Macromolecular Research, Vol. 15, No. 1, pp 31-38 (2007)

Titanium Complexes: A Possible Catalyst for Controlled Radical Polymerization

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Received August 22, 2006; Revised November 14, 2006

Abstract: Pentamethylcyclopentadienyltitanium trichloride, bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2), and bis(pentamethylcyclopentadienyl)titanium dichloride were used in the polymerization of styrene without the aid of Group I-III cocatalysts. The properties of the resulting polymer indicated that polymerization was more controlled than in thermal polymerization. The kinetic studies indicated that a lower level of termination is present and that the polymer chain can be extended by adding an additional monomer. To elucidate the mechanism of polymerization, a series of experiments was performed. All results supported the involvement of a radical mechanism in the polymerization using Cp_2TiCl_2. The possibility of atom transfer radical polymerization (ATRP) mechanism was investigated by isolating the intermediate species. We could confirm the activation step from the reaction of 1-PECl with Cp_2TiCl by detecting the coupling product of the generated active radicals. However, the reversible deactivation reaction competes with other side reactions, and it detection was difficult with our model system.

Keywords: titanium complexes, catalyst, controlled radical polymerization, atom transfer radical polymerization.

Introduction

Titanium complexes have been widely used as catalysts for a range of polymerizations. In coordination polymerizations, cocatalysts such as Group I-III metal alkyl or hydride compounds are usually used with titanium complexes to reduce them to lower oxidation states and to generate the active Ti-alkyl cations. The Lewis acid character of titanium complexes also makes it possible for them to act as cationic initiators. On the other hand, the use of titanium compounds in radical polymerization is relatively rare.[1-3] In recent years, a large number of transition metal complexes have been used as catalysts for free radical polymerization, either as conventional redox initiators or in atom transfer radical polymerization (ATRP). Most of the metals are middle or late transition metals, including Cu,[4-8] Ru,[9-11] Fe,[12-16] Ni,[17-19] Pd,[20] Co,[21] Rh,[22,23] Re,[24,25] and Mo.[26] Especially in ATRP, there have been very few reports of using early transition metal complexes. Early transition metal complexes show high catalytic activities in many organic reactions and polymerizations, but they have limitations when used with polar functional groups in some applications. This is due to their highly oxophilic nature, which leads to deactivation by coordination with hard Lewis bases like oxygen. However, the cyclovoltametric analysis revealed that the Ti(III)/Ti(IV) pair has a very low half-wave potential.[27] Therefore, this redox pair should be capable of modulating the equilibrium in an atom transfer reaction, and hence, can be a candidate as a very active catalyst system for ATRP. In this study, we used various titanium complexes in the polymerization of styrene and MMA without Group I-III compounds. Polymerizations with various conditions were performed to elucidate the mechanism of polymerization.

Experimental

Materials and Characterizations. NMR spectra were measured in $CDCl_3$ or toluene-d_8 on GE 300 spectrometer, operating at 300 MHz. Elemental analyses were performed by the Atlantic Microlab Inc. Gas chromatography (GC) was performed on either a HP 5890 equipped with MS detector, or a HP 6890 with a FID detector, using non-polar HP-5 or medium polar HP-INNOWAX capillary column for the separation. Gel permeation chromatography/light scattering

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(GPC/LS) were performed using Hewlett-Packard (HP) 1050 series liquid chromatography pump equipped with a Wyatt Dawn DSP-F laser photometer and a Wyatt/Optilab interferometer using tetrahydrofuran (THF) as the mobile phase. Separation was effected by a multiple series of Polymer laboratory Mixed C columns at a flow rate of 1 mL/min at 25 °C.

Materials including bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2), pentamethyl-cyclopentadienyltitanium trichloride (Cp^*TiCl_3), bis(pentamethylcyclopentadienyl)-titanium dichloride ($Cp^*_2TiCl_2$), titanium trichloride ($TiCl_3$), titanium tetrachloride ($TiCl_4$), copper(II) bromide ($CuBr_2$), pentamethyldiethylene-triamine (PMDETA), bis(cyclopentadienyl)magnesium (Cp_2Mg), zinc metal, TEMPO, galvinoxyl, and 1-octanethiol were obtained from commercial suppliers and used without further purification. Styrene, ethyl vinyl ether and methyl methacrylate (MMA) were dried over CaH_2 overnight, and distilled twice under reduced pressure from CaH_2 prior to use. Benzoyl peroxide (BPO) was purified by dissolving in $CHCl_3$ at room temperature and adding an equal amount of methanol. α,α'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallizing from acetone. 1-Phenylethyl chloride (1-PECl)[28] and 1-(2,2,6,6-tetramethylpiperidinyloxy)-1-phenylethane (1-PE-TEMPO)[29] were prepared following literature procedures with a few modifications. Toluene and THF were dry and oxygen-free using a process described by Pangborn, *et al.*[30]

Synthesis of Bis(cyclopentadienyl)titanium Chloride (Cp_2TiCl). A mixture of 2 g of $TiCl_3$ and 2 g of Cp_2Mg in 5 mL of THF was prepared in 25 mL of Schlenk flask equipped with reflux condenser and 3-way stopcock in drybox. The flask was taken out of the drybox, and attached to a vacuum line. With a slow and continuous flow of argon, the flask was heated to reflux for 1.5 h. After reaction, THF was removed by applying vacuum, and the remaining solid was purified by sublimation. The first collection of dark red oil was discarded. The solid sublimed at 170 °C was collected, and characterized by elemental analysis as a Cp_2TiCl. (Calc'd for ($C_{10}H_{10}TiCl$): C, 56.25; H, 4.72; Cl, 16.60. Found: C, 56.27; H, 4.65; Cl, 16.72.

General Methods of Polymerization. In a drybox, all polymerization components including monomer, initiator, metal catalyst, additives, and solvent were added to a 5 mL tube having a stirring bar. The reaction tube was taken out of the drybox, degassed three times using freeze-thaw method, and sealed under vacuum. The sealed tube was immersed in an oil bath thermostated at desired temperature, and polymerization proceeded with continuous stirring. After reaction, the seal was broken, and THF or methylene chloride was added to dissolve or dilute the polymerization mixture. Conversion was checked either by gravimetry after precipitating polymeric product from methanol following by drying overnight under vacuum, or by directly injecting this solution to GC and determining the remaining monomer content compared with the internal standard. For other characterization such as GPC and NMR, the polymer was purified as metal-free either/both by repeated dissolving in THF-precipitating from methanol, or/and by passing short column of active alumina column.

Isolation of Activation Steps in ATRP. In a drybox, a solution of 5.5 mg of Cp_2TiCl (2.5×10^{-5} mol), 7.3 mg of 1-PECl (5×10^{-5} mol), and 0.6 mL of toluene-d_8 was prepared at room temperature. On adding 1-PECl, the green color of the Cp_2TiCl solution was immediately changed to red, and after few minutes, red solid precipitated out. The solution was added to NMR tube having airtight valve. The tube was taken out of the box, and ^{1}H-NMR spectrum of the solution was taken. The NMR tube was then put in an oil bath at 130 °C. After certain interval, ^{1}H-NMR spectrum of the solution was taken to follow the reaction.

Isolation of Deactivation Steps in ATRP. In a drybox, a solution of 6.2 mg of Cp_2TiCl_2 (2.5×10^{-5} mol), 6.5 mg of 1-PE-TEMPO (2.5×10^{-5} mol), and 0.6 mL of toluene-d_8 was prepared at room temperature. The solution was added to NMR tube having airtight valve. The tube was taken out of the box, and ^{1}H-NMR spectrum of the solution was taken. The NMR tube was then put in an oil bath at 130 °C. After certain interval, ^{1}H-NMR spectrum of the solution was taken to follow the reaction.

Results and Discussion

Controlled Polymerization of Styrene Using Titanium (IV) Complexes. Styrene was polymerized in the presence of bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2) and pentamethylcyclopentadienyltitanium trichloride (Cp^*TiCl_3) with 1-phenylethyl chloride (1-PECl) at 130 °C (Table I). With all the components, prepared polystyrene possesses controlled molecular weight and narrow molecular weight distribution (Run 1). The absence of 1-PECl (Run 2) or the titanium complex (Run 3), results in a large increase in the molecular weight and the molecular weight distribution became broader. In comparison with a normal radical polymerization using benzoyl peroxide (BPO) as a radical initiator (Run 4), or the thermal polymerization of styrene (Run 5), the rate of polymerization was slower, but molecular weight of the resulting polystyrene was low, and molecular weight distribution was narrow.

