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In Situ and Readily Prepared Metal Catalysts and Initiator for Living Cationic Polymerization of Isobutyl Vinyl Ether: Dual-Purpose Salphen as a Ligand Framework for $ZrCl_4$ and an Initiating Proton Source

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A salphen complex [salphen = *N,N'-o*-phenylene-bis(3,5-di-*tert*-butyl-salicylidene-imine)], synthesized in situ by mixing a salphen ligand with a metal chloride is shown to be an effective catalyst in cationic polymerization for the first time. Furthermore, The salphen/$ZrCl_4$ system induced the living cationic polymerization of isobutyl vinyl ether proceeded in toluene at 0 °C with quantitative initiation from the HCl simultaneously generated upon the complex formation.

The expansion of the scope of substrates or monomers in organic reactions or polymerization, respectively, is often sparked by the development of new metal catalysts with well-designed ligands. For example, various elaborately designed polymerization catalysts have enhanced tolerance towards polar groups and catalytic activity, widening the choice of polymerizable monomers in the field of olefin metathesis polymerization[1,2], transition metal-catalyzed living radical polymerization or ATRP[3–5], and the coordination polymerization of polar vinyl monomers[6-8]. This explosive growth in precise organic synthesis and polymerization can be attributed to the variable and/or controllable activity of metal complex catalysts with various carefully designed ligands. Their diverse activity is attained by tuning the electron density of the central metals and/or the redox potential of the complexes through the interaction of the designed ligands with the central metals.

The rather limited scope of monomers in cationic polymerization for high polymers may be improved if well-defined metal catalysts with various ligands are available. A distinct opportunity for the utility of designed metal complexes as catalysts in cationic polymerization was shown by our recent development of initiating systems for base-assisting living cationic polymerization. These systems consist of a metal halide and an externally-added base, the interaction of which is key to successful living polymerization[9]. Among various combinations, an alcohol or acetylacetone with an appropriate metal halide permitted in situ ligand exchange, generating a real catalytic species inducing living polymerization[10,11]. These results encouraged us to pursue the goal of designing metal complex catalysts for precise polymer synthesis using cationic polymerization. Despite the potency of metal complex catalysts, catalyst design using various ligands has been limited in cationic polymerization[9,12,13], although ligand design or in situ complex formation was demonstrated to be effective for achieving the stereoselective cationic polymerization of alkyl vinyl ethers[14] or styrene derivatives[15,16].

The difficulty in the use of metal-complex catalysts for cationic polymerization lies in maintaining sufficient catalytic activity with a highly nucleophilic ligand and/or preventing the termination. In fact, the amount of nucleophilic additive is a decisive factor for controlled polymerization, particularly when an ammonium salt or an amine/amide compound is employed as the additive[17–19]. The polymerization is readily inhibited by an excess of such relatively strong nucleophilic additives, even if their absolute concentration is very low. In addition, our previous study showed that an alkoxy group on certain Lewis acid catalysts dissociates from the central metal to react with the propagating carbocation[10]. Hence, catalyst design to date in this field has focused on relatively simple compounds containing alkoxy or phenoxy groups[10,11,14,20].

To circumvent the abovementioned problems, the use of a Schiff base ligand would be effective because the chelating effect of the ligand is expected to suppress any ligand exchange reactions that might lead to the deactivation of the polymerization. Furthermore, a family of Schiff base ligands, known as one of the most useful ligands, can coordinate with many different metals[21,22], yielding catalysts capable of achieving a variety of synthetic transformations. In particular, various transition metals are available for complex

