A Novel Catalyst System for Cationic Polymerization of Styrene Derivatives. Combination of Platinum(0) Complex and Methyldichlorosilane

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ABSTRACT: Polymerizations to give polymers with relatively high number average molecular weight ($> M_n = 10000$) are demonstrated for styrene, α-methylstyrene, 4-methylstyrene, 4-methoxystyrene, and 4-chloromethylstyrene by the combination of platinum(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex [Pt(0)(DVTMDS)$_2$] (0.1 mol%) and methyldichlorosilane (10 mol%) in CH$_2$Cl$_2$. Poly(4-chloromethylstyrene) obtained by this polymerization system has linear structure as elucidated by ^{1}H NMR, although chain transfer is noticed in the polymerization. When the polymerization of ethyl vinyl ether was quenched with methanol followed by the treatment with 0.1N HCl, the resulting polymer showed a resonance at 9.76 ppm in ^{1}H NMR arising from an aldehyde group. This result provides a strong evidence for the relevance of a carbocationic polymerization mechanism.
KEY WORDS Cationic Polymerization / Platinum(0) Complex / Methyldichlorosilane / Styrene Derivatives / Linear Poly(4-chloromethyl styrene) / Stereoregularity /

The late-transition metal catalyzed polymerizations have become of significant importance in the field of polymer synthesis during the past decade due to the wide applicability to prepare structurally well-defined polymers. Particular interest has grown in the use of Group 10 metal complexes (Ni or Pd) as catalysts for the coordination polymerization of α-olefins[1] and controlled radical polymerization.[2] Increasing attention has been also paid to analogous Pt complexes.[3] However, Pt complexes are relatively inactive for the coordination polymerization of α-olefins because of the difficulty of migratory insertion of α-olefin into Pt-alkyl bond.[3c,4] They are used as excellent structural models for the important intermediate, in the Pd catalyzed systems, which is difficult to be evidenced.

Recently, late-transition metal cationic complexes[5] have been noticed to function as the initiator for the polymerization of electron-rich olefins such as vinyl ethers and N-vinylcarbazole, which are well-known to readily polymerize *via* carbocationic process. For example, diaryldiazabutadiene (ArDAB) Pt$^+$ cationic complex [Pt(ArDAB)(Me)(NCMe)]$^+$BF$_4^-$ was reported to initiate the carbocationic polymerization of vinyl ethers and N-vinylcarbazole.[6] Since late-transition metal cationic complexes merely function as the initiator and not as the counter ion of propagating end, this polymerization system provides little opportunity to control the polymer structures such as chemical structure and stereoregularity, and they do not seem to have any no advantages over the conventional carbocationic polymerization systems.

In order to precisely control the polymer structure, new Pt catalyzed polymerization system which possesses Pt$^-$ anionic complex as the counter anion is required, and this system is expected to open the new way in the field of polymerization of electron-rich olefin monomers like α-olefins and vinyl ethers. Our interest was focused on the platinum(0) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex [Pt(0)(DVTMDS)$_2$],[7] which is well-known as the very efficient catalyst for the hydrosilylation of unsaturated compounds. As is generally accepted for Pt catalyzed hydrosilylation of olefin, the mechanism involves the oxidative addition of hydrosilane to Pt(0)(DVTMDS)$_2$ at the first step, followed by insertion of olefin into Pt-H bond of H-Pt(II)L$_2$-SiR$_3$ complex and reductive elimination from R-Pt(II)L$_2$-SiR$_3$ complex.[8] In this mechanism, the metal center of H-Pt(II)L$_2$-SiR$_3$ complex seems to be weakly electron-deficient due to the existence of silicon atom with lower electronegativity and labile ligand (DVTMDS). Therefore, this Pt complex is expected to exhibit unique reactivity different from ordinary H-Pt(II)L$_2$-alkyl complexes, when the labile ligand is replaced by strongly nucleophilic ligand like chlorine anion. Namely, the combination of protonic acid (HX) and H-Pt(II)L$_2$-SiR$_3$ might produce proton (H$^+$) with Pt$^-$ counter ion [Pt(II)LX(SiR$_3$)H]$^-$, and might serve as a new initiator for the cationic polymerization of electron-rich olefin monomers.

In this paper, we report the results of the new polymerization system of styrene derivatives such as styrene (St), α-methylstyrene (α-MSt), 4-methylstyrene (MeSt), 4-methoxystyrene (MOSt) and 4-

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chloromethylstyrene (CMSt), and ethyl vinyl ether (EVE) using the combination of Pt(0)(DVTMDS)$_2$ and methyldichlorosilane (MeCl$_2$SiH). These new unprecedented polymerization systems were found to proceed *via* carbocationic polymerization mechanism. In addition, our new carbocationic polymerization system successfully afforded linear poly(4-chloromethylstyrene) (PMCSt), which has attracted much attention as the important precursor of various functional materials.