To investigate the characteristics of the polymerization in detail, we performed kinetic studies of the styrene polymerization using several different titanium(IV) complexes. Three commercially available titanium complexes were used, Cp_2TiCl_2, Cp^*TiCl_3, and bis(pentamethylcyclopentadienyl) titanium dichloride ($Cp^*_2TiCl_2$). Figure 1 shows the first order kinetic plots of monomer conversion as a function of time for the polymerization of styrene. After an initial nonlinear increase in conversion, the plot shows a linear relationship between $\ln([M]_0/[M])$ and polymerization time for all three titanium complexes, indicating approximately constant num-

Table I. Polymerization of Styrene Under Various Conditions at 130 °C

Run[a]		Time (h)	Conversion (%)	M_n	PDI
1	Cp_2TiCl_2/1-PECl/Styrene	2	17	6,300	1.57
2	Cp_2TiCl_2/Styrene	2	25	89,300	1.72
3	1-PECl/Styrene	2	16	133,300	1.78
4	BPO/Styrene	1.5	high	46,100	1.87
5	Styrene	7.5	high	263,000	1.66

[a] Polymerization conditions; $[styrene]_0$=8.7 M (bulk); $[styrene]_0/[1\text{-}PECl]_0$=100; $[styrene]_0/[Cp_2TiCl_2]_0$=100; $[styrene]_0/[BPO]_0$=200.

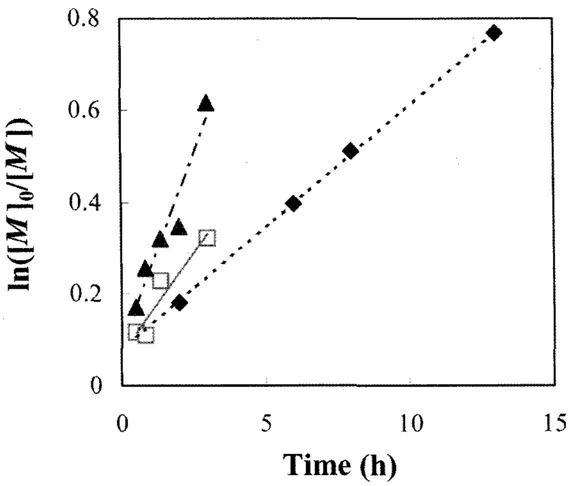


Figure 1. Kinetic of the polymerization of styrene using various titanium complexes at 130 °C, (a) Cp_2TiCl_2 (◆, ---); (b) Cp^*TiCl_3 (□ , —); (c) $Cp^*_2TiCl_2$ (▲, - · -). See Table I for conditions.

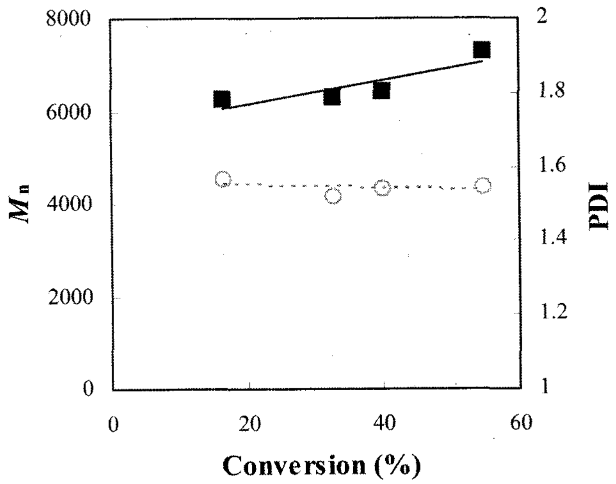


Figure 2. Plots of number average molecular weight (M_n, ■, —) and polydispersity index (PDI, o, ---) of the polymer and monomer conversion for the polymerization of styrene using Cp_2TiCl_2/1-PECl at 130 °C. See Table I for conditions.

ber of active species during the reaction. Number average molecular weight (M_n) and polydispersity index (PDI) of the resulting polymers were lower than those of polymers prepared thermally, indicating that polymerizations were under a higher degree of control (Figure 2). However, molecular weight of the product polymer remains almost constant throughout all conversion range after an increase at the initial stage of polymerization.

To check the living characteristic of our system, chain extension reactions were performed. Polystyrene was prepared with 1-PECl and Cp_2TiCl_2 in bulk at 130 °C. The isolated and purified polystyrene (M_n=6,300; PDI=1.57) was dissolved in additional styrene monomer containing Cp_2TiCl_2, and heated to 130 °C for 20 h. Figure 3 is the gel permeation chromatogram (GPC) of the resulting polymer. It shows that molecular weight distribution of the product polymer was unimodal and the molecular weight shifts to the higher molecular weight region (M_n=53,300; PDI=1.75). This indicates that most of initial polymer was reactivated and available to react with more monomer.