Table 1. Cationic polymerization of IBVE using the salphen/MCl_n initiating systems[a]

entry	MCl_n	temp (ºC)	time	conv (%)[c]	$M_n \times 10^{-3}$ (calcd)[d]	$M_n \times 10^{-3}$ (obs)[e]	M_w/M_n[e]	*meso* dyad (%)[f]
1	$ZrCl_4$	0	18.5 h	98	7.6	7.3	1.15	66
2		60	2.5 h	94	7.2	5.0	1.18	59
3		30	7 h	99	7.6	7.4	1.16	62
4		–30	98 h	96	7.4	8.9	1.37	70
5		–78	1410 h	59	1.5	3.2	1.49	75
6[b]		0	2 h	82	6.3	7.3	1.26	61
7	$SnCl_4$	0	20 min	94	7.3	10.5	1.37	65
8	$FeCl_3$	0	5 s	90	7.0	11.5	1.57	61
9	$ZnCl_2$	0	6 h	97	7.5	17.3	1.94	60
10	$TiCl_4$	0	168 h	12	0.9	n.d.	n.d.	n.d.
11	$AlCl_3$	0	430 h	2	0.2	n.d.	n.d.	n.d.

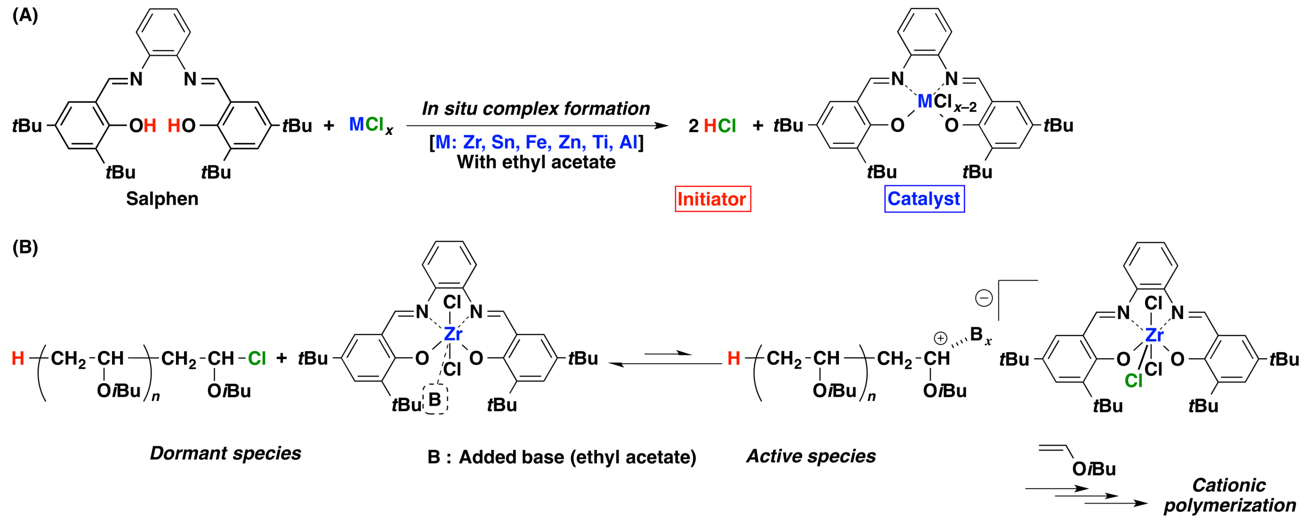
[a] $[IBVE]_0$ = 0.76 M, $[MCl_n]_0$ = 5.0 mM for entries 1–4 and 6–11, 15 mM for entry 5, [salphen ligand]$_0$ = 5.0 mM for entries 1–4 and 6–11, 15 mM for entry 5, [ethyl acetate] = 1.0 M, [heptane] = 5.0 vol % in toluene at 0 ºC. [b] In dichloromethane. [c] Determined by gas chromatography. [d] Calculated from concentration of salphen ligand[27]. [e] Determined by GPC (polystyrene standards). [f] Determined by ^{13}C NMR analysis (see Figure S4 for the spectra).

formation with Schiff base ligands, which permits the precise tuning of catalytic activity[23] based upon the unique properties of each transition metal. Another feature of the ligand is that the electronic and geometric characteristics of catalysts are readily adjusted[22,24] because Schiff base ligands are prepared by a condensation reaction between aldehydes and amines with various substituents. In this study, therefore, we examined catalyst design using a chelating Schiff base ligand for the cationic polymerization of a vinyl ether.

As a first step toward catalyst design, an in situ complexation method was investigated for catalyst modification using a salphen ligand [salphen = *N*,*N'*-*o*-phenylene-bis(3,5-di-*tert*-butyl-salicylideneimine)]. The salphen ligand, a tetradentate Schiff base ligand, is easily synthesized by the condensation of equivalent quantities of a specific salicylaldehyde and *o*-phenylenediamine. A salphen complex was synthesized simply by mixing the ligand and a metal chloride in dichloromethane, and the resulting solution was directly added to a monomer solution in toluene. In addition, the ligand performs another role: during complex formation, HCl is generated and can function as a protonogen, or an initiator, for the cationic polymerization of a vinyl ether.

The polymerization was conducted in toluene using an as-prepared salphen complex solution, obtained simply by mixing equivalent amounts of a metal chloride and a salphen ligand at 0 °C in the presence of ethyl acetate in dichloromethane (Scheme 1). The advantage of this method over a common, previously reported method[22] is the greatly facilitated synthetic procedure without purification and the in situ generation of toxic HCl as a proton source, as observed with the systems using alcohol or acetylacetone in conjunction with metal chlorides[10,11].

The choice of metal halide was crucial for achieving controlled polymerization. Among the metal halides examined, $ZrCl_4$ combined with the ligand catalyzed the polymerization in the best-controlled manner (Table 1, entry 1). The reaction proceeded quantitatively at a moderate rate[25] in a homogeneous system in the presence of ethyl acetate as an added base[26] in toluene at 0 °C. The obtained polymers had narrow molecular weight distributions (MWDs), which shifted toward higher molecular weight regions with increasing monomer conversion. It is noteworthy that their M_n values increased linearly along the theoretical line calculated based on the molar ratio of IBVE to the phenoxy groups in the salphen ligand[27] (Fig. S1†). These results also indicate the quantitative formation of the metal complex



Scheme 1. (A) In situ complex formation between the salphen ligand and a metal chloride and (B) polymerization mechanism of IBVE using the salphen/$ZrCl_4$ initiating system.

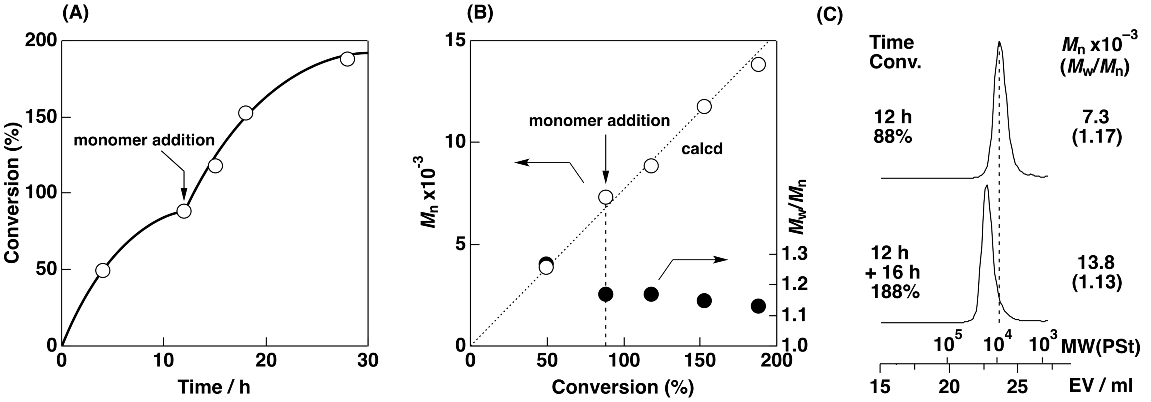


Fig. 1. (A) Time–conversion curves for the polymerization, (B) M_n (calculated M_n, dotted line) and M_w/M_n and (C) MWD curves for poly(IBVE)s obtained using the salphen/$ZrCl_4$ initiating system ($[IBVE]_0 = [IBVE]_{added} = 0.76$ M, $[ZrCl_4]_0 = 5.0$ mM, [salphen ligand]$_0$ = 5.0 mM, [ethyl acetate] = 1.0 M, [heptane] = 5.0 vol % in toluene at 0 ºC).

from the mixture of a salphen ligand and $ZrCl_4$ along with a protonogen to initiate polymerization (Scheme 1A). ^{1}H NMR analysis of the product polymer also showed the suppression of undesired side reactions[28,29] during the polymerization (Fig. S2†).