EXPERIMENTAL

General

St (Wako; purity > 99%), α-MeSt (Tokyo Kasei; purity > 99%), MeSt (Tokyo Kasei; purity > 96%), and MOSt (Tokyo Kasei; purity > 95%) were washed with 10% aqueous sodium hydroxide, and distilled over calcium hydride before use. CMSt (Acros; purity 90%) was passed through an alumina column, and distilled over calcium hydride before use. Hydrogen hexachloroplatinate (IV) hexahydrate (Wako; purity 98.5%) and MeCl$_2$SiH (ShinEtsu Chemicals) were used without purification. Toluene, CH$_2$Cl$_2$, n-hexane, AcOEt, Et$_2$O, and THF (solvent) were purified by the usual methods.

The 500 MHz ^{1}H NMR and 125 MHz ^{13}C NMR spectra were obtained in CDCl$_3$ on Varian 500 MHz spectrometer model Unity INOVA. Chemical shifts are reported in ppm relative to CHCl$_3$ (δ 7.26, ^{1}H) and CDCl$_3$ (δ 77.0, ^{13}C). IR spectra were obtained on a JASCO VALOR-III spectrophotometer. GC-Mass analyses were carried out on Shimadzu QP-500 mass spectrometer. Size exclusion chromatography (SEC) analyses were performed on a JASCO HPLC with the combination of Shodex KF-803L (exclusion limit: $M_n = 4 \times 10^5$, polystyrene) and KF-804 (exclusion limit: $M_n = 7 \times 10^4$, polystyrene) columns using the tetrahydrofulan (THF) as an eluent.

Typical Polymerization Procedure

Ethanol (0.5 mL) and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (0.0186 g, 0.1 mmol) were added to H$_2$PtCl$_6$ 6 H$_2$O (0.0026 g, 0.005 mmol, 0.1 mol%), and the resulting reaction mixture was stirred at 50°C for 90 min to give Pt(0)(DVTMDS)$_2$. After removal of the solvent *in vacuo*, toluene (0.0342 g, 0.37 mmol) and methyldichlorosilane (0.0575 g, 0.5 mmol, 10 mol%) were added to the solution of Pt(0)(DVTMDS)$_2$ in CH$_2$Cl$_2$ (1.0 mL) at 0°C. The polymerization was initiated by adding CMSt (0.7831 g, 5.0 mmol) into a mixture of Pt(0)(DVTMDS)$_2$ and MeCl$_2$SiH, and continued at r.t. for 2.0 h. During the polymerization, monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR with toluene as an internal standard. After adding methanol (0.5 mL), reaction mixture was poured into methanol (100 mL), and white precipitates were collected and dried *in vacuo*.

Poly(4-chloromethylstyrene) [Poly(CMSt)]

^{1}H NMR δ (ppm) 1.40 (brs, 2 H, –CH$_2$), 1.58–2.52 (br, 1 H, –CH), 4.53 (s, 2 H, –CH$_2$Cl), 6.50 (brs, 2 H, m–Ph), 7.06 (brs, o–Ph); ^{13}C NMR δ (ppm) 40.2 (–CH), 41.2–44.8 (m, –CH$_2$), 46.3 (–CH$_2$Cl), 127.8 (m–Ph), 128.4 (o–Ph), 134.9 ($ipso$–Ph), 145.1 (p–Ph); IR (KBr, cm^{-1}) 3052, 3026, 2924, 2850, 1612, 1511, 1266, 836, 675.

One-Pot Copolymerization of MOSt and St

To a solution of Pt(0)(DVTMDS)$_2$ (0.1 mol%) and MeCl$_2$SiH (10 mol%) in CH$_2$Cl$_2$ (1.0 mL), a mixture of MOSt (0.3355 g, 2.5 mmol), St (0.2604 g, 2.5 mmol), and hexamethyldisilane (0.0137 g, 0.094 mmol) was added at −50°C, and stirred at the same temperature for 10 min. After 150 min under stirring at 0°C, polymerization was quenched by adding methanol (0.5 mL), and the resulting polymer was analyzed by ^{1}H NMR and GPC. During the polymerization, monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR with hexamethydisilane as an internal standard.

Trapping of Propagating End in the Polymerization of EVE

To a solution of Pt(0)(DVTMDS)$_2$ (0.1 mol%) and MeCl$_2$SiH (10 mol%) in CH$_2$Cl$_2$ (1.0 mL), EVE (0.3606 g, 5.0 mmol) was added at 0°C, and stirred at the same temperature for 15 min. After adding methanol (0.5 mL), the reaction mixture was filtered with neutral silica gel to remove the catalyst, and removal of the solvent afforded poly(EVE). The hydrolysis of the obtained poly(EVE) was carried out in a mixture of Et$_2$O (2.0 mL) and 0.1N HCl (2.0 mL). Organic phase was separated and dried over anhydrous MgSO$_4$. Removal of the solvent afforded the poly(EVE) having an aldehyde group at ω-terminal (95% yield).

RESULTS AND DISCUSSION

Polymerization of α-Methylstyrene (α-MeSt)

Polymerization of α-MeSt was initially examined in the presence of Pt(0)(DVTMDS)$_2$ (0.1 mol%) and MeCl$_2$SiH under the various reaction conditions (temperature, amount of MeCl$_2$SiH, and solvent). The results were summarized in Table I. When the reaction was conducted at r.t. using 1.0 mol% of MeCl$_2$SiH

Table I. Polymerization of α-methylstyrene
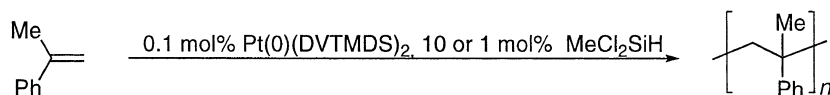
| Entry	MeCl$_2$SiH/mol%	Solvent	Temp./°C	Time/min	Conv./%[a]	Yield/%[b]	M_n[c]	M_w/M_n[c]
1	1.0	Toluene	r.t.	30	100	0[d]	–	–
2	1.0	Toluene	0	30	94	72	980	6.0
3	1.0	Toluene	−10	30	90	85	1400	7.4
4	1.0	Toluene	−20	720	44	31	2700	3.1
5	10.0	Toluene	−10	30	100	84	740	9.7
6	10.0	Toluene	−20	30	100	88	4000	4.0
7	10.0	Toluene	−30	30	100	86	7000	3.7
8	10.0	Toluene	−50	720	73	65	13000	3.4
9	1.0	CH$_2$Cl$_2$	r.t.	30	100	0[e]	–	–
10	10.0	CH$_2$Cl$_2$	0	30	100	89	470	4.7
11	10.0	CH$_2$Cl$_2$	−50	30	100	90	8400	2.6
12	10.0	CH$_2$Cl$_2$	−70	30	100	92	13000	2.5
13	10.0	*n*-hexane	0	720	47	32	1600	5.5
14[f]	10.0	*n*-hexane	−10	720	69	65	1600	10.7
15	10.0	AcOEt	0	720	58	20	720	1.8
16	10.0	AcOEt	−10	720	0	–	–	–
17	10.0	Et$_2$O	0	720	0	–	–	–
18	10.0	THF	0	720	0	–	–	–

All reactions were carried out in solvent ([α-MeSt] = 5.0 M) in the presence of platinum catalyst prepared *in situ* by mixing H$_2$PtCl$_6$ 6H$_2$O (0.1 mol%) and DVTMDS at 50°C for 90 min. [a]Determined by ^{1}H NMR. [b]Isolated yields after reprecipitation into MeOH. [c]Estimated by GPC (THF as an eluent) with polystyrene standard. [d]Terminal olefin dimer **1a** was obtained in 54% yield (refer to isolated yield after chromatography). [e]Terminal olefin dimer **1a** was obtained in 41% yield (refer to isolated yield after chromatography). [f]Precipitation of polymer occured during the polymerization.

in toluene or CH$_2$Cl$_2$, oligomers, and terminal olefin dimer **1a**[9] were produced without formation of any other dimmers such as internal olefin dimer **1b**[9] or indene dimer **1c**[9] *via* Friedel–Crafts reaction (entries 1 and 9). On the other hand, oligomers with higher molecular weight were obtained at lower temperature with incomplete monomer conversion (entries 2–4). Changes in the amount of MeCl$_2$SiH from 1.0 mol% to 10 mol% caused an increase in conversion and molecular weight (entries 5–8), in particular, the highest molecular weight (M_n = 13000) was observed at −50°C (entry 8).

The effect of the solvent on polymerization was also investigated in the presence of Pt(0)(DVTMDS)$_2$ (0.1 mol%) and MeCl$_2$SiH (10 mol%) in various solvents such as CH$_2$Cl$_2$, *n*-hexane, AcOEt, Et$_2$O, and THF (entries 10–18). Although the *n*-hexane was relatively efficient solvent as well as toluene, precipitation of polymer was observed during the course of polymerization at −10°C (entry 14). Among above solvents, AcOEt, Et$_2$O, and THF which contain heteroatom were found to inhibit the polymerization (entries 15–18), whereas the use of CH$_2$Cl$_2$ as polar solvent afforded poly(α-MeSt) with high molecular weight (M_n = 13000) and slightly narrower molecular weight distri-

bution (MWD) in good yield with complete monomer conversion. Furthermore, this polymerization was relatively rapid (30 min) even at −70°C (entry 12). For example, the monomer conversion for entries 8 and 12 were 26% (60 min) → 49% (240 min) → 73% (420 min) → 73% (720 min), and 32% (3 min) → 81% (15 min) → 100% (30 min) in toluene and in CH$_2$Cl$_2$, respectively. Thus, the polymerization using the combination of Pt(0)(DVTMDS)$_2$(0.1 mol%) and 10 mol% of MeCl$_2$SiH at low temperature in CH$_2$Cl$_2$ was found to cause the complete conversion of monomer to form high molecular weight poly(α-MeSt).

In the polymerization of α-MeSt, as temperature is lowered, increase in molecular weight and decrease in MWD were observed, indicating that chain transfer and termination reactions are suppressed at lower temperature. Furthermore, polymerizations using less polar solvent dramatically slowed down the rate of polymerization. These trends are apparently in line with conventional carbocationic polymerization of α-MeSt.[10] However, poly(α-MeSt)s obtained in CH$_2$Cl$_2$ and toluene showed different stereoregularity, for example, triad tacticity[11] of the polymers obtained by polymerization at −50°C are *rr*:*mr*:*mm* = 83:17:0 in CH$_2$Cl$_2$, and *rr*:*mr*:*mm* = 49:40:11 in toluene (entries 8 and 12). In

Table II. Polymerization of styrene derivatives
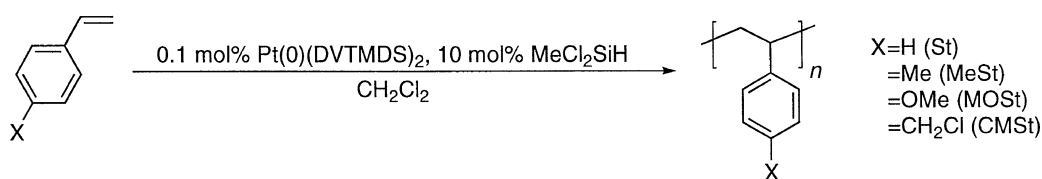
Entry	X =	Temp./°C	Time/min	Conv./%[a]	Yield/%[b]	M_n^c	M_w/M_n^c
1	H	r.t.	720	41	36	13000	3.0
2	H	0	30	100	98	11000	3.3
3	H	−10	720	49	43	27000	2.9
4	Me	r.t.	15	100	94	15000	3.6
5	Me	0	15	100	93	36000	2.7
6	Me	−10	15	100	98	28000	3.5
7	Me	−30	15	100	98	67000	2.2
8	OMe	r.t.	15	100	98	23000	4.6
9	OMe	0	15	100	95	15000	5.4
10[d]	OMe	−10	15	100	99	14000	3.2
11[d]	OMe	−30	15	100	99	12000	3.0
12	CH$_2$Cl	r.t.	120	100	96	11000	3.6
13	CH$_2$Cl	0	540	100	92	6600	3.3
14[e]	CH$_2$Cl	−10	720	82	62	6700	2.9

All reactions were carried out in solvent ([monomer] = 5.0 M) in the presence of platinum catalyst prepared *in situ* by mixing H$_2$PtCl$_6$ 6H$_2$O (0.1 mol%) and DVTMDS at 50°C for 90 min. [a]Determined by ^{1}H NMR. [b]Isolated yields after reprecipitation into MeOH. [c]Estimated by GPC (THF as an eluent) with polystyrene standard. [d]Monomer concentration was 2.5 M. [e]0.5 mol% of Pt(0)(DVTMDS)$_2$ was used.

other words, this result is not consistent with the view that polarity of the solvent hardly affected the stereoregularity in the conventional carbocationic polymerization of α-MeSt.[10b,c] These observations indicate that even if this polymerization proceeds *via* carbocationic mechanism, polymerization mechanism under the influence of the Pt(II) counter anion may be different from the conventional carbocationic polymerization.

