Preparation of Narrow Polydispersity Polycaprolactone Catalyzed by Cationic Zirconocene Complexes

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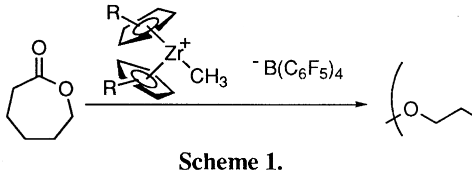
Various cationic zirconocene complexes effectively catalyzed polymerization of ε-caprolactone in a living fashion at ambient temperature to afford polycaprolactone possessing narrow molecular weight distribution (Mw/Mn = 1.06-1.3). The efficiency of the catalyst in the polymerization was enhanced by modifying the structure of cyclopentadienyl ligands.

Cationic group-4 metallocenes have been regarded as models of catalytic species involved in Ziegler-Natta olefin polymerization.[1] Recently these compounds have been reported to exhibit catalytic activities in synthetic reactions[2] and in polymerization other than simple α-olefins: for example, it has been reported that both *syndio*-[3] and *iso*-specific[4] polymerizations of methyl methacrylate (MMA) were effectively promoted. Alkyl lanthanocene having a similar electronic structure to the cationic zirconocene also behaved as effective catalyst in polymerizations of MMA and lactones as well as α-olefins.[5] In the case of lactones, polymerization proceeded in a living fashion; however, efficiency of the catalyst (E.C.)[6] did not reach sufficient levels. During the course of our study on chemical behavior of cationic zirconocene complexes, it was found that ring-opening polymerization of ε-caprolactone was quite smoothly catalyzed by these complexes in a living fashion. Also the ligand of the complexes was found to influence on reactivity and efficiency of catalyst in this polymerization.

Cationic zirconocene $Cp_2ZrMe^+B(C_6F_5)_4^-$ was generated by treating Cp_2ZrMe_2 (**1a**) with an equimolar amount of $Ph_3CB(C_6F_5)_4$ in the presence of 100 molar amount of ε-caprolactone. After stirring for a few hours at room temperature, polycaprolactone was isolated in a quantitative yield by usual work up.[7] Thus formed polymer was shown to possess high molecular weight (Mw = 38000) and very narrow molecular weight distribution (Mw/Mn = 1.06) by GPC analysis.[8] The linear correlation was also observed between molecular weight and initial molar ratio of monomer / catalyst. These results suggested that the polymerization proceeded in a living fashion with 30% calculated efficiency of the catalyst.



Scheme 1.

In order to examine the effects of the center metals and Cp ligands of various metallocenes on the polymerization of ε-caprolactone, the corresponding dimethyl complexes **1-6** were prepared according to the reported methods.[9] Dimethyl hafnocene **1b** catalyzed the polymerization as fast as zirconium complex **1a** though efficiency was not improved as shown in Table 1 (entries 1 and 2). Titanium complex **1c** has no catalytic activity in the polymerization of ε-caprolactone (entry 3).

Table 1. Polymerization of ε-caprolactone catalyzed by various group-4 metallocene complexes

Entry[a]	Complexes		Conversion / %	Mn (Mw/Mn)[c]
1	$Cp_2Zr(CH_3)_2$	**1a**	100	36000[d] (1.06)
2	$Cp_2Hf(CH_3)_2$	**1b**	100	36000[d] (1.08)
3	$Cp_2Ti(CH_3)_2$	**1c**	No Reaction[b]	

[a] Reaction conditions: monomer/**1** = 100; at room temperature; for 2 hours. [b] Reactions period was longer than 24 h. [c] Mw: weight-average molecular weight Mn: number-average molecular weight. [d] Efficiency of catalyst were calculated to 30%.

Efficiency of the catalyst was dependent on the structure of Cp ligands of zirconocene as shown in Table 2: that is, by using a complex **2** containing 1,3-dimethylcyclopentadienyl ligand, efficiency of the catalyst was slightly increased to 45%. When more sterically hindered complex **3** was used, efficiency of the catalyst reached 100% though the polymerizations rate was extremely decreased even at higher temperature (entry 4).

Based on the results, it was considered that a complex having both Cp and Cp* ligands would improve efficiency and polymerization rate at ambient temperature. Then, the complex $CpCp^*ZrMe_2$ (**4**) was synthesized from Cp^*ZrCl_3 and CpLi in two steps and polymerization of ε-caprolactone was examined. As expected, the polymerization proceeded quantitatively at room temperature with 100% of efficiency to afford polycaprolactone possessing narrow molecular weight distribution (entry 5). The complexes containing indenyl ligands, Ind_2ZrMe_2 (**5**), $Et(Ind)_2ZrMe_2$ (**6**), gave rather unsatisfactory results: lower conversion and efficiency. The polymerization mechanism of this catalyst system was assumed to proceed via cationic mechanism,[10] since oxetane, generally regarded to be polymerized via only cationic mechanism,[11] was readily polymerized also with this catalyst system. This finding suggests that the polymerizations proceed via the cationic mechanism and differ from anionic living ring opening polymerization promoted by several metal alkoxide complexes.[12] Further study on the mechanisms of the polymerization is now in progress.

Thus, a new function of cationic zirconocene complexes was demonