Cationic Zinc Enolates as Highly Active Catalysts for Acrylate Polymerization

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Zinc enolates are important reagents widely employed in organic synthesis because of their desired features that combine admirable reactivity with functional group tolerance.[1] A recent stride in structural characterizations of a series of discrete zinc enolate complexes[2] has provided much needed structural information for a fundamental understanding of behavior and further exploration in catalytic reactions of zinc enolates. There is also growing interest in the utilization of discrete zinc complexes for ring-opening polymerization of heterocyclic monomers such as epoxides and lactides;[3] however, to the best of our knowledge, there were no prior open literature reports on the use of *discrete zinc enolates* for polymerization of any monomers.[4]

Group 4 metallocene enolates, upon treatment with suitable activators, are highly effective catalysts/initiators for the controlled/living polymerization of *methacrylates*.[5] They are poor catalysts, however, for the polymerization of *acrylates* (containing active α-H) owing to the presence of facile chain-termination processes through the key back-biting cyclizations involving the activated antepenultimate ester group of the growing polymer chain; thus, only a monomer conversion of 47% can be achieved at room temperature even with a high catalyst loading of 1.0 mol % to monomer.[6] This crucial limitation of these early transition metallocene enolate-based catalysts in acrylate polymerization prompted us to investigate other discrete metal enolates for effective acrylate polymerization and ultimately led us to the structurally characterized binuclear zinc enolate complexes **1−4** supported by the dibenzofuran bis-(amidoamine) ligand (Scheme 1). Communicated herein are the three most remarkable features about this polymerization system: (a) generation and structural characterization of the unprecedented cationic zinc enolate, (b) a novel activation mode involving the use of B(C₆F₅)₃, and (c) high activity and the ability to produce high molecular weight ($M_n = 5.40 \times 10^5$ g/mol; polydispersity index, PDI = 2.15) poly(*n*-butyl acrylate) with a catalyst loading as low as 0.02 mol %.

Control runs using either neutral zinc enolate complexes (**1** and **2**) or the activator B(C₆F₅)₃ under our catalyst screening conditions ([monomer]/[catalyst] = 200, 23 °C, 2 h) showed no activity for polymerization of *n*-butyl acrylate (*n*-BA). However, the mixing of **1** with 1 equiv of B(C₆F₅)₃ yielded a highly active polymerization system that achieved quantitative monomer conversions within 10 min for the [*n*-BA]/[**1**] ratios from 200 to 800 (entries 1−4, Table 1);[7] the polymerization was in fact complete within 5 min even for the 1000:1 ratio run (entry 5). Polymer M_n increases linearly with the [*n*-BA]/[**1**] ratio until it reached $M_n = 1.89 \times 10^5$ at the 800:1 ratio. All polyacrylates produced exhibit unimodal molecular weight distributions but with typical PDI values being in the range from 2.2 to 2.9, indicative of a nonliving polymerization. The high activity was not noticeably affected by the addition of the potent

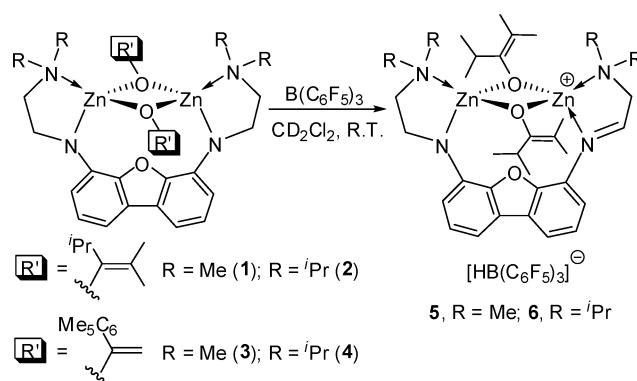† Colorado State University.
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Scheme 1

Table 1. *n*-BA Polymerizations in CH₂Cl₂ at 23 °C [B = B(C₆F₅)₃]

run no.	[*n*-BA]/[cat]	catalyst	time (min)	conversion[a] (%)	M_n[b] (kg/mol)	PDI[b] (M_w/M_n)
1	200	**1**/B	10	100	58.6	2.61
2	400	**1**/B	10	100	85.3	2.39
3	600	**1**/B	10	100	149	2.76
4	800	**1**/B	10	100	189	2.75
5	1000	**1**/B	5	100	172	2.87
6	1000	**1**/2B	2	100	200	2.96
7	5000	**1**/B	180	60[c]	540	2.15
8	5000	**1**/2B	60	56[c]	453	2.26
9	1000	**5**	10	100	185	2.82
10	1000	**6**	10	100	203	2.59

[a] By ¹H NMR. [b] By GPC. [c] Halted stirring because of high viscosity caused moderate conversions under current conditions.

radical inhibitor galvinoxyl[8] (1 or 5 equiv), arguing against involvement of possible radical polymerization processes.

Subsequently, we examined effects of polymerization temperature, activator stoichiometry, and zinc enolate structure on polymerization characteristics. First, polymerizations at 0 °C are similarly rapid,[7] but the resulting polyacrylates have considerably higher M_n than those produced at 23 °C (e.g., 3.16×10^5 at 0 °C vs 1.89×10^5 at 23 °C for the 800:1 ratio runs). Second, use of 2 equiv of B(C₆F₅)₃ to complex **1** renders more rapid polymerization than that using just 1 equiv of the borane (entry 6 vs 5, 8 vs 7). Remarkably, the polymerization with a low catalyst loading of only 0.02 mol % (the 5000:1 ratio) produces high M_n polymer of 5.40×10^5 g/mol with the smallest PDI of 2.15 (entry 7). Third, zinc enolate **2**, upon activation with 1 equiv of B(C₆F₅)₃, is also highly active, achieving quantitative monomer conversions within 10 min for the [*n*-BA]/[**2**] ratios from 200 to 1000, but the polyacrylates obtained exhibit ∼10 to 35% higher M_n than those produced by **1**,[7] reflecting modulation of the R groups at the amine *N* atoms on the electrosteric feature of the zinc center. Complexes **3** and **4** bearing the enolate moiety derived from permethylated acetophenone, when activated with B(C₆F₅)₃, are ∼ 30-fold less reactive than the active species
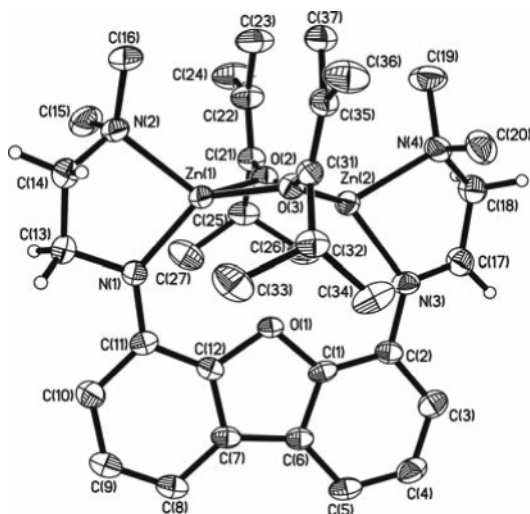
Figure 1. Structure of **5**. Hydrogens at the $C_2H_4(H_3)$ linkers are shown, while other hydrogens and the $[HB(C_6F_5)_3]^-$ anion are omitted for clarity.

derived from zinc enolates **1** and **2**,[7] presumably owing to relative nucleophilicity of the alkyl versus aryl enolate moieties.

To probe the structure of the active species, we investigated the reaction of zinc enolates **1** and **2** with $B(C_6F_5)_3$ (1 and 2 equiv). Thus, mixing of colorless **1** (or **2**) with 1 equiv of $B(C_6F_5)_3$ in CD_2-Cl_2 immediately yielded dark red ion pair **5** (or **6**) as a result of instantaneous apparent hydride abstraction from the lower CH_2 group in the C_2H_4 sidearm linker by the borane,[9] Scheme 1. The solution structure of the active species can be inferred from the following five most characteristic NMR changes/features observed during the reaction of **1** with $B(C_6F_5)_3$: (a) the time-average symmetry in solution is lowered from C_{2v} (**1**) to C_s (the cation of **5**); (b) the enolate moieties remain intact, except for the anticipated changes in chemical shifts; (c) the upper CH_2 protons on the cation side are shifted to downfield by 1.24 ppm; (d) one of the lower CH_2 protons in the linker now appears at 8.88 ppm (t,$^3J_{HH}$ = 4.2 Hz, =CH), downfield shifted by 5.58 ppm, whereas the other becomes BH at 1.12 ppm (d,$^1J_{HB}$ = 6.6 Hz), upfield shifted by 2.18 ppm; and (e) the ^{19}F NMR spectrum of the anion $[HB(C_6F_5)_3]^-$[10] reveals a small chemical shift difference of <3 ppm $[\Delta(m,p\text{-}F)$ = 2.97 ppm in **5**] between the *para*- and *meta*-fluorines, indicating that the anion is not coordinated to the cation.[11] Activation of complex **2** with $B(C_6F_5)_3$ proceeds in the same fashion, yielding the cationic zinc enolate ion pair **6**. Both isolated **5** and **6** showed the same high activities (entries 9 and 10) as the in situ generated catalysts. The reaction of **1** with 2 equiv of $B(C_6F_5)_3$ gives the identical product **5** with the second equiv of the borane remaining in the solution, showing that a plausible dicationic zinc enolate species is not generated. Thus, the rate enhancement observed for the acrylate polymerization with 2 equiv of $B(C_6F_5)_3$ is attributed to monomer activation by excess of this Lewis acid. Interestingly, the reaction of **1** with 1 or 2 equiv of $Al(C_6F_5)_3$ gives a mixture of unidentifiable species with no indications for formation of ion pairs analogous to **5**. Consistent with this finding, the *n*-BA polymerization by **1**/$Al(C_6F_5)_3$ is ~100-fold less reactive than **5**, producing only low M_n polymer.

The molecular structure (Figure 1) of the active species **5** was confirmed by single-crystal X-ray diffraction, featuring ion pairs of the zinc enolate cation and the uncoordinated borate anion $[HB(C_6F_5)_3]^-$ (B–H = 1.07(3) Å). The cation portion consists of a pair of four-coordinate zinc centers in which the Zn–N dative bond lengths [Zn(2)–N(4) = 2.068(3), Zn(2)–N(3) = 2.036(2), and Zn(1)–N(2) = 2.078(3) Å] are longer than the covalently bound

one [Zn(1)–N(1) = 1.937(3) Å], thus giving a clear assignment of neutral Zn(1) and cationic Zn(2) centers. Accordingly, the newly formed N(3)–C(17) double bond length of 1.304(4) Å is distinctive of other N–C single bonds [1.434(4)–1.482(4) Å]. Metric parameters of the neutral zinc center in **5** compare well to those of **1**;[2] however, the Zn–O bonds at the cationic zinc enolate center are 0.05 Å (av) shorter than those of the neutral zinc center, resulting in an unsymmetrical Zn_2O_2 core. The whole tetradentate ligand set (ignoring the 4 Me's at N) presents a quasi-mirror plane [the least-square plane containing C(1) to C(14), C(17)–C(18), O(1), N, and Zn atoms was refined to Δ = 0.0734 Å], of which two O-bridging enolates are located at each side and oriented approximately perpendicular to the Zn–Zn axis. Overall, the ligand set strikes the right balance for providing stabilization and reactivity of the cationic active species resulted from the amido → imino transformation involving $B(C_6F_5)_3$.

Regarding the polymerization mechanism, it is tempting to suggest that monomer additions occur at the active, cationic site of the zinc enolate in which the datively bound, "axial like" amino *N* is displaced by monomer in the initiation step, embarking a coordinative-anionic addition polymerization as the acrylamide polymerization by the cationic metallocene enolates.[12] However, mechanistic details about this polymerization system are currently unknown, and our efforts are underway to address these issues.

In summary, we have generated the unprecedented cationic zinc enolates via the unique activation approach and utilized these species as highly active catalysts for the production of high molecular weight polyacrylates at ambient temperature.

Supporting Information Available: Experiment details and crystallographic data (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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