Several common metal chloride catalysts induced uncontrolled or no polymerization (Table 1, entries 7–11). The combination of $SnCl_4$, $FeCl_3$, or $ZnCl_2$ with the salphen ligand induced uncontrolled polymerization. The GPC profiles of the products obtained with these metal chlorides had broad MWDs with noticeable tailing. The M_n values of the polymers obtained from the salphen/$SnCl_4$ and $ZnCl_2$ systems increased linearly, although they were higher than the calculated values. The higher M_n values likely result from a smaller proton source concentration (HCl) due to insufficient complex formation. In sharp contrast, no polymerization occurred for the combination of the salphen ligand with $TiCl_4$ or $AlCl_3$. The inactivity is attributable to the absence of vacant sites that exhibit Lewis acidity on the central metals, as opposed to the Zr-salphen complexes [Zr(salphen)Cl_2], which have a labile coordination (a vacant) site because of their ability to form seven-coordinate structures[30–33] (Scheme 1B). Therefore, metal chlorides can be classified into three groups according to their polymerization behavior: catalysts inducing living/controlled polymerization mediated by living/long-lived species ($ZrCl_4$); uncontrolled polymerization ($SnCl_4$, $FeCl_3$, and $ZnCl_2$); and no reaction ($TiCl_4$ and $AlCl_3$).

To confirm the living nature of the polymerization with the salphen/$ZrCl_4$ initiating system, a monomer addition experiment was conducted under the optimized conditions. As shown in Fig. 1, after the addition of a fresh feed of the monomer, the MWD of the products shifted toward the higher molecular weight region with no original polymer remaining. A linear increase of the M_n values against the monomer conversion was also confirmed. Moreover, the ^{1}H NMR spectra of these polymers showed the quantitative generation of the terminal acetal group[34] and the undetectable undesired side reactions[28,29] (Fig. S3†). These results demonstrate the progression of living polymerization using the complex prepared in situ from salphen and $ZrCl_4$.

The stereoregularity of the product polymers was determined from the peaks of the methylene carbons of the main chains in the ^{13}C NMR spectra recorded in $CDCl_3$ (Fig. S4†). The *meso* dyad values of the polymer prepared with the examined salphen/MCl_n systems ranged from 60 to 66%, a range similar to the range obtained using simple metal halides as catalysts (61–67%)[14,35]. These results indicate that the direction of the insertion of the monomer molecules to the propagating carbocation is not affected by the steric hindrance around the catalysts produced by the salphen framework employed in the present study.

Table 1 also summarizes the polymerization results under various conditions, demonstrating the importance of temperature and the polarity of the solvent. The polymerization using this initiating system in toluene was examined at various temperatures (Table 1, entries 1–5). The polymerizations proceeded successfully even at higher temperatures (0–60 ºC), producing polymers with relatively narrow MWDs (Fig. S5†). However, the polymerization reactions at low temperatures (–30 and –78 °C) yielded polymers with broad MWDs and M_n values that were higher than the theoretical ones. The M_n of the polymers obtained at –30 °C and the linear first–order plots for the polymerization (Fig. S6†) indicated that the broadening of the MWDs was not attributable to undesired side reactions, but instead, to slow initiation reaction kinetics. The polymerization in dichloromethane at 0 °C quantitatively yielded a polymer with a unimodal, although slightly broader MWD (Table 1, entry 6). In addition, the M_n was higher than the theoretical values (Fig. S7†). The results obtained under various conditions demonstrate that the polymerization in toluene at 0 °C is most suitable for the salphen/$ZrCl_4$ system.

