

Well-Defined Polymers Containing 1,3-Dichloro-tetra-*n*-butyl-distannoxane Moiety: Synthesis, Mechanism, and Applications in Catalysis

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ABSTRACT: A series of well-defined different chain lengths polymers, which contain the organometallic 1,3-dichloro-tetra-*n*-butyl-distannoxane core in the main chain, was obtained in one-pot via a novel 1,3-dichloro-tetra-*n*-butyl-distannoxane (complex **A**)/azobisisobutyronitrile (AIBN) initiating system used in reverse atom transfer radical polymerization of styrene in different concentrations. The introduction of organotin complex **A** was supported by ¹H-NMR, ¹³C-NMR, and the Inductive Coupled Plasma Emission Spectrometer analysis of the organotin-containing polymer. Moreover, the mechanism of polymerization was investigated by changing the ratio of complex **A** to

AIBN. It was concluded that the complex **A** not only acted as an important part of the initiator system but also introduced the functional organometallic group into the polymer chain. Additionally, the organotin-containing polymer could be used as catalyst for esterification, and the reaction products' conversion could reach high up to 99% and does not decrease after four successive cycles. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3485–3494, 2012

Key words: polymer synthesis; 1,3-dichloro-tetra-*n*-butyl-distannoxane; reverse ATRP; organotin-containing polymer; catalysis

INTRODUCTION

The introduction of organometallic compounds into polymers brings novel and potentially useful physical and chemical properties to the final polymeric complex.¹ This kind of metal-containing molecules has given rise to important technological applications in catalysis, biochemistry, nanoscience and advanced materials. Since the mid 1990s, scientists have paid more attention to the development of new, easily processed materials via the incorporation of metal centers into synthetic polymer chains. The polymers containing different kinds of metals, such as Fe, Ru, Pt, Pd, and Ni,^{2–15} were successfully synthesized in the past five decades. In comparison, the introduction of Sn complex into polymer is scant. Angiolini et al.^{16–19} synthesized a series of polymers containing the tributyltin carboxylate moiety. However, their pro-

tolol is synthetically tedious. For example, it involves the esterification of both bis(tributyltin) oxide in the polymers and carboxylic groups or the polymerization of monomers containing organotin which is prepared beforehand. Moreover, the result is also unsatisfied in transesterification reactions using these polymers containing tributyltin carboxylate moiety as catalysts.

The organotin compound, 1,3-dihalo-tetra-alkyl-distannoxane, is a stable, easy-to-handle Lewis acid that has been used as catalyst for various reactions as esterification, acetalization, and deacetalization, etc.^{20–24} It is noteworthy that this kind of tin complex can easily self-assemble through intermolecular halide-tin interaction.²⁵ Hence, introducing the 1,3-dihalo-tetra-alkyl-distannoxane unit into polymer has the potential to give rise to tin-containing macromolecular catalysts.

On the other hand, atom transfer radical polymerization (ATRP) facilitates the preparation of polymers with predetermined molecular weights and narrow molecular weight distributions from versatile monomers under mild reaction conditions.^{26,27} A great deal of well-defined metallo-polymers has been synthesized via ATRP including the side group metallo-polymers^{28,29} and metallo-supra-molecular block copolymers.³⁰ In most cases, the polymerization strategy involves metal-containing monomers or the ligation of species by metal-coordination. Some scientists use the initiator containing the transition metal complex to synthesize the metallo-polymers.^{31,32} Recently,

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we found that the organometallic, 1,3-dihalo-tetra-alkyl-distannoxane, can perform the ATRP of styrene in bulk as an initiator including the Sn-Cl bond.³³ But this ATRP can only be achieved successfully in low concentration solution. It is difficult for the synthesis of the polymer with low-molecular weight in this methodology.

In this article, we described a novel reverse ATRP initiated by azobisisobutyronitrile (AIBN) and 1,3-dihalo-tetra-*n*-butyl-distannoxanes (complex **A**). The reverse ATRP could be performed in a wide concentration range of the initiator system (1,3-dihalo-tetra-*n*-butyl-distannoxanes/AIBN). Using this strategy, a series of well-defined different chain lengths copolymers which contain the 1,3-dihalo-tetra-*n*-butyl-distannoxane unit in the main chain (PS-*b*-A-*b*-PS), was straightforwardly synthesized in a one-pot approach.

EXPERIMENTAL

Material

Styrene was purchased from Aldrich in Shanghai (99%), stirred with CaH₂ overnight at room temperature, and distilled before use. AIBN was purchased from Aldrich, purified by recrystallization from ethanol twice. Cupric chloride (CuCl₂), cuprous chloride (CuCl), acetic acid, *n*-butyl alcohol, and toluene were purchased from Acros in Beijing (99%), 4,4'-dinonyl-2,2'-bipyridine (dNbipy) from Nanjing Chemzham Pharmtech Co. (99%), and all used as received. 1,3-dichloro-tetra-*n*-butyl-distannoxane (complex **A**) was prepared as previously report.³⁴ All other commercial solvents were purified using standard procedures. All other commercial solvents were purchased from the sixth factor of Tianjin chemical reagent.

Instrumentation

NMR spectra were recorded on a Varian Mercury plus 400 (1H 400 Hz) spectrometer using CDCl₃ as solvent and tetramethylsilane as internal standard. Conversions were measured by ¹H-NMR of the raw products. Molecular weights were estimated by ¹H-NMR. Molecular weight distributions were measured using a Waters gel permeation chromatography (GPC) [Waters 1515 liquid chromatography connected with three Waters styragel GPC columns (HT2, HT3, HT4) and a Waters 2414 refractive index detector; with tetrahydrofuran (THF) as eluent; flow rate, 1 mL/min; temperature, 40°C]. Calibration was achieved with mono-dispersed polystyrenes as standards. The Sn contribution of the polymer was measured by Inductively Coupled Plasma Emission Spectrometer (ICP) [ICP-9000 (N + M), Therom Jarrell-Ash Corp].

Polymerization

A 50 mL Schlenk tube was charged with the appropriate copper compound/ligand [cuprous chloride (40 mg, 0.4 mmol), cupric chloride (260 mg, 2 mmol), and dNbipy (1480 mg, 3.6 mmol)], AIBN (160 mg, 1 mmol), and 1,3-dichloro-tetra-*n*-butyl-distannoxane (1106 mg, 1 mmol). The flask was sealed with a rubber stopper and cycled between vacuum and argon three times to remove oxygen. Styrene (10 mL, 87.3 mmol) was then added quickly with a syringe. Three "freeze-pump-thaw" cycles were performed to remove oxygen for the second time. Schlenk tube was then sealed in a vacuum line and immersed into a preheated, 110°C oil bath for given time in the Table I. At various time, 0.5 mL aliquots of the reaction mixture was tapped using a purged syringe and then diluted with CDCl₃ to determine the conversion by ¹H-NMR on the basis of comparison the ethenyl group of unreacted styrene with the two hydrogen atoms at *ortho*-position of phenyl group. The residue was diluted with THF, filtered through a small column of alumina, precipitated with methanol, filtered, washed, and then dried under vacuum for GPC determination.

Esterification catalyzed by the polymer

A test tube with a condenser pipe was charged with acetic acid (180 mg, 3 mmol), *n*-butyl alcohol (148 mg, 2 mmol), toluene (1 mL), and the organotin-containing polymer catalyst (*M_n* = 4000, 200 mg, 0.05 mmol). The test tube was placed in a preheated oil bath at 110°C and magnetically stirred. After the reaction was completed, the product was distilled under vacuum from the reaction mixture, and the remnant solid was dried under vacuum, washed with methanol (3 × 5 mL), and reused for a new catalytic run. The yield of the esterification reaction was determined by ¹H-NMR of the reaction solution at the end of the 48 h. By comparison of the peak integration area of methylene group connected to the ester group ($\delta = 4.1$ ppm) with that of the hydroxymethyl group ($\delta = 3.6$ ppm), we could obtained the yield of the esterification reaction.

RESULTS AND DISCUSSION

Due to the self-assembly property of 1,3-dichloro-tetra-*n*-butyl-distannoxane, the ATRP initiated by single complex **A** was unsuccessful in high initiator concentration (styrene : initiator = 87.3 : 1) in our previous report (Scheme 1).³³ As a continuation of our ongoing work, we try to improve the efficiency of the organometallic initiator by decomposing the self-assembly of complex **A**. In the normal ATRP

TABLE I
Bulk Polymerization Initiated by 1,3-dichloro-tetra-*n*-butyl-distannoxane/AIBN at 110°C

Entry	Time (h)	Conv. (%) ^a	<i>M_n</i> , cal (g/mol) ^b	<i>M_n</i> , NMR (g/mol) ^c	PDI (<i>M_w</i> / <i>M_n</i>) ^d
1 ^e	12	23	3204	3281	–
2 ^e	15	32	4012	3874	1.13
3 ^e	18	42	4957	4663	1.12
4 ^e	21	48	5474	5490	1.12
5 ^e	27	57	6320	6365	1.12
6 ^f	24	15	6410	6308	1.18
7 ^f	33	25	10,162	10,259	1.16
8 ^f	36	29	11,812	11,893	1.12
9 ^f	42	36	14,133	14,199	1.13
10 ^f	48	38	14,867	14,861	1.09
11 ^f	57	51	19,888	19,597	1.16
12 ^g	24	4	5039	5149	1.10
13 ^g	48	22	21,345	21,267	1.26
14 ^g	60	29	27,641	27,524	1.27
15 ^g	72	39	36,547	36,681	1.21
16 ^g	84	46	43,033	42,587	1.25

^a The conversions were determined by ¹H-NMR of the raw products.

^b $M_{n,cal} = [\text{Styrene}] \times 104.15 \times \text{Conv.}/[\text{initiator}] + 1106$ (MW of the initiator).

^c $M_{n,NMR}$ determined by ¹H-NMR.

^d PDI were obtained from GPC determination.

^e Bulk: [styrene]₀ = 8.73M; [CuCl₂]₀ = [CuCl]₀ × 5 = [dNbipy]₀/1.5 = 0.2M; [complex A]₀ = 0.1M.

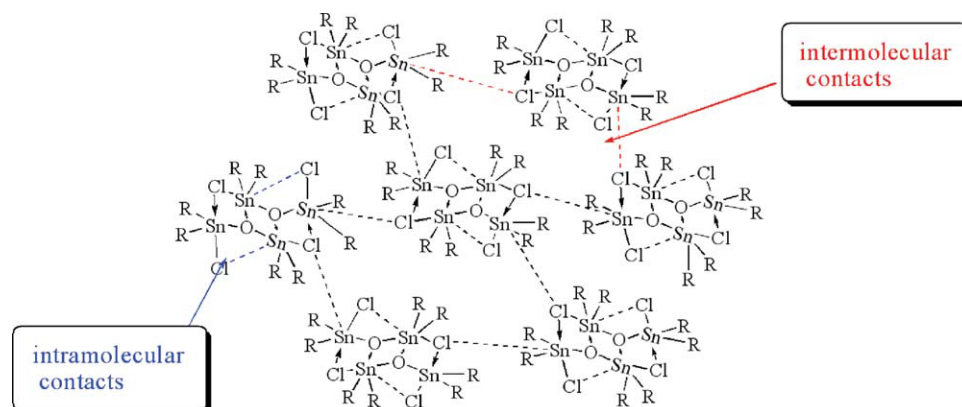
^f Bulk: [styrene]₀ = 8.73M; [CuCl₂]₀ = [CuCl]₀ × 5 = [dNbipy]₀/1.5 = 0.05M; [complex A]₀ = 0.025M.

^g Bulk: [styrene]₀ = 8.73M; [CuCl₂]₀ = [CuCl]₀ × 5 = [dNbipy]₀/1.5 = 0.02M; [complex A]₀ = 0.01M.

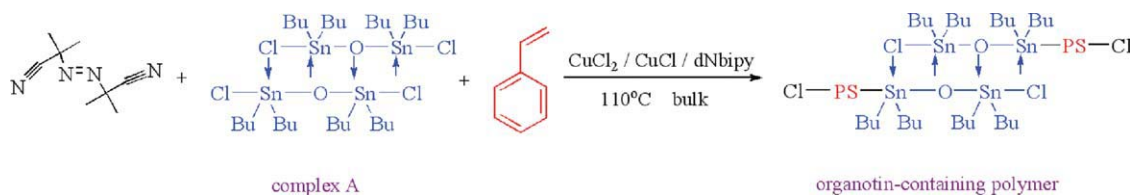
initiated by single complex **A**, the initiating tin radicals are generated from complex **A** in the presence of a transition metal in its lower oxidation state. In contrast, the radicals are generated initially from conventional radical initiators AIBN in the reverse ATRP. These radicals can subsequently destroy the self-assembly of complex **A** by radical transfer to Sn-Cl in complex **A**. Therefore, we explored this new strategy to perform the reverse ATRP initiated by 1,3-dichloro-tetra-*n*-butyl-distannoxane/AIBN for the synthesis of the organotin-containing macromolecules (Scheme 2). Herein, the polymerization was

performed at 110°C using a transition-metal compound at higher oxidation state, CuCl₂, coordinated with a suitable ligand, 4,4'-dinonyl-2,2'-bipyridine (dNbipy) as a catalyst ([styrene]₀ = 8.73M; [CuCl]₀ = 0.2M; [CuCl₂]₀ = 1.0M; [dNbipy]₀ = 0.3M; [complex A]₀ = 0.1M).

For comparison, the common reverse ATRP initiated by single AIBN was also performed. As shown in Table II, when the concentrations of single AIBN or 1,3-dichloro-tetra-*n*-butyl-distannoxane/AIBN were 0.1M, the monomer conversion was 92% after 16 h in the former single initiator but only 38% in



Scheme 1 intramolecular and the intermolecular contacts of 1,3-dichloro-tetra-*n*-butyl-distannoxane [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].



Scheme 2 The synthetic route of the organotin-containing polymer [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

the latter mixed initiator (Table II, Entries 1 and 2). This remarkable change indicated that the complex **A** played an important role in the polymerization process. The low monomer conversion of our strategy may be caused by the process of radical transfer from AIBN to complex **A** or the lower reactivity of the tin radical. Nevertheless, the polydispersity (M_w/M_n) of the organotin-containing polymer by using complex **A**/AIBN (0.1M) as the initiator was 1.06, which was as low as the polydispersity of the polymer initiated by single AIBN. This experimental result indicated that the polymerization process was still controllable after adding the complex **A** to the polymerization system. Moreover, it is worthwhile to note that the ATRP reaction could not proceed by using the single 1,3-dichloro-tetra-*n*-butyl-distannoxane as the initiator under the same concentration condition. However, by using 1,3-dichloro-tetra-*n*-butyl-distannoxane/AIBN as coinitiators in this novel reverse ATRP, we herein could successfully introduce the organometallic distannoxane into the main chain of polymer and further afford the functional, low-molecular weight, well-defined organometallic polymer.

Subsequently, the influence of different ratio of complex **A** to AIBN was also investigated. When the ratio of complex **A** to AIBN was decreased to 0.5, the monomer conversion was 69% after 16 h (Table II, Entry 3). However, the polydispersity (M_w/M_n) was increased significantly to 1.40. Further reducing the ratio of complex **A** to AIBN to 0.25, the monomer conversion was as high as 80% after 16 h but the polydispersity was 1.44 (Table II, Entry 4). These two high polydispersity index (PDI) maybe

attributed to the two different pathways in the polymerization: (1) only AIBN initiated reverse ATRP reaction; (2) complex **A**/AIBN initiated reverse ATRP reaction. In detail, when the ratio of complex **A** to AIBN was 1 : 1, all of the radicals generated from AIBN are completely transferred to complex **A**, which guarantees the unitary pathway in the complex **A**/AIBN initiated reverse ATRP reaction. In contrast, as for the ratio of complex **A** to AIBN in 0.5 or 0.25, the amount of the complex **A** was smaller than the AIBN, thus one part of radicals from AIBN was transferred to complex **A** to initiate the reverse ATRP, and the other part of radicals from AIBN directly initiated the reverse ATRP. Consequently, this polymerization proceeds via two paths which complicates the polymerization. As a result, the PDI was relatively high. When the ratio of complex **A** to AIBN was increased to 2.0, the monomer conversion was only 44% after 16 h with a high PDI of 1.33. The slight increasing of conversion maybe assigned to the increasing amount of complex **A**, which makes the radical transfer faster than in the case of the ratio of 1 : 1. The increase of PDI can result from the incompletely disruption of the self-assembled complex **A**. Moreover, 41% of complex **A** was recovered after polymerization, which confirms the complex **A** was indeed not fully disassembled and part of the organometallic initiator did not participate in the polymerization. In summary, the above experimental results indicated that complex **A** acted as an important component in the initiation step. This is because that the PDI of the polymer would always remain high no matter how the ratios change.

The introduction of the complex **A** into the polymer chain via our novel reverse ATRP was also

TABLE II
Bulk Polymerization Initiated by Different Ratio of 1,3-dichloro-tetra-*n*-butyl-distannoxane to AIBN or Single AIBN at 110°C for 16 h

Entry	AIBN	Complex A	CuCl ₂ ^a	Conv. (%) ^b	PDI (M_w/M_n) ^c
1	0.1	0	0.2	92	1.05
2	0.1	0.1	0.2	38	1.06
3	0.1	0.05	0.2	69	1.40
4	0.1	0.025	0.2	80	1.44
5	0.1	0.2	0.2	44	1.33

^a $[\text{CuCl}_2]_0 = [\text{CuCl}]_0 \times 5 = [\text{dNbipy}]_0/1.5 = 0.2M$.

^b The conversions were determined by ¹H-NMR of the raw products.

^c PDI were obtained from GPC determination.

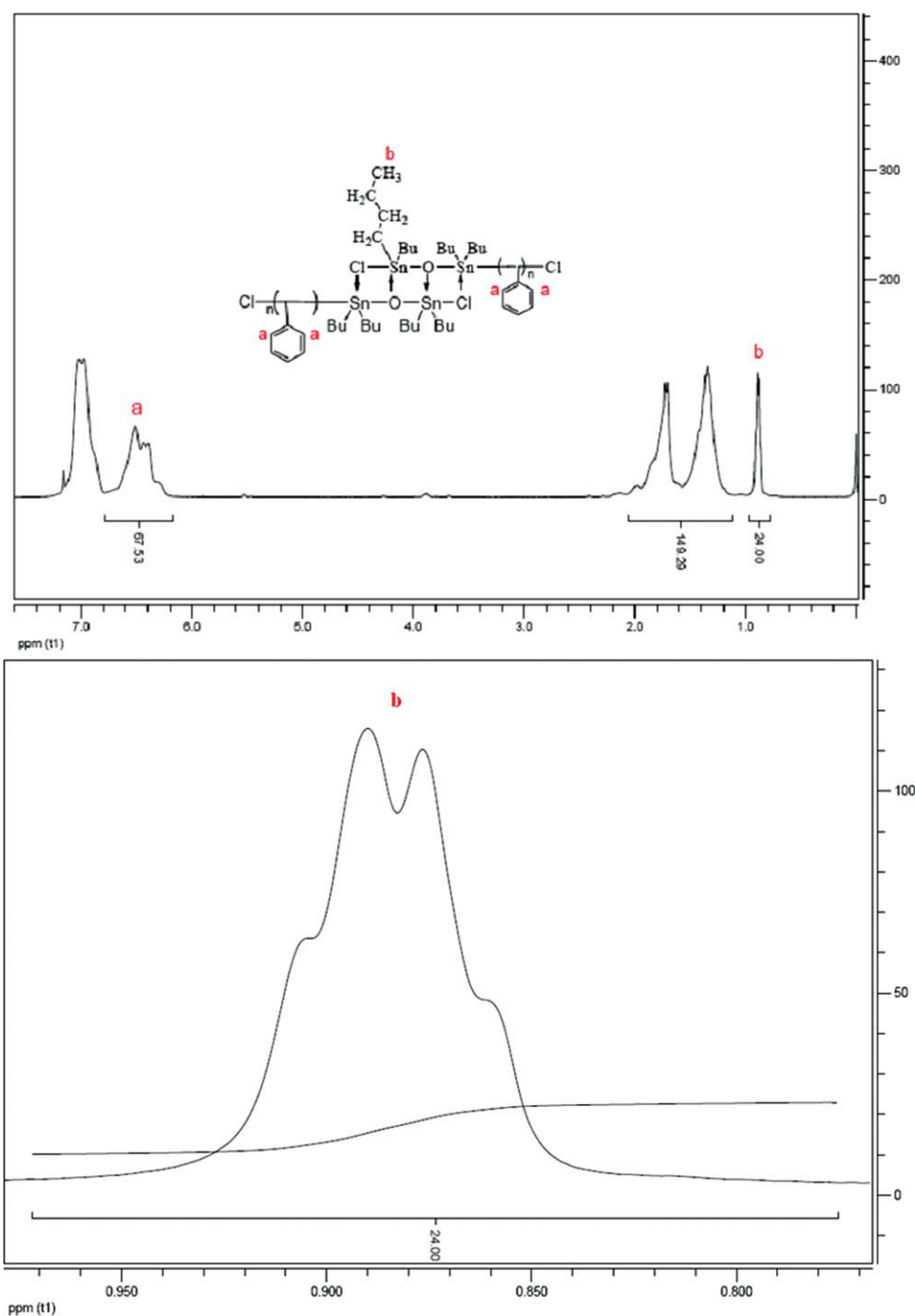


Figure 1 $^1\text{H-NMR}$ of organotin-containing polymer produced by using complex A/AIBN (0.1M : 0.1M) as the initiator at 110°C for 16 h [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

supported by NMR spectral data on the organotin core in the resulting products. Figure 1 presents the $^1\text{H-NMR}$ spectrum of organotin-containing polymer produced by using complex A/AIBN (0.1M : 0.1M) as the initiator at 110°C for 16 h. The peak marked **b** at ca. 0.8 ppm is assigned to the CH_3 in butyl group of the 1,3-dichloro-tetra-*n*-butyl-distannoxane moiety in the polymer. Moreover, comparison of the integration of the signals of group **b** with those of group **a** in the main chain of organotin-containing polymer

gives a molecular weight, $Mn, \text{NMR} \approx 4636$, close to the one calculated from conversion ($Mn, \text{cal} = [\text{Styrene}] \times 104.15 \times \text{Conv.}/[\text{initiator}] + 1106$ (molecular weight (MW) of the initiator)), $Mn, \text{cal} \approx 4560$. The $^{13}\text{C-NMR}$ clearly displays two different butyl group resonances (due to the formal Bu_2SnO (endo) and Bu_2SnCl (exo) tin moieties of the distannoxane unit) (Fig. 2). The ^{119}Sn NMR spectrum was also recorded, but unfortunately, it displays no any signal. The reason remained unclear currently.

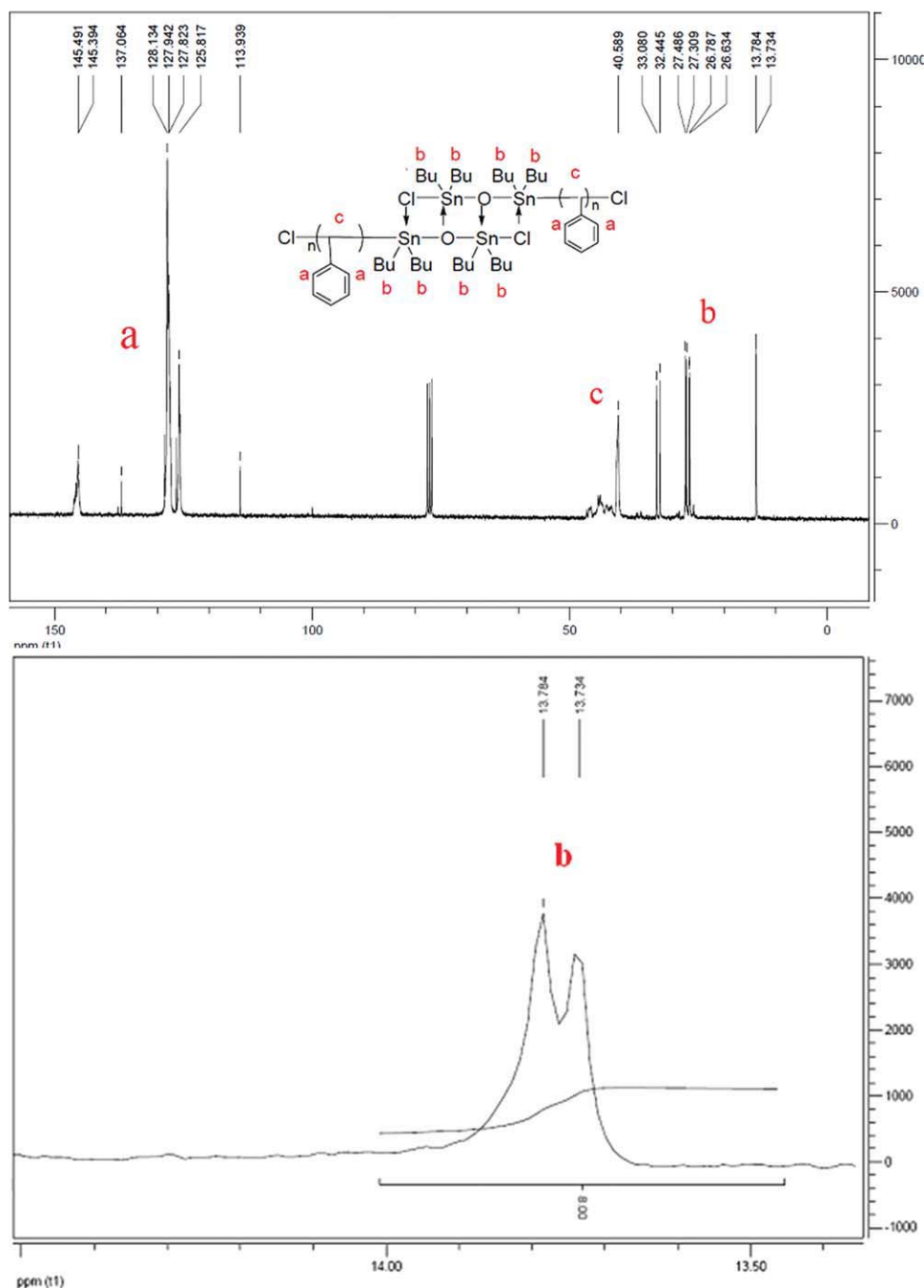


Figure 2 ^{13}C -NMR of organotin-containing polymer produced by using complex A/AIBN (0.1M : 0.1M) as the initiator at 110°C for 16 h [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com)].

Moreover, the ICP analysis was also measured to confirm the presence of the Sn element in the polymer. The polymer ($Mn, \text{cal} \approx 4560$) was determined to contain the mass percentage ca. 10.2% of tin, in agreement with the expected value of 10.4%. These two experimental results strongly support the involvement of the complex A initiated pathway in our novel reverse ATRP.

