Structure of Polymer-Bound Titanocene Analogues and Reactivity of Their Dinitrogen Complexes

Mikio KOIDE, Tetsuo MASUBUCHI, Yoshimi KURIMURA,*
and Eishun TSUCHIDA

*Department of Polymer Chemistry, Waseda University,
3-4-1, Ohkubo, Shinjuku-ku, Tokyo 160, Japan.*

**Department of Chemistry, Ibaraki University,
2-1-1, Bunkyo, Mito, Ibaraki 310, Japan.*

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ABSTRACT: Various titanocene polymers in which titanium ion of titanocene dichloride (TiCp_2Cl_2) was covalently bound to polystyrene [or poly(carboxylic acid)] were synthesized. These polymer-bound titanocene species were found to be active catalysts for the reduction of dinitrogen molecule under mild conditions. When poly[styrene-co-styrylchlorobis(η -cyclopentadienyl)-titanium] and poly[styrene-co-bis(η -cyclopentadienyl) (*p*-vinylbenzoyloxy)titanium chloride] were cross-linked with divinylbenzene, the NH_3 yield was relatively higher than that of the corresponding non-crosslinked homogeneous system. The NH_3 yield increased with the percentage of cross-linking in the order $8\% > 2\% > 1\%$.

KEY WORDS Titanocene Polymer / Dinitrogen Molecule / Dinitrogen Complex / Reduction / Ammonia /

Most of low-valency transition metals are well-known for their ability to bind molecular nitrogen as end-on or side-on type.¹⁻⁴ The synthesis of polymeric dinitrogen complexes involves the utilization of dinitrogen molecules in air as the nitrogen source of NH_3 and various aminated substances.

A dinitrogen complex such as $(\text{Cp}_2\text{TiR})_2\text{N}_2$ ($\text{R}=\text{aryl}$) is known to be stable due to the delocalization (π -back donation) of the π electrons from the phenyl groups via the Ti atoms to the N_2 ligand.⁵⁻⁷ However, these binuclear complexes are catalytically inactive for the reduction of the coordinated dinitrogen molecule. We have studied the chemical behavior of the transition-metal complexes with polymeric ligand and found that the dimerization of metal complexes was inhibited by the polymer chain.⁸ This paper is concerned with the syntheses of various polymer-bound titanocene dichlorides and the reduction of the coordinated dinitrogen in the polymer-bound titanocene complexes.

EXPERIMENTAL

Materials

Polystyrene was prepared by the radical polymerization of styrene initiated by azobisisobutyronitrile (AIBN). The number-average molecular weight of polystyrene calculated from vapor pressure osmometer was 13500. Bio-Beads SX polystyrene resins cross-linked by 1%, 2%, and 8% divinylbenzene in the form of white beads (200—400 mesh) from Bio-RAD Laboratories were used without further purification.

Commercial grade of titanocene dichloride (TiCp_2Cl_2), butyllithium (15% hexane solution), anhydrous aluminum trichloride, acetyl chloride, and potassium permanganate were used without further purification. Tetrahydrofuran, carbon disulfide, and isopropyl alcohol were purified in the ordinary way.

Preparations of Poly[styrene-co-styrylchlorobis(η -cyclopentadienyl)titanium] and Cross-linked Poly[styrene-co-styrylchlorobis(η -cyclopentadienyl)titanium]

Poly(*p*-bromostyrene) was obtained by the bromination of polystyrene. Poly[styrene-*co*-styrylchlorobis(η -cyclopentadienyl)titanium] (polymer I) was obtained as follows. Poly(*p*-bromostyrene) (10 g 31.5 mmol Br) was added to butyllithium (3.0 ml 15% hexane solution) drop by drop at 0°C in THF (120 ml). The reaction mixture was stirred and the temperature was allowed gradually to warm to room temperature. After the reaction proceeded for 30–60 minutes at room temperature, a solution of titanocene dichloride (0.87 g) was added to the reaction mixture, and stirred for 3 hours. This solution was poured into methanol and filtered. The precipitate was dried in vacuum for two days yielding 8.8 g of products.⁹ Polymer I was synthesized at various titanium content (Ti mol%, 0.63, 2.3, 3.7, 6.3, and 9.0). Cross-linked poly[styrene-*co*-styrylchlorobis(η -cyclopentadienyl)titanium] (polymer II) was synthesized in a manner similar to that of polymer I from cross-linked polystyrene.

*Preparation of Poly[styrene-*co*-bis(η -cyclopentadienyl)-(acryloyloxy)titanium Chloride]*

Styrene-acrylic acid copolymer was prepared by the radical polymerization initiated by α, α' -azobisisobutyronitrile (AIBN) and purified twice by reprecipitation. Poly[styrene-bis(η -cyclopentadienyl)-(acryloyloxy)titanium chloride] (polymer III) was obtained from styrene-acrylic acid copolymer by reaction with TiCp_2Cl_2 .