Effects of the Radical Inhibitors. To check the mechanism of the polymerization, sets of control experiments were performed. First, we used radical inhibitors such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) or galvinoxyl (2,6-di-*t*-butyl-α-(3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-

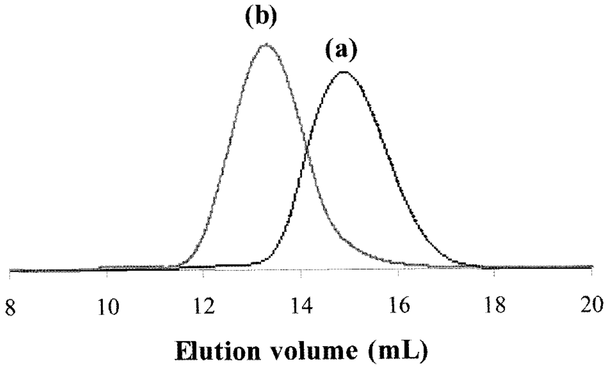


Figure 3. Gel permeation chromatogram traces of (a) initial polystyrene before the chain extension reaction; (b) final polystyrene after the reaction using Cp_2TiCl_2. Conditions; $[styrene]_0$=8.7 M; $[styrene]_0$/[initial polystyrene chain]$_0$=100; $[Cp_2TiCl_2]_0$/[initial polystyrene chain]$_0$=1.

p-tolyl-oxy). Table II shows the effects of the radical inhibitor on the polymerization. When TEMPO was used, the reaction rate was decreased, but the polymerization was not completely inhibited. Even though TEMPO is usually a very good inhibitor for radical polymerizations, the C-O bond between terminated polymer chain and TEMPO unit can be cleaved homolytically to regenerate radical species at the high temperature of 130 °C. When galvinoxyl was used as radical inhibitor, the polymerizations were completely inhibited, and no polymer was formed even after 100 h at 100 °C. As a comparison, we also used the common cationic initiators, $TiCl_3$ and $TiCl_4$. As expected, polymers were still formed in the presence of galvinoxyl, although the polymerization rates were decreased. These results also support a radical mechanism for the polymerization using Cp_2TiCl_2 and Cp^*TiCl_3.

Effects of the Radical Chain Transfer Agents. One of the experimental setups to discriminate the coordination mechanism from the radical one is using radical chain transfer agents. We used 1-octanethiol for this purpose. Table III shows the results when 20 equivalent 1-octanethiol was used in the polymerization of styrene. When Cp_2TiCl_2 was used in the polymerization along with the chain transfer agent, the molecular weight of the product polystyrene decreased along with increasing value of the PDI. These results support the view that there is an active radical chain transfer reaction in the polymerization.

Copolymerization of Styrene and Ethyl Vinyl Ether. Styrene and ethyl vinyl ether have quite different reactivities in radical and cationic polymerizations due to the electronic character of the vinyl substituents, even though both monomers can be polymerized to varying degrees by both polymerization mechanisms. In radical polymerization, the reactivity ratios of these two monomers in copolymerization are $r_{styrene}=90$ and $r_{ethyl\ vinyl\ ether}=0$, whereas the reactivity of ethyl vinyl ether in cationic polymerizations is higher than that of styrene. The copolymerization results are shown in Table IV. The copolymer prepared using Cp^*TiCl_3 had a styrene content of 33%, which was close to the values for the cases of cationic initiators, such as $TiCl_3$ and $TiCl_4$. On the other hand, when Cp_2TiCl_2 was used, the styrene content in copolymer was as high as 83%. These results also support presence of the radical intermediates for the polymerization using Cp_2TiCl_2.