Polymerization of Styrene Derivatives

Further experiments for the polymerization of styrene derivatives such as St, MeSt, MOSt, and CMSt to probe the efficacy of this polymerization system were carried out in the presence of Pt(0)(DVTMDS)$_2$ (0.1 mol%) and MeCl$_2$SiH (10 mol%) in CH$_2$Cl$_2$ at various temperatures. The results were summarized in Table II. In the polymerization of St, the polymerization temperature significantly affected monomer conversion, namely the monomer conversion was not consumed completely at r.t. or −10°C even with a prolonged reaction time (entries 1 and 3), whereas the polymerization at 0°C led to the formation of poly(St) (M_n = 11000) with complete monomer conversion and quantitative polymer yield (entry 2). The highest molecular weight (M_n = 27000) of the polymer was obtained at −10°C with only 49% monomer conver-

sion in 720 min (entry 3) among the polymerizations were carried out at these temperatures, indicating that lower polymerization temperature leads to the suppression of chain termination and propagation simultaneously. On the contrary, polymerizations of MeSt and MOSt having an electron-donating group at *para* position are rapid (15 min), and the resulting poly(MeSt) and poly(MOSt) with high molecular weight (> M_n = 12000) were obtained in good yield (> 93%) regardless of reaction temperature (entries 4–11). However, molecular weight of the obtained polymers is still much lower, about one tenth of the calculated molecular weight (calcd. M_n = $M_{monomer}$ × [monomer]/[Pt]), indicating that chain transfer reaction still frequently occurred. In the ^{13}C NMR spectra, the resonances of the *ipso* carbon of polystyrene derivatives consist of the partially resolved multiplets, diagnostic disordered of stereochemical environments, thus the obtained polymers were found atactic.

To demonstrate the utility of this polymerization system, our interest was focused on the synthesis of linear poly(CMSt) because it has been widely used as the precursor of functional materials. It is also known that linear poly(CMSt) is difficult to obtain without cross-linking of the main chain. Our polymerization system afforded the linear poly(CMSt) in 96% yield
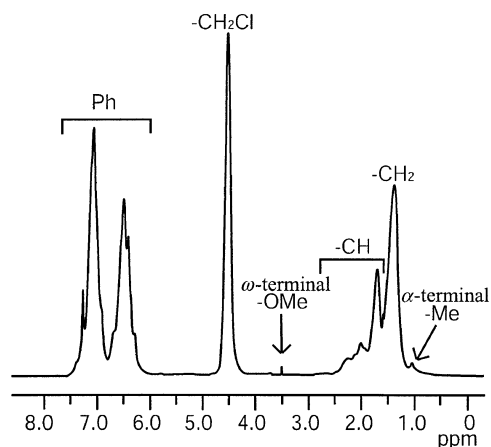
Figure 1. ^{1}H NMR (500 MHz) spectrum of poly(CMSt) (M_n = 11000, M_w/M_n = 3.6).

with relatively high molecular weight (M_n = 11000) at r.t. (entry 12). The evidence for linear structure was given by the comparison of integral ratio between chloromethyl group and aromatic group in ^{1}H NMR (Figure 1).[12] The integral ratio is 1:1, which indicates that the obtained poly(CMSt) is linear without any cross-linking. Further evidence for the existence of chloromethyl group was also given by IR ($-CH_2Cl$: 1266 and 675 cm^{-1}). The polymerization at lower temperature gave the poly(CMSt) with lower molecular weight, but all of the obtained poly(CMSt)s were also found to be linear (entries 13 and 14).

To check the living nature of the polymerization, synthesis of block copolymer using this polymerization system was attempted by monomer-addition method and one-pot method to obtain the MOSt$_n$-b-MeSt$_m$ and MOSt$_n$-b-St$_m$ block copolymers. In the monomer-addition method, MeSt as the second monomer was added to the reaction mixture at $-30°C$ just before initial polymerization of MOSt at $-30°C$ had been finished (96% conversion, M_n = 9900, M_w/M_n = 2.7). Added MeSt was smoothly consumed within 15 min (100% conversion). After the monomer addition, however, molecular weight of the obtained polymer decreased (M_n = 4100), and the MWD became broader (M_w/M_n = 5.0) than that of original poly(MOSt) (M_w/M_n = 2.7). Almost similar result was obtained in the one-pot method for the copolymerization of MOSt and St. The copolymerization at $-50°C$ led to the 100% conversion of MOSt and 0% conversion of St within 5 min (M_n = 9100, M_w/M_n = 2.9), higher polymerization temperature ($0°C$) after consumption of MOSt led to the 48% conversion of St within 120 min. The molecular weight of the resulting polymer somewhat increased (M_n = 9600), but the MWD became broader (M_w/M_n = 4.1) than that of original poly(MOSt) (M_w/M_n = 2.7). These results indicate