*Preparation of Poly[styrene-*co*-bis(η -cyclopentadienyl)-(p-Vinylbenzoyloxy)titanium Chloride]*

Carboxypolystyrene was prepared by the Friedel-Crafts reaction of polystyrene and then, by hydrolysis of the product.^{10,11} Poly[styrene-*co*-bis(η -cyclopentadienyl)-(p-vinylbenzoyloxy)titanium chloride] (polymer IV) was obtained from carboxypolystyrene by reaction with TiCp_2Cl_2 . The cross-linked analog (polymer V) was synthesized in a manner similar to that of polymer IV.

*Preparation of Cross-linked Poly[styrene-*co*-bis(η -cyclopentadienyl)-(maloyloxy)titanium chloride]*

Styrene-maleic anhydride alternating copolymer was obtained by AIBN-initiated radical polymerization. Cross-linked poly[styrene-*co*-bis(η -cyclopentadienyl)-(maloyloxy)titanium chloride]

Table I. Characteristics of titanocene polymers

Materials	Structure	M_w
Polymer I	$\begin{array}{c} \text{---}(\text{CH}_2\text{---CH})\text{---}(\text{CH}_2\text{---CH})\text{---} \\ \qquad \qquad \\ \text{C}_6\text{H}_4 \qquad \text{C}_6\text{H}_4 \\ \qquad \qquad \\ \text{Cp}_2\text{TiCl} \end{array}$	13500
II	$\begin{array}{c} \text{---}(\text{CH}_2\text{CH})\text{---}(\text{CH}_2\text{---CH})\text{---}(\text{CH}_2\text{CH})\text{---} \\ \qquad \qquad \qquad \qquad \\ \text{C}_6\text{H}_4 \qquad \text{C}_6\text{H}_4 \qquad \text{C}_6\text{H}_4 \\ \qquad \qquad \qquad \qquad \\ \text{Cp}_2\text{TiCl} \qquad \text{---}(\text{CH}_2\text{---CH})\text{---} \end{array}$	—
III	$\begin{array}{c} \text{---}(\text{CH}_2\text{---CH})\text{---}_x \text{---}(\text{CH---CH})\text{---} \\ \qquad \qquad \\ \text{COO} \qquad \text{C}_6\text{H}_4 \\ \qquad \qquad \\ \text{Cp}_2\text{TiCl} \end{array}$	11800
IV	$\begin{array}{c} \text{---}(\text{CH}_2\text{---CH})\text{---}(\text{CH}_2\text{---CH})\text{---}(\text{CH}_2\text{---CH})\text{---} \\ \qquad \qquad \qquad \qquad \qquad \\ \text{COOH} \text{ COO} \qquad \text{C}_6\text{H}_4 \qquad \text{CO} \\ \qquad \qquad \qquad \qquad \qquad \qquad \\ \text{Cp}_2\text{TiCl} \qquad \text{NH} \qquad \text{CH} \qquad \text{NH} \\ \qquad \qquad \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{CO} \qquad \text{CO} \\ \qquad \qquad \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{---}(\text{CH}_2\text{---CH})\text{---} \end{array}$	5000
V	$\begin{array}{c} \text{---}(\text{CH}_2\text{---CH})\text{---}(\text{CH}_2\text{---CH})\text{---} \\ \qquad \qquad \\ \text{C}_6\text{H}_4 \qquad \text{C}_6\text{H}_4 \\ \qquad \qquad \\ \text{COO} \qquad \text{Cp}_2\text{TiCl} \end{array}$	13500
VI	$\begin{array}{c} \text{---}(\text{CH}_2\text{---CH})\text{---}(\text{CH}_2\text{---CH})\text{---}(\text{CH}_2\text{---CH})\text{---} \\ \qquad \qquad \qquad \qquad \\ \text{C}_6\text{H}_4 \qquad \text{C}_6\text{H}_4 \qquad \text{C}_6\text{H}_4 \\ \qquad \qquad \qquad \qquad \\ \text{COO} \qquad \text{Cp}_2\text{TiCl} \qquad \text{---}(\text{CH}_2\text{---CH})\text{---} \end{array}$	—

(polymer VI) was prepared by the reaction of styrene-maleic acid copolymer cross-linked with hexamethylenediamine with TiCp_2Cl_2 .