The semilogarithmic kinetic plot of $\ln([M]_0/[M])$ vs. time for the bulk reverse ATRP of styrene at 110°C was linear when the ratio of styrene/initiator

was 87.3/1, corresponding to a high initiator concentration (Table I, Entries 1–5, Fig. 3). Retardation was also observed. It can be attributed to the process of radical transfer from AIBN to complex A. The number-averaged molecular weights increased linearly with the monomer conversions and fit satisfactorily the expected molecular weights [Fig. 4(A)]. The PDI of about 1.12 for the polymers are lower than that of the single complex A initiating ones except for Entry 1 whose PDI is difficult to obtain because of the low molecular weights.³³

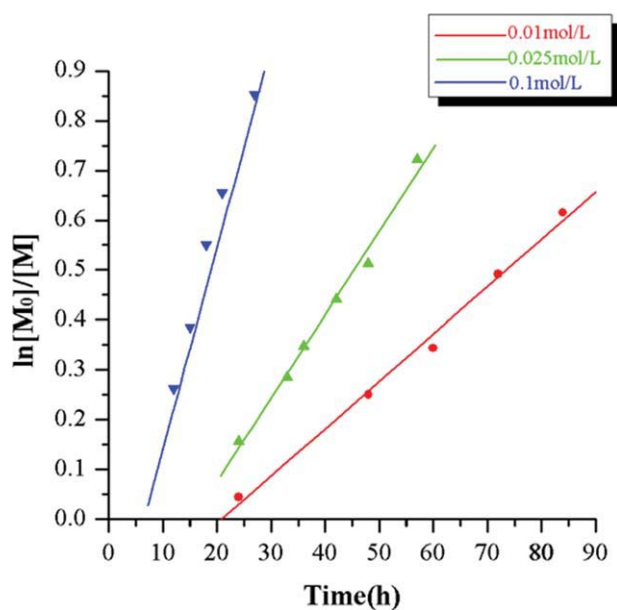


Figure 3 Semilogarithmic kinetic plots for the reverse ATRP of styrene initiated with complex A/AIBN at 110°C. Blue line: Bulk: $[\text{styrene}]_0 = 8.73\text{M}$; $[\text{CuCl}_2]_0 = [\text{CuCl}]_0 \times 5 = [\text{dNbipy}]_0/1.5 = 0.2\text{M}$; $[\text{complex A}]_0 = 0.1\text{M}$. Green line: Bulk: $[\text{styrene}]_0 = 8.73\text{M}$; $[\text{CuCl}_2]_0 = [\text{CuCl}]_0 \times 5 = [\text{dNbipy}]_0/1.5 = 0.05\text{M}$; $[\text{complex A}]_0 = 0.025\text{M}$. Red line: Bulk: $[\text{styrene}]_0 = 8.73\text{M}$; $[\text{CuCl}_2]_0 = [\text{CuCl}]_0 \times 5 = [\text{dNbipy}]_0/1.5 = 0.02\text{M}$; $[\text{complex A}]_0 = 0.01$ [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

It is worthwhile to note that no complex A was recovered after polymerization, which indicates that full amount of the organometallic initiator was involved in the polymerization.

When increasing the ratio of styrene/initiator to 349/1 and 873/1, a linear plot was obtained for $\ln([M]_0/[M])$ against time (Fig. 3). Retardation was also observed, and its duration increased on a decreasing concentration of the initiator. This is attributed to the decrease of the concentration of the radicals decelerated in the process of radical transfer from AIBN to complex A. The molecular weights are in good agreement with the expected values for both concentrations [Fig. 4(B,C)]. Moreover, the polydispersities, $M_w/M_n < 1.2$ for Entries 6–11 and $M_w/M_n < 1.3$ for Entries 12–16, were lower than that of the single complex A initiating ones in the same concentration, which indicated a better controllable process.

As a result, a series of polymers with well defined, different chain lengths which contain the organotin core in the main chain were straightforwardly obtained in a one-pot process through the novel 1,3-dichloro-tetra-*n*-butyl-distannoxane/AIBN initiating system in different concentrations by the reverse ATRP process.

We propose a mechanism for this novel reverse ATRP (Scheme 3). Initially, AIBN is cleaved at 110°C to generate the radical I·. The radical I· is stabilized by the highly oxidized transition-metal species (CuCl_2), like for a classical reverse ATRP. As shown in Step 3, the radical was transferred to the oligomer of complex A with concomitant abstraction of a Cl atom from the oligomer of complex A to form the radical B. It is proposed that the transfer process from radical I· to complex A is faster than that of radical I· transferring to the monomer. Thus, the radical I· should be prone to transfer to complex A rather than the monomer. In this step, the participation of radical I· would break the coordination at the level of the weakly bound Sn-Cl-Sn bridge between the clusters. The oligomer of complex A would thus be cleaved to the dimeric radical B. In Step 4, the highly oxidized transition-metal species, CuCl_2 , would subsequently donate the halogen atom Cl to the radical B with the formation of the reduced transition-metal species, CuCl, and the dormant species, complex A. This radical transfer process is believed to ensure that all of the complex A participates into the polymer chain build-up by the combination of 1,3-dichloro-tetra-*n*-butyl-distannoxane with AIBN which breaks the self-assembly of complex A and further enhances the reactivity of the Sn-Cl bond which would be determinant for the successful reverse ATRP. In the subsequent steps, the transition-metal species, CuCl, promotes the typical ATRP process. The molecular weights are consistent with the expected ATRP process and the low polydispersities are owed to this reverse ATRP process.