Structures of **1**
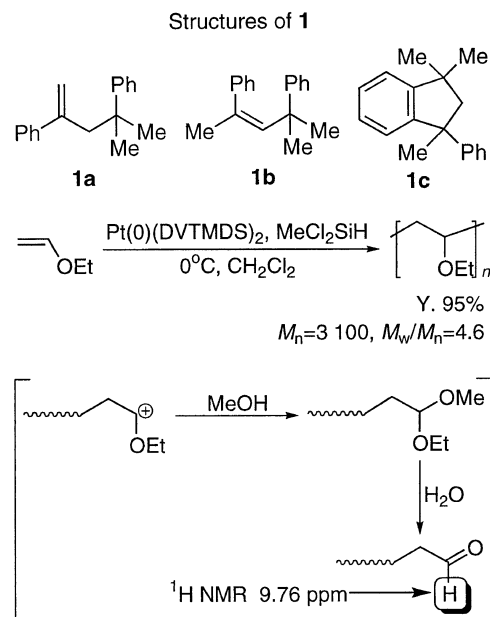
Scheme 1.

that the finally obtained polymers are a mixture of each homopolymers. Homoploymerization of second monomer (MeSt) or unreacted monomer (St) occurred by the initiating species arising from the frequent chain transfer reaction during the course of the initial polymerization. A better understanding of these results might lead to a possibility of one-pot copolymerization by taking advantage of different monomer reactivity, if chain transfer reaction can be complete suppressed.

Trapping of Propagating End in the Polymerization of Ethyl Vinyl Ether (EVE)

To obtain the evidence for cationic polymerization process, polymerization of EVE was carried out in the presence of Pt(0)(DVTMDS)$_2$ (0.1 mol%) and MeCl$_2$SiH (10 mol%) in CH$_2$Cl$_2$ at $0°C$ for 15 min, and quenched with methanol followed by the treatment with 0.1N HCl (Scheme 1). If the polymerization proceeds *via* cationic species on the propagating chain end, an aldehyde group should be formed at the polymer chain end (ω-terminal). The aldehyde group arises from hydrolysis of the acetal group formed by nucleophilic attack of methanol on the carbenium center of the propagating end as reported for the PEVE prepared by the conventional cationic polymerizations.[13]

A ω-terminal group analysis of the obtained poly(EVE) exhibited a weak resonance at 9.76 ppm in ^{1}H NMR (Figure 2). In addition, ω-terminal group analysis of the obtained poly(CMSt) also exhibited a weak resonance of methoxy group at 3.51 ppm in ^{1}H NMR (Figure 1). This polymer also exhibited methyl group as the α-terminal group. Indeed, these observations strongly suggest a carbocationic polymerization mech-
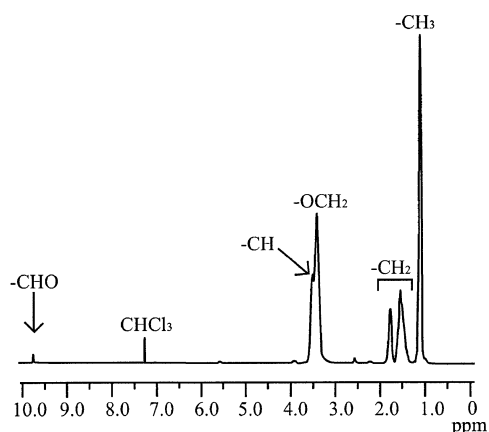
Figure 2. ^{1}H NMR (500 MHz) spectrum of poly(EVE) quenched by methanol followed by treatment with 0.1 N HCl.

anism.

Mechanistic Considerations

In this cationic polymerization system, the initiating species is most likely a proton (H^{+}) generated by the hydrolysis of $MeCl_2SiH$ with water (arising from $H_2PtCl_6 6 H_2O$ or adventitious water), because α-terminal group of the obtained poly(CMSt) was found to be methyl group (1.05 ppm, in Figure 1). To clarify this point, polymerization of α-MeSt using the combination of $Pt(0)(DVTMDS)_2$ (0.1 mol%) and $MeCl_2SiH$ (10 mol%) was examined in CH_2Cl_2 at −30°C in the presence of 10 mol% of 1,8-bis(dimethylamino)naphthalene as the proton trap. As expected, polymerization was completely suppressed, and ^{1}H NMR analysis of the reaction mixture indicated the formation of disiloxane HClMeSiOSiMeClH [δ 0.55 (d, $J = 1.9$ Hz, 6 H, Si<u>Me</u>) and 5.58 (q, $J = 1.9$ Hz, 2 H, Si<u>H</u>)]. Thus, these results strongly suggest that proton is serving as the initiator for this polymerization.