Table I shows the characteristics of titanocene polymers obtained. The composition of each titanocene polymer was determined by elemental analyses, Volhard's method, Waltz-Taylor method,^{12,13} and diantiprylmethane method.¹⁴

Reduction of Dinitrogen by Titanocene Polymers

When lithium naphthalide was added to a tetrahydrofuran (THF) of titanocene polymers and stirred for 1 day under N_2 atmosphere, dinitrogen complexes of titanocene polymers were obtained. Dinitrogen complexes of titanocene polymers could be identified by visible spectra measurements and the absorption maxima were 564, 645 nm.^{5,9} To

the dinitrogen complexes of titanocene polymers in THF was added isopropyl alcohol (*i*-PrOH) and then, the evolved ammonia was captured by hydrochloric acid solution through an introduced tube. Ammonia and hydrazine were determined by an indothymol reagent¹⁵ and *p*-(dimethylamino)-benzaldehyde reagent,¹⁶ respectively.

RESULTS AND DISCUSSION

Table II shows the reduction yield of dinitrogen molecule in the polymer-bound titanocene systems. The NH₃ yields in heterogeneous system (polymer II and V) were higher than those of the corresponding homogeneous systems (polymer I and IV). In a heterogeneous system, the flexibility of the polymer chain was prevented by the networks. Polymer VI in which titanocene analogue units were bound to the diamine cross-linked to styrene-maleic acid copolymer, was inactive for the formation of NH₃. The flexibility of the chain in polymer VI was higher than that of other systems since the main chain was composed of maleic acid and styrene. Also, titanocene was easily bound to the adjacent groups since carboxyl groups were close with each other. Thus, polymer VI tended to form a binuclear complex⁶ and the NH₃ yield thus became low in the polymer VI system. However, the titanocene analogue bound *via* the carboxyl groups to the polymer chain (polymer III, IV, and V) could easily fix the dinitrogen molecules. The NH₃ yield in the polymer bound titanocene *via* the carboxyl groups (polymer III, IV, and V) was higher than that of polymer-

bound titanocene *via* the phenyl groups (polymer I and II). It is suggested that the ligand having carboxyl groups raises the *d*-electron energy levels on the metal atom and thus facilitates the reduction of the dinitrogen because the carboxyl groups act as a *d*-electron donor through oxygen.

Figure 1 shows the time dependence of the ammonia concentration in the reduction of dinitrogen molecule after the addition of *i*-PrOH in the system (polymer II). The yield of NH₃ in this system was relatively high in comparison with that of homogeneous systems: in the former case, NH₃ was formed 50–65 mol per titanium mol. The dependence of the NH₃ yield on the percentage of cross-linking can be explained by the fact that the mononuclear complex species in the polymer system with higher degree of cross-linking is predominant owing to the flexibility of the polymer chains being low and, furthermore, the titanocene content of the polymer chain is low. However, the reason as to why the NH₃ yield is saturated with the elapse of time may be the removal of two cyclopentadienyl (Cp) groups from the titanocene as CpLi during the reduction process.

Table III shows the effect of the percentage of cross-linking on the reduction yield in the polymer II system. The NH₃ yield was high as the titanocene content in the polymer became small as in the case of homogeneous systems. When titanocene moieties were dispersed on the polymer chain, the mononuclear dinitrogen complex species, considered as the active species, became more predominant. Thus, it is suggested that NH₃ is formed more effectively as the

Table II. Reduction of dinitrogen molecules at various titanocene polymers^a

Materials	Percentage of cross-linking %	Ti	NH ₃
		mol%	mol per Ti mol
Polymer I	0	0.60	41.7
II	8	0.30	67.8
III	0	0.14	150
IV	1	0.20	123
V	0	0.58	55.0
VI	10	0.30	0.37

^a [C₁₀H₈], 1.0 g; [Li], 0.2 g; [Polymer], 0.1 g; [*i*-PrOH], 20 ml; reaction temp, 25°C; reaction time, 24 h, in THF.

Figure 1. Time dependence of the reduction of dinitrogen molecule by polymer II-LiNp systems in THF at room temperature: ●, 8%; ○, 2%; △, 1%; [Polymer II], 0.1 g; [C₁₀H₈], 1.0 g; [Li], 0.2 g; [*i*-PrOH], 20 ml.

Table III. Effect of the percentage of cross-linking on the reduction of dinitrogen molecule^a

Percentage of cross-linking	Ti	NH ₃
	mol%	mol per Ti mol
1	0.47	49.5
1	0.71	41.3
1	1.50	18.5
2	0.65	57.2
2	1.22	23.6
8	0.30	67.8

^a [C₁₀H₈], 1.0 g; [Li], 0.2 g; [Polymer II], 0.1 g; [*i*-PrOH], 20 ml; reaction temp, 20°C; reaction time, 24 h, in THF.

Table IV. Effect of the proton source on the reduction of dinitrogen molecule^a

Proton source	NH ₃	NH ₃
	mol	mol per Ti mol
<i>i</i> -PrOH	231	57.2
HCl	105	26.1
H ₂ SO ₄	97.7	24.2

^a [C₁₀H₈], 1.0 g; [Li], 0.2 g; [Polymer II], 0.1 g; percentage of cross-linking, 2%; [Ti mol], 0.65; reaction temp, 25°C; reaction time, 24 h, in THF.