1,3-dichloro-tetra-*n*-butyl-distannoxane has been used extensively in the past as a catalyst for various functional group transformations such as esterification, acetalization, and deacetalization, etc.^{20–22} Considering that many organometallic catalysts have been incorporated into polymers to extend the application scope and to enhance the potential to recycle, we investigated the catalytic activity as well as the recycling potential of 1,3-dichloro-tetra-*n*-butyl-distannoxane incorporated in polystyrene as above described. Esterification was selected as a model reaction for this purpose. In view of their boiling point and solubility, acetic acid and *n*-butyl alcohol were chosen as substrates. The esterification was performed in toluene at 110°C in the presence of 2.5 mol % polymer catalyst ($M_n = 4000$). The yield of esterification could reach up to 99% in 48 h, which was as high as the yield of esterification using the precursor complex A. When decreasing the concentration of organotin-containing polymer catalyst to 0.25 mol %, the yield of esterification still remained 94% with the same reaction time. To assess the recycling potential of the macromolecular catalyst, a

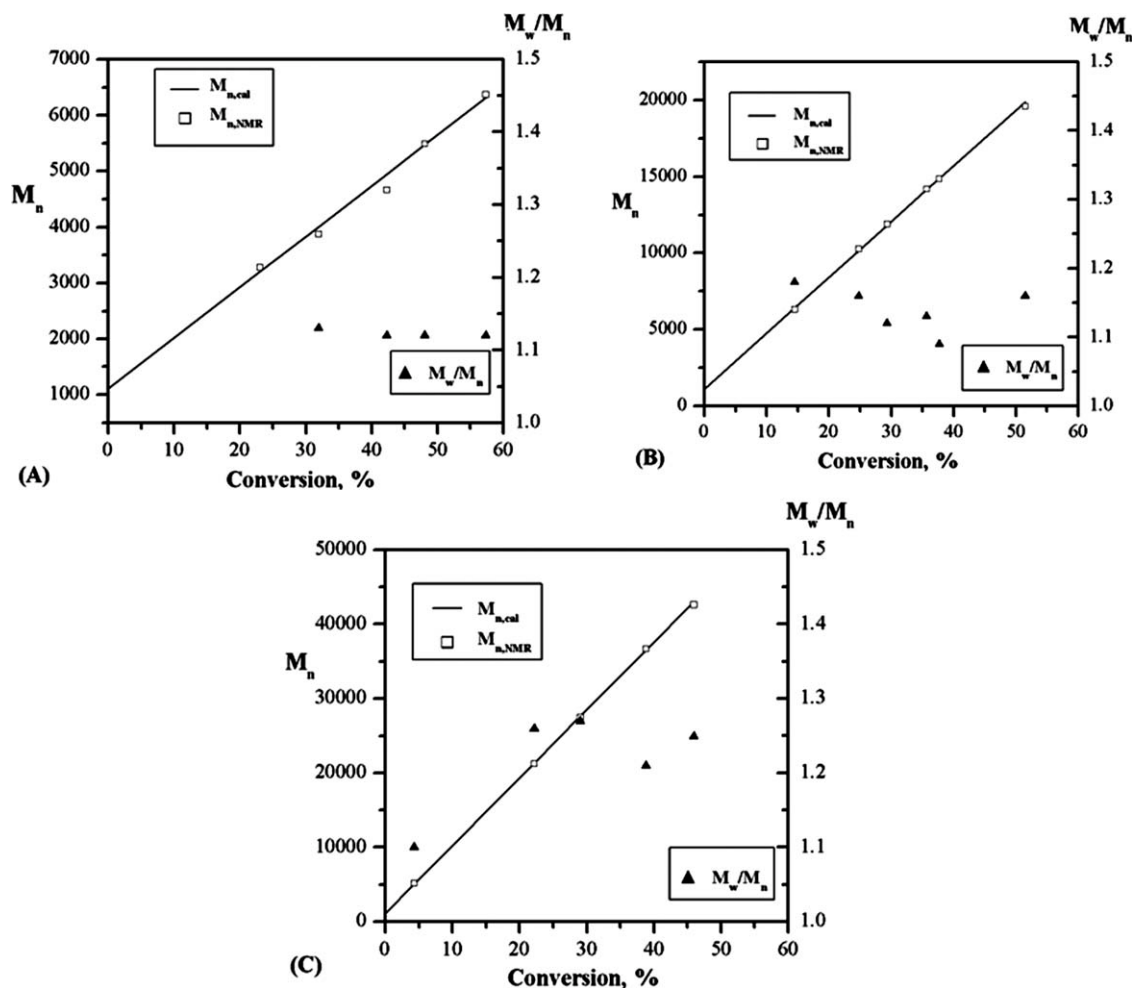


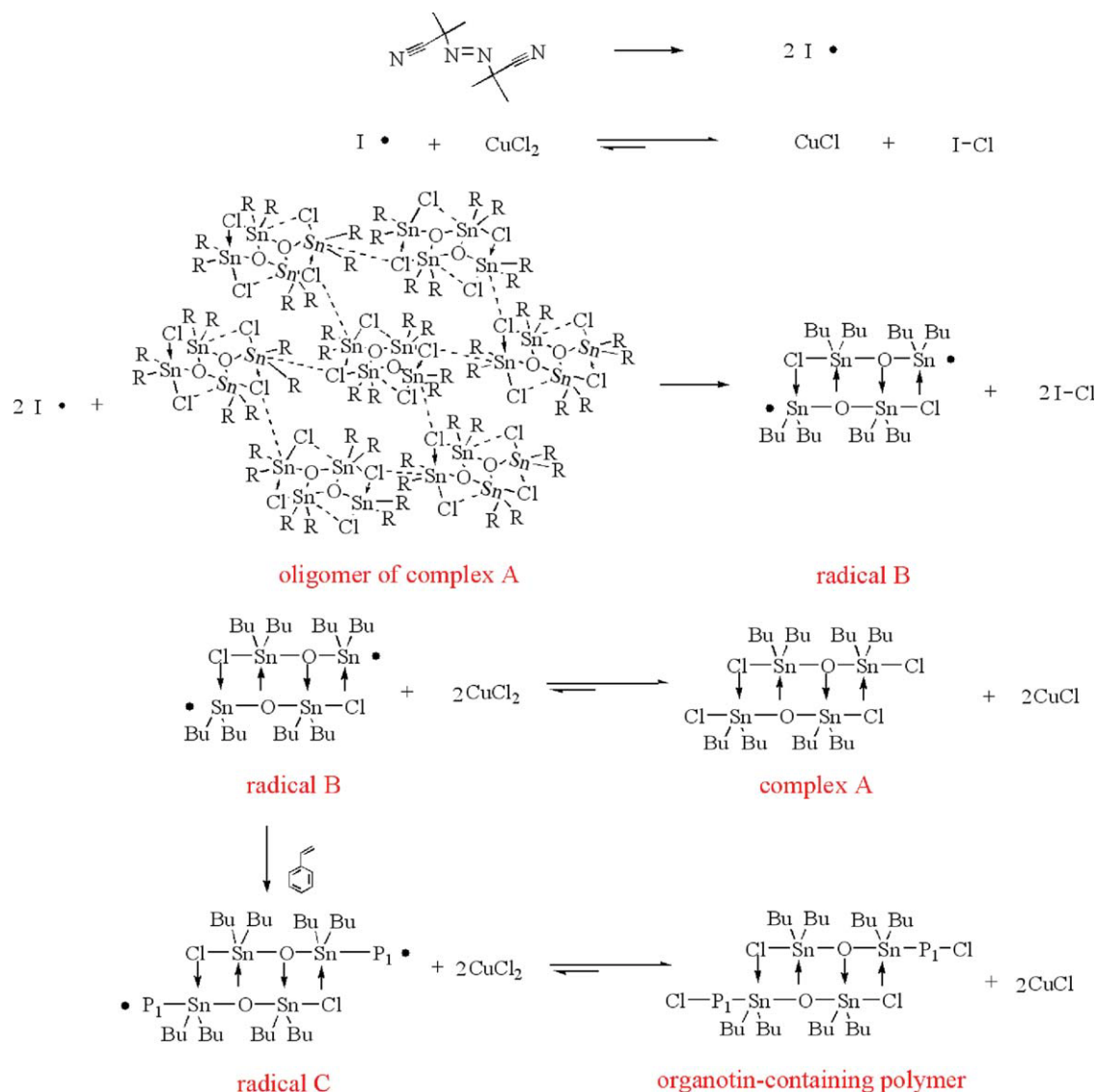
Figure 4 Evolution of molecular weight, M_n , and molecular weight distribution, M_w/M_n , with monomer conversion for the reverse ATRP of styrene initiated with complex A/AIBN at $110^\circ C$. (A) Bulk: $[styrene]_0 = 8.73M$; $[CuCl_2]_0 = [CuCl]_0 \times 5 = [dNbipy]_0/1.5 = 0.2M$; $[complex\ A]_0 = 0.1M$. (B) Bulk: $[styrene]_0 = 8.73M$; $[CuCl_2]_0 = [CuCl]_0 \times 5 = [dNbipy]_0/1.5 = 0.05M$; $[complex\ A]_0 = 0.025M$. (C) Bulk: $[styrene]_0 = 8.73M$; $[CuCl_2]_0 = [CuCl]_0 \times 5 = [dNbipy]_0/1.5 = 0.02M$; $[complex\ A]_0 = 0.01M$.

series of five consecutive runs were performed in toluene at $110^\circ C$. At the end of each reaction run of 48 h, the catalyst was dried under vacuum, washed with methanol, and reused in a new reaction run. As shown in Table III, the yield of butyl acetate remained unchanged even after four runs. Thus, it demonstrated that the polymer incorporating the 1,3-dichloro-tetra-*n*-butyl-distannoxane core in the main chain is an outstanding and recyclable catalyst for esterification, at least with a primary alcohol. Moreover, the characteristic of the organotin-containing polymer catalyst could be changed conveniently by altering the chain length or the species of the monomer.