Some model reactions were also examined in CH_2Cl_2 at −30°C by using the α-MeSt. When HCl or a combination of HCl and $Pt(0)(DVTMDS)_2$ were employed, polymerization did not take place (0% monomer conversion). Use of the combinations of $Pt(0)(DVTMDS)_2$ and $MeSiCl_3$ or $SiCl_4$ (generation of HCl *in situ*) was also inefficient for the polymerization (0% monomer conversion). These results obviously indicated that HCl or simple combination of HCl and $Pt(0)(DVTMDS)_2$ are not the initiating species, and combination of hydrosilane (Si–H) and $Pt(0)(DVTMDS)_2$ seems necessary. The effect of the substituents at the silicon atom on the polymerization system was also investigated by using various hydrosilanes such as $(EtO)_3SiH$, $Me(Me_2N)_2SiH$, Et_3SiH, $MePh_2SiH$, $MePhSiH_2$, $MePhClSiH$, Me_2ClSiH, and Cl_3SiH. Among above hydrosilanes, only Cl_3SiH

(10 mol%) caused the polymerization of α-MeSt in the presence of $Pt(0)(DVTMDS)_2$ (0.1 mol%) in CH_2Cl_2 even at −70°C (92% yield, $M_n = 8600$, $M_w/M_n = 2.3$). In addition, the combination of HCl and $Pt(0)(DVTMDS)_2$ was examined in the presence of Me_2ClSiH which is an inactive silane component for the polymerization although it has similar structure with $MeCl_2SiH$ (containing Si–H and Si–Cl groups). The reaction only gave the dimer **1a** in 7% yield as determined by ^{1}H NMR. These results suggest that existence of both Si–H group and two or more Si–Cl groups is essentially for this polymerization system. In other words, existence of Si–H and Si–Cl groups are necessary to give H-Pt(II)L$_2$–SiMeCl$_2$ species, and HCl is required to form active initiating species.

From above results, we propose Figure 3 as a plausible reaction mechanism. The initiation involves the hydrolysis of $MeCl_2SiH$ and oxidative addition of $MeCl_2SiH$ to $Pt(0)(DVTMDS)_2$ to give HCl and H-Pt(II)L$_2$–SiMeCl$_2$. Following the reaction of HCl with H-Pt(II)–SiMeCl$_2$ gives proton with platinum anionic counter ion, namely, H[+][Pt(II)LCl(SiMeCl$_2$)H][−] as the initiating species. In this mechanism, two or more Si–Cl groups are probably needed to stabilize the platinum anionic counter ion during the course of the polymerization. In the propagation, the nature of the ion pair between carbocation and platinum anionic complex seems relatively tight (not free ion) even in the polar solvent such as CH_2Cl_2 judging from the facts of unusual formation of linear poly(CMSt) and of the formation of poly(α-MeSt) with different tacticity from the polymers obtained by conventional cationic initiating system. Further evidence for the tight ion might be also given by the formation of **1a** without **1c** in the dimerization of α-MeSt.[9] Main chain transfer reaction is considered to involve the spontaneous β-elimination of proton (path a) and/or abstraction of the β-proton by monomer (path b). ^{1}H NMR analysis of the obtained poly(α-MeSt) showed resonance of terminal olefin group at 4.99 and 4.60 ppm arising from chain transfer reaction, although α-terminal could not be observed. The integral ratio of α-terminal (methyl group) and ω-terminal (methoxy group) of methanol quenched poly(CMSt) was 7.5:1 (α-terminal:ω-terminal, Figure 1). The ratio of ω-terminal is much higher than that of poly(α-MeSt), but still not to be 1:1.
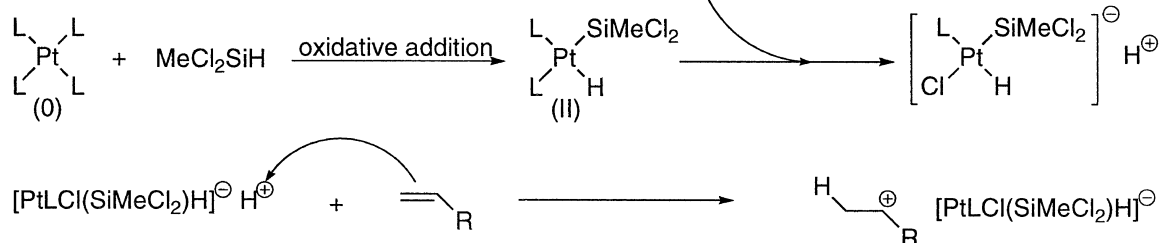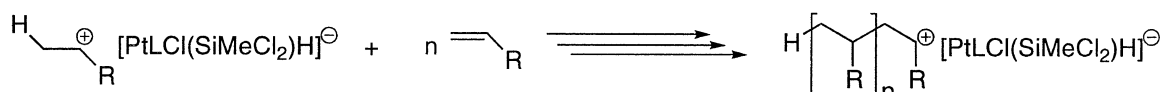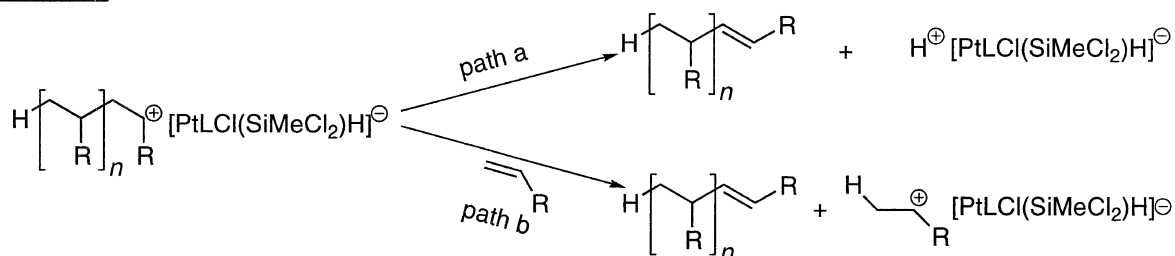
CONCLUSION