Table V. Effect of reduction temperature on the reduction dinitrogen molecule^a

Reaction temp	N ₂ H ₄	NH ₃
	mol per Ti mol	mol per Ti mol
°C		
-78	0.94	7.81
-20	0.84	10.3
0	0.81	18.2
25	0.75	26.1

^a [C₁₀H₈], 1.0 g; [Li], 0.2 g; [Polymer II], 0.1 g; percentage of cross-linking, 2%; [Ti mol], 0.65; [HCl], 10 ml; reaction time, 24 h, in THF.

titanocene content in the polymer becomes small. The flexibility of that chain for the cross-linked titanocene polymer is probably depressed and consequently, the formation of a binuclear complex such as $\text{Ti}-\text{N}=\text{N}-\text{Ti}$ is prevented. Therefore, the NH₃ yield of the polymer II is larger than that of polymer I.

Table IV shows the effect of the proton source on the reduction yield of nitrogen. When hydrochloric acid or sulfuric acid was used for the proton supply source, NH₃ was formed. The NH₃ yield for hydrochloric acid and sulfuric acid systems were less than that for *i*-PrOH system: the NH₃ yields were 26.1 mol/Ti mol for hydrochloric acid and 28.3 mol/Ti mol for sulfuric acid. This fact indicates that the decomposition of the dinitrogen complex proceeded along with the reduction of the dinitrogen in the presence of these strong acids.

Table V shows the reduction yield of dinitrogen by the addition of hydrochloric acid. Both NH₃ and N₂H₄ were observed when hydrochloric acid was added. The NH₃ yield increased with the rise of the temperature, but the N₂H₄ yield decreased as the temperature increased. From these results, following reaction scheme is considered to apply.

The binuclear dinitrogen complex was easily formed at low temperatures. When hydrochloric acid was added to the binuclear dinitrogen complex, it tended to react with the acid to give N₂ and H₂.⁶ On the other hand, the coordinated dinitrogen reacted predominantly with the acid to give NH₃ via the mononuclear dinitrogen complex.

Figure 2 shows the relationship between the *i*-PrOH amount and NH₃ yield. The NH₃ yield showed a maxima when the yield was 57 mol per titanium mol at *i*-PrOH 20 ml. When large amounts of *i*-PrOH was added, *i*-PrOH reacted with lithium naphthalide to give lithium alcoholate. When an argon atmosphere was used instead of a N₂ atmosphere following the addition of *i*-PrOH,

Figure 2. Effect of *i*-PrOH amounts of the reduction of dinitrogen molecule; [Polymer II], 0.1 g; percentage of cross-linking, 2%; [C₁₀H₈], 1.0 g; [Li], 0.2 g.

Figure 3. Effect of reduction reagent amount of the reduction of dinitrogen molecule; [Polymer II], 0.1 g; [C₁₀H₈], 1.0 g; [*i*-PrOH], 20 ml.

stoichiometric amounts of NH₃ (2 ml/Ti mol) were formed. But the NH₃ yield became large (30 ml per titanium mol) when the system conditions were changed from an argon atmosphere to a nitrogen atmosphere. But NH₃ was scarcely formed in air.

The effect of the amounts of the reductant on the NH₃ yield is shown in Table VI and Figure 3. The NH₃ yield depended on the amount of polymer when the reductant amount was a constant. Consequently, the NH₃ yield increased with a decrease in the amount of polymer. The NH₃ yield was saturated when lithium naphthalide was added 2000 fold per titanium mol. 57.2 mol of NH₃ were formed in the polymer II system. The NH₃ yield also depended on the amount of lithium when the

Table VI. Effect of reduction reagent amount of the reduction of dinitrogen molecule^a

Materials	Reduction reagent		NH ₃
	[C ₁₀ H ₈][Li]		
g	g		mol per Ti mol
0.05	1.0	0.2	57.5
0.1	1.0	0.2	57.2
0.1	0.5	0.1	19.9
0.1	0.2	0.05	8.0
0.2	1.0	0.2	24.1
0.5	1.0	0.2	4.6

^a [Polymer II, Ti mol], 0.65; percentage of cross-linking, 2%; [*i*-PrOH], 20 ml; reaction temp, 25°C; reaction time, 24 h, in THF.

content was constant and the amount of reduction reagent (naphthalene was 1.0 g) was changed in the polymer II system. In this case the NH₃ yield was saturated at Li 0.6 g. Thus, the NH₃ yield depended on the amount of polymer and reduction reagent. The reason why excess amount of lithium naphthalide must be added is that lithium alcoholate is inactivated as a reductant.

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