CONCLUSIONS

A series of well-defined polymers with different chain lengths that contain 1,3-dichloro-tetra-*n*-butyl-distannoxane unit in the main chain were conven-

iently obtained in one-pot reaction using a novel reverse ATRP of the styrene initiated by 1,3-dichloro-tetra-*n*-butyl-distannoxane/AIBN in bulk in a wide range of concentrations of the initiator system. Using different ratios of complex A to AIBN enabled us to prove that complex A could not only act as an important part of the initiator system but also introduce the functional organotin compound into the polymer chain. The 1H -NMR, ^{13}C -NMR, and ICP analyses also evidenced that the 1,3-dichloro-tetra-*n*-butyl-distannoxane was completely incorporated to the polymer chain by this novel reverse ATRP. Moreover, the organotin-containing polymer could be used as catalyst for esterification, achieving conversions high up to 99% in 48 h. And the activity remained after four successive cycles. In view of the self-assembly property of 1,3-dichloro-tetra-*n*-butyl-distannoxane, we intend to prepare micelles or vesicles as micro-reactors which could be widely used in catalysis and biosynthesis.



Scheme 3 The mechanism of reverse ATRP initiated by 1,3-dichloro-tetra-*n*-butyl-distannoxane/AIBN [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

TABLE III

Recycling of the Organotin-Containing Polymer Catalyst in the Esterification of Acetic Acid and *n*-butyl alcohol in Toluene at 110°C^a

	organotin-containing polymer				
	Fresh	1st	2nd	3rd	4th
Yield (%) ^b	99	99	99	99	99

^a Reaction conditions: [acetic acid] = 3M; [*n*-butyl alcohol] = 2M; [organotin-containing polymer] = 0.05M; $M_n^{\text{organotin-containing polymer}} = 4000$.

^b Yield was determined by ¹H-NMR.

The synthesis of the water-soluble polymers such as poly4VP or poly(*N,N*-dimethylacrylamide) containing the 1,3-dichloro-tetra-*n*-butyl-distannoxane is presently in progress.

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