A novel cationic polymerization system using the combination of platinum(0) complexes (0.1 mol%) and methyldichlorosilane (10 mol%) has been demonstrated for the various styrene derivatives such as

Initiation

1. HCl generation

$$MeCl_2SiH + 1/2\ H_2O \longrightarrow HCl + 1/2\ MeClHSiOSiHClMe$$

2. Cationation

$$\begin{array}{c}L \\ L\end{array}\!\!Pt\!\!\begin{array}{c}L \\ L\end{array}\ (0) + MeCl_2SiH \xrightarrow{\text{oxidative addition}} \begin{array}{c}L \\ L\end{array}\!\!Pt\!\!\begin{array}{c}SiMeCl_2 \\ H\end{array}\ (II) \longrightarrow \left[\begin{array}{c}L \\ Cl\end{array}\!\!Pt\!\!\begin{array}{c}SiMeCl_2 \\ H\end{array}\right]^{\ominus} H^{\oplus}$$

$$[PtLCl(SiMeCl_2)H]^{\ominus}\ H^{\oplus} + \overset{}{=}\!\!\backslash_R \longrightarrow H\backslash\!\!\overset{\oplus}{\diagup}_R\ [PtLCl(SiMeCl_2)H]^{\ominus}$$

Propagation

$$H\backslash\!\!\overset{\oplus}{\diagup}_R\ [PtLCl(SiMeCl_2)H]^{\ominus} + n\ \overset{}{=}\!\!\backslash_R \rightleftharpoons H\!\!\left[\begin{array}{c} \\ R\end{array}\right]_n\!\!\overset{\oplus}{\diagup}_R\ [PtLCl(SiMeCl_2)H]^{\ominus}$$

Chain transfer

$$H\!\!\left[\begin{array}{c} \\ R\end{array}\right]_n\!\!\overset{\oplus}{\diagup}_R\ [PtLCl(SiMeCl_2)H]^{\ominus}$$

path a → $H\!\!\left[\begin{array}{c} \\ R\end{array}\right]_n\!\!\diagup\!\!=\!\!_R + H^{\oplus}[PtLCl(SiMeCl_2)H]^{\ominus}$

path b → $H\!\!\left[\begin{array}{c} \\ R\end{array}\right]_n\!\!\diagup\!\!=\!\!_R + H\backslash\!\!\overset{\oplus}{\diagup}_R\ [PtLCl(SiMeCl_2)H]^{\ominus}$

Figure 3. Plausible polymerization mechanism.

styrene, α-methylstyrene, 4-methylstyrene, 4-methoxystyrene, and 4-chloromethylstyrene. This novel cationic polymerization system gave the polymers with relatively high number average molecular weight ($> M_n = 10000$) in all cases, and unusual formation of linear poly(4-chloromethylstyrene) was observed. Furthermore, evidence for the cationic polymerization process was successfully obtained by the trap of carbocation in the polymerization of ethyl vinyl ether. Polymerization mechanism may involve the generation of proton and anionic platinum complex, which serve as initiator and counter anion, respectively. Further studies of detailed polymerization mechanism, stereospecific polymerization, and living polymerization are now in progress.

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