We examined the cationic polymerization of IBVE using an isolated salphen complex to confirm the occurrence of a quantitative, fast initiating reaction in the salphen/$ZrCl_4$ system. Because the HCl generated during the complex formation was also removed during solvent evaporation, the adduct of IBVE with HCl (IBVE–HCl) was used as a cationogen for polymerization. The cationic polymerization of IBVE using the isolated catalyst proceeded in a controlled manner in the presence of ethyl acetate in toluene at 0 °C (Fig. S8†). The obtained polymers were similar in molecular weight and MWD to the products prepared from the in situ prepared salphen complex system. This result supports the hypothesis that the salphen/$ZrCl_4$ initiating system, prepared in situ, led to quantitative complexation and a successive initiating reaction due to the generated HCl.

Conclusions

In conclusion, a well-defined metal complex was demonstrated to be effective for catalyzing the living cationic polymerization of an alkyl vinyl ether. The as-prepared salphen/ZrCl$_4$ complex induced the living cationic polymerization of IBVE in the presence of ethyl acetate as an added base in toluene at 0 °C. The use of tetradentate Schiff base ligands, which are easily tunable electronically and sterically, is expected to expand the available synthetic strategies for the precise control of cationic polymerization reactions, such as the adjustment of the catalytic activity and stereoselectivity of the catalyst. We are currently investigating polymerization reactions using various combinations of metal chlorides and salen ligands to reveal the relationship between the structure of the complex and its catalytic activity, especially by comparing the polymerization behavior of salphen and salen ligands, which will be reported in a forthcoming study.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental section and additional data. See DOI: 10.1039/c000000x/

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23 A polymerization using 2,6-diisopropylphenol and *o*-phenylenediamine with ZrCl$_4$ was conducted as a control experiment. The equimolar amounts of the three components were mixed to give a catalytic solution. The polymerization using the solution proceeded but the monomer conversion leveled off at around 30% (150 h, 31%). On the other hand, the reaction using 2,6-diisopropylphenol and ZrCl$_4$ without the diamine induced controlled polymerization in a manner similar to the polymerization using the alcohol/MCl$_n$ initiating system[10]. Thus, the superiority of the salphen complex over the catalysts with these model compounds is that both the electronic and geometric characteristics can be readily tuned because of the versatility of the ligand design and the multidentate ligation.

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25 In this system, it is difficult to tune polymerization rate without changing target molecular weights because the initiator and Lewis acid catalysts should be always mixed at the same concentrations.

26 An "added base" is a weak Lewis base that is used for living/controlled cationic polymerization. A weak Lewis base such as ethyl acetate, 1,4-dioxane, and THF controls the polymerization through its interaction with a Lewis acid catalyst, the propagating carbocation, and/or the counteranion.

27 The generated HCl during complex formation was employed as a protonogen, or an initiator, for the cationic polymerization of a vinyl ether. Hence, the theoretical M_n values were calculated based on the concentration of the generated HCl ($[HCl]_{theoretical}$ = 2 × $[\text{salphen ligand}]_0$ = 10 mM except for entry 5 or 30 mM for entry 5 in Table 1).

28 The product polymers had no irregular structures originating from undesired side reactions, such as β-proton elimination, dealcoholization, and the generation of aldehyde groups at chain ends[29], which was confirmed by ^{1}H NMR (Figure S2 and S3).

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34 The functionality of the terminal acetal group was determined from the peak integral ratio of the methyl proton of the initiating group (3H, peak a in Figure S3) and the methine proton of the end group (1H, peak g). The integral ratio a/g was 3.0/1.03, which indicates that quantitative functionality was achieved.

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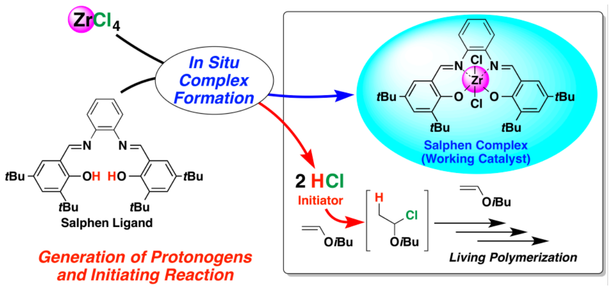

A well-defined catalyst, generated quantitatively in situ simply by mixing $ZrCl_4$ and a salphen ligand was shown to induce the living cationic polymerization of isobutyl vinyl ether.