Polymerization of Methyl Methacrylate. We tried to polymerize MMA using titanium complexes to rule out the cationic mechanism (Table V). The polymerization of MMA using titanium complexes proceeded in high yields. Moreover, the rate of polymerization was faster than that of the styrene polymerizations. Compared with the polymerization using conventional radical initiators, the rate was slower and the molecular weight of resulting polymer was very high. However, molecular weight distribution of product polymer was narrower. The microstructure of polymer was examined by ^{1}H-NMR. The fraction of triads was calculated by the

Table II. Effect of Radical Inhibitor on the Polymerization of Styrene Using Titanium Complexes[a]

Ti Complex	Radical Inhibitor	Temp (°C)	Time (h)	Conversion (%)	M_n	PDI
Cp_2TiCl_2	none	130	25	85	10,400	1.31
	TEMPO	130	100	62	3,140	1.34
	galvinoxyl	100	100	no polymer		
Cp^*TiCl_3	none	130	15	64	6,510	1.35
	TEMPO	130	100	48	2,180	1.36
	galvinoxyl	100	100	no polymer		
$TiCl_3$	none	130	2	58	2,130	1.57
	TEMPO	130	100	64	3,080	1.46
	galvinoxyl	100	20	62	3,650	2.05
$TiCl_4$	none	25	10 min	83	5,430	1.51
	galvinoxyl	130	20	36	3,320	3.71

[a]Polymerization conditions; $[styrene]_0=8.7$ M (bulk); $[styrene]_0/[1\text{-PECl}]/[Ti\ complex]_0=100/1/1$; $[radical\ inhibitor]_0/[Ti\ complex]_0=5$.

Table III. Effect of Radical Chain Transfer Agent (1-Octanethiol) on the Polymerization of Styrene Using Titanium Complexes at 130 °C[a]

Ti Complex	1-Octanethiol	Time	Conversion (%)	M_n	PDI
Cp_2TiCl_2	without	24 h	60	10,300	1.67
	with	24 h	30	2,330	2.70

[a]Polymerization conditions; $[styrene]_0=8.7$ M (bulk); $[styrene]_0/[1\text{-PECl}]/[Ti\ complex]_0=100/1/1$; $[1\text{-octanethiol}]_0/[Ti\ complex]_0=20$.

Table IV. Copolymerization of Styrene and Ethyl Vinyl Ether Using Various Titanium Complexes at 100 °C[a]

Ti Complex	Time (h)	Conversion (%)	M_n	PDI	Styrene Content in Copolymer (%)
Cp_2TiCl_2	100	16	7,760	1.704	83
Cp^*TiCl_3	100	8	73,950	3.072 (multiple peak)	33
$TiCl_3$	3	75	22,220	1.639 (multiple peak)	12
$TiCl_4$	100	> 95	6,830	1.581 (multiple peak)	28

[a]Polymerization conditions; $[\text{styrene}]_0=4.3$ M; $[\text{ethyl vinyl ether}]_0=4.3$ M; $[\text{monomers}]_0/[\text{1-PECl}]_0/[\text{Ti complex}]_0=100$.

Table V. Polymerization of Methyl Methacrylate (MMA) Using Titanium Complexes at 100 °C[a]

Initiating System	Time (h)	Conversion (%)	M_n	PDI
Cp_2TiCl_2/1-PECl	3	34	197,500	1.667
Cp^*TiCl_3/1-PECl	1.5	93	309,600	1.874
Cp_2TiCl_2/BPO	1	46	40,480	3.136
Cp^*TiCl_3/BPO	1	47	66,650	2.319
BPO	1	71	277,400	2.886

[a]Polymerization conditions; $[\text{MMA}]_0=9.3$ M (bulk); $[\text{MMA}]_0/[\text{1-PECl}]_0/[\text{Ti complex}]_0=100/1/1$; $[\text{MMA}]_0/[\text{1-BPO}]_0/[\text{Ti complex}]_0=100/0.5/1$.

Table VI. Polymerization of Styrene Using $Cp_2Ti^{III}Cl$ and 1-PECl at Various Temperatures

Run[a]	Temp. (°C)	Time (h)	Conversion (%)	M_n	PDI
1	30	24	90	136,080	2.09
2	70	12	21	31,010	1.73
3	90	12	69	39,360	1.82
4	110	12	80	25,760	1.82
5	130	12	86	24,950	1.72

[a]Polymerization conditions; $[\text{styrene}]_0=4.4$ M (50%, v/v, in toluene); $[\text{styrene}]_0/[\text{1-PECl}]_0/[Cp_2TiCl]_0/[\text{decane}]_0=100/1/1/10$.

integration of 0.7-1.3 ppm regions for α-methyl resonance. The stereoregularity of PMMA formed using titanium complexes was very similar to that of polymers prepared by conventional radical methods. These data all indicate that the polymerization proceeded by a radical mechanism.

