $CH_3CHBrCO_2CH_3$ (98%), $CH_3CHClCO_2CH_3$ (97%), CHI_3 (99%), $C(CH)_3I$ (95%), and nBu_4NBr (99%) were from Aldrich. $CHCl_2CO_2CH_3$ (99+%) was from TCI. All were used without purification. The ligand 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) was prepared according to the reported procedure.[28] *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA, 99%) as the ligand was from Aldrich, and ethyl acetate (EtOAc) (solvent) was from Fisher. They were both used as received.

Polymerization. Bulk: To dry glass tubes with metal salt were added, using degassed syringes, ligand, degassed monomer, and initiator. Three freeze−pump−thaw cycles were performed, and the tubes were sealed under vacuum and placed in an oil bath held by a thermostat at the desired temperature. At timed intervals, the polymerizations were stopped by cooling the tubes into ice−water. Afterward, the tubes were opened and the contents dissolved in THF.

Solution. A dry round-bottom flask was charged with $Fe(OAc)_2$. The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed monomer, solvent, and amine ligand were added using degassed syringes. The flask was immersed in an oil bath held by a thermostat at the desired temperature. Initiator was then added and timing was started. At timed intervals, samples were withdrawn from the flask using degassed syringes and added to THF.

Block Copolymerization. To a glass tube with CuBr and dNbpy was added a solution of the pVOAc−CCl_3 macroinitiator dissolved in degassed monomer (styrene or *n*-butyl acrylate). Three freeze−pump−thaw cycles were performed, and the tubes were sealed under vacuum and placed in an oil bath held by a thermostat at the desired temperature. After the desired amount of time, the tube was removed from the bath, and the reaction mixture was dissolved in THF.

Characterization. Monomer conversion was determined from the concentration of residual monomer using a Shimadzu GC-14 gas chromatograph equipped with a J&W Scientific 30 m DB-WAX column with a Shimadzu CR501 Chromatapac. Size exclusion chromatography (SEC) for molecular weight and molecular weight distribution was performed using a Waters 712 WISP autosampler, 510 HPLC pump, 410 differential detector, and the following PSS columns: guard, 10^5, 10^3, 10^2 Å. All samples were run in THF at 35 °C with a flow rate of 1.0 mL/min. Linear polystyrene standards were used for calibration. ^{1}H NMR spectra were recorded using a Bruker AM 300. For purification of pVOAc for ^{1}H NMR analysis, the reaction mixture dissolved in THF was first passed through an aluminum column to remove any metal-containing species. Polymer was then obtained by precipitation in hexane for five times and then dried under reduced pressure for 48 h.

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