Polymerization of Styrene Using Titanium(III) Complex. The previous results gathered from the various polymerization runs to verify the mechanism, all support the radical pathway for the polymerization using Cp_2TiCl_2. Because of their low costs and ubiquitous use in commercial polymerization processes, our goal is to use early transition metal complexes, such as titanium complexes, as ATRP catalysts. Especially interesting is the Ti(III)/Ti(IV) redox pair, which has a very low half-wave potential and could be a candidate for a very active ATRP catalyst. In our previous experiments, we used higher-oxidation state Ti(IV) complex and 1-PECl as starting materials. In this paradigm, the initial radicals should be generated from the auto-initiation reaction of monomers, which is one of the reasons for slow polymerization. To test the activity of titanium complexes as ATRP catalyst under more conventional conditions, we used lower-oxidation state $Cp_2Ti^{III}Cl$ and 1-PECl as an initiation system.

The polymerization of styrene was performed with this Cp_2TiCl and 1-PECl in toluene. The polymerization mixture was prepared in drybox at room temperature. To a heterogeneous solution of Cp_2TiCl in styrene and toluene, was added 1-PECl. The color of the solution changed from green to red immediately upon addition of the 1-PECl. This indicates that the green colored Cp_2TiCl reacts very fast with 1-PECl to generate the red-colored Cp_2TiCl_2. After removal from the drybox, the reaction tube was immersed in oil bath thermostated at the desired temperature. Table VI shows the results of polymerization of styrene at various temperatures. In general, as the temperature increases, the rate of polymerization increases and molecular weight of product polymer decreases. It is thought that these results are related to the thermal initiation reaction of the styrene monomer, i.e., as the temperature increases, more radicals are generated by the thermal Diels-Alder reaction of styrene. The increased concentration of radical then increases the rate of polymerization, and decreases the molecular weight of the product polystyrene.

We also performed kinetic studies of polymerization at 90 °C. The first order kinetic plot of monomer concentration is linear after an initial fast stage of polymerization, which is similar to the case of polymerization using Cp_2TiCl_2 (Figure 4). The molecular weight of the product polymer as a function of conversion is also similar to that for the polymerization using Cp_2TiCl_2, and shows a gradual increase after a big increase in the low conversion region (Figure 5). However, molecular weight of the product polymer was higher than that of polymer prepared using Cp_2TiCl_2. If the polymerization follows the ATRP mechanism, radicals would be generated by chlorine transfer reaction between 1-PECl and Cp_2TiCl at room temperature, which is evidenced by the color change. Therefore, the large portion of 1-phenylethyl

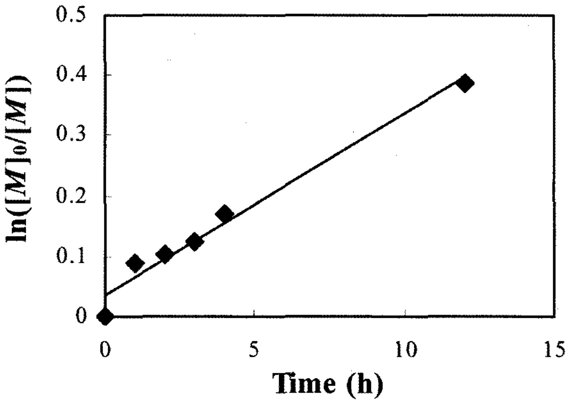


Figure 4. Kinetic plots of $\ln([M]_0/[M])$ vs. time for the bulk polymerization of styrene using Cp_2TiCl at 90 °C. See Table VI for conditions.

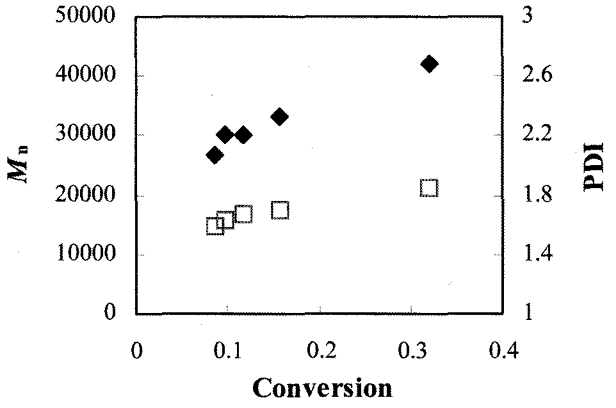
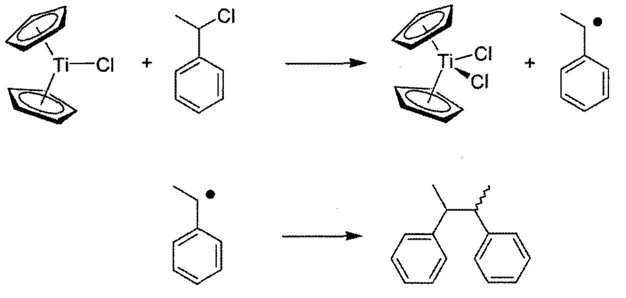


Figure 5. Plots of number average molecular weight (M_n, ◆) and polydispersity index (PDI, ☐) of the polymer and monomer conversion for the polymerization of styrene using Cp_2TiCl at 90 °C. See Table VI for conditions.

radicals could be consumed before reaching the reaction temperature by propagation and/or termination reactions. In this case, the real components participating in the polymerization at reaction temperature would be Cp_2TiCl_2 and a reduced amount of 1-PECl. As we have seen in Table I, 1-PECl has an effect of decreasing molecular weight of product polymer. Hence, in this experiment, reduced concentration of 1-PECl could increase the molecular weight of polystyrene.

Checking Atom Transfer Reactions. From the kinetic studies using Cp_2TiCl and 1-PECl, we could not confirm that the polymerization follow an ATRP pathway. Next, we tried to isolate intermediate species from each step to see if the polymerization using Cp_2TiCl proceeds by ATRP mechanism. Scheme I depicts the strategy of isolating activated products from the suspected ATRP reaction. If atom transfer reaction takes place, chlorine atom would transfer from 1-PECl to Cp_2TiCl to generate Cp_2TiCl_2 and 1-phenylethyl radicals. These radicals would react each other to form 2,3-diphenylbutane. Figure 6 shows the ^{1}H-NMR spectrum of the product of the reaction. It is found that new peaks appear at chemical shift of 2.6-2.8 and 0.9-1.2 ppm corresponding methyne and methyl proton of 2,3-diphenylbutane, respectively. This ^{1}H-NMR result and color change support the hypothesis that activation step in the atom transfer reaction is present in the polymerization of styrene using Cp_2TiCl_2.

The isolation of products from the deactivation step of the atom transfer reaction was carried out using the trapping reactions. The 1-phenylethyl-TEMPO adduct (1-PE-TEMPO) was mixed with Cp_2TiCl_2 in toluene-d_8, and heated at 130 °C. At high temperature, 1-PE-TEMPO cleaves homolytically to generate TEMPO and the 1-phenylethyl radical. If atom transfer reaction takes place, chlorine atom would transfer from Cp_2TiCl_2 to 1-phenylethyl radical to generate Cp_2TiCl and 1-PECl (Scheme II). Figure 7 shows the ^{1}H-NMR spectrum of the reaction mixture, which reveals unexpected results. Instead of the expected peaks for 1-PECl, new peaks for styrene appear at 5.2, 5.8, and 6.8 ppm. We believe the potential pathways for the formation of styrene as follows. It has been reported that the 1-PE-TEMPO spontaneously thermally decomposes to styrene and TEMPO by a *β*-hydro-



Scheme I. Isolation of the activation reaction.

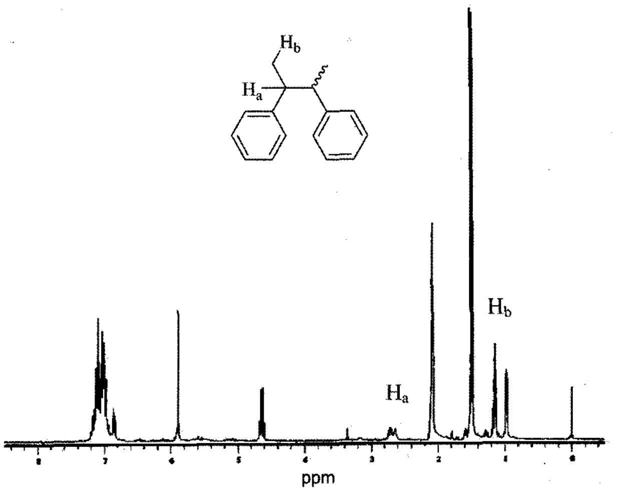
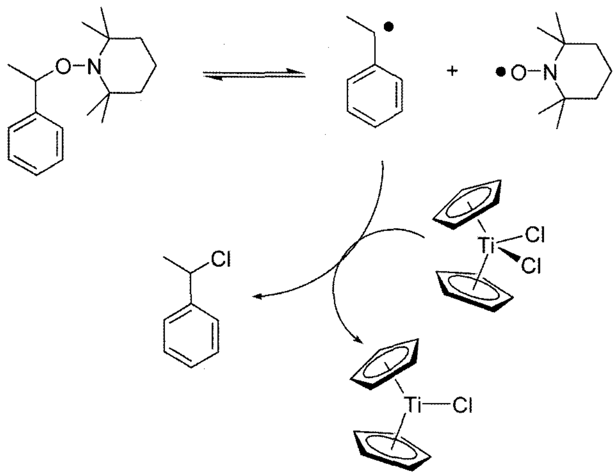


Figure 6. ^{1}H-NMR spectrum of Cp_2TiCl and 1-phenylethyl chloride in toluene-d_8.



Scheme II. Isolation of the deactivation reaction.

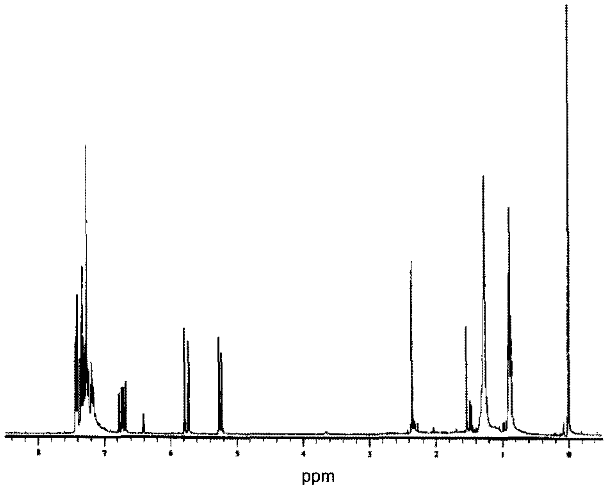
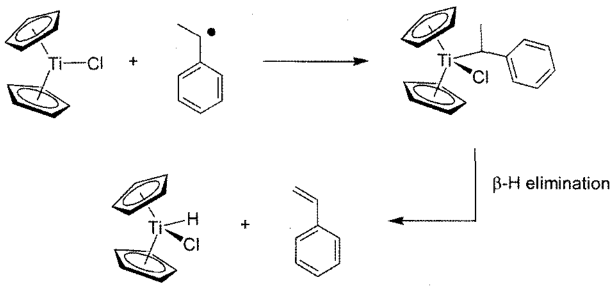


Figure 7. ^{1}H-NMR spectrum after reaction between 1-phenylethyl-TEMPO adduct and Cp_2TiCl_2 at 130 °C in toluene-d_8.

gen transfer.[31] The 1-phenylethyl radical or 1-PECl also can decompose to styrene by the chain end degradation reactions that were described as side reactions of ATRP.[32] Scheme III depicts another potential reaction for the formation of styrene. The 1-phenylethyl radical and the paramagnetic Cp_2TiCl complex can combine to form Ti-alkyl complexes, and this Ti-alkyl complex then undergoes *β*-hydrogen elimination reaction to generate styrene and the titanium hydride complex.

Conclusions

We used various titanium complexes in the polymerization of styrene. The properties of resulting polymer indicate that polymerization was more controlled compared with thermal polymerization. The kinetic studies indicated that lower level of termination is present and the polymer chain can be extended by adding additional monomer. Because the reaction conditions are different from the cationic polymerization or coordination polymerization that is the usual polymerization mechanism using titanium complexes, polymerizations with various conditions were performed to elucidate the mechanism of polymerization. The polymerization was completely inhibited with the use of galvinoxyl radical, and the molecular weight of resulting polymers decreased with the use of 1-octanethiol, radical chain transfer agent. The copolymerization of styrene with ethyl vinyl ether using Cp_2TiCl_2 resulted the similar copolymer composition as when BPO was used as radical initiator. It was also possible to polymerize methyl methacrylate with these same titanium complexes. PMMA formed using titanium complexes shows very similar stereoregularity with polymers prepared by conventional radical methods. All these results support that the polymerization mechanism involves radical mechanism. We tried to isolate intermediate species from each step to see if the polymerization using titanium complexes proceeds by ATRP mechanism. We could confirm the activation reaction from the 1-PECl and Cp_2TiCl to generate active radical. However, the reversible deactivation reaction competes with other side reactions, and hard to be detected with our model system.



Scheme III. Degradation of Ti-alkyl compound.

Acknowledgements. This work was supported by the Soongsil Universisty Research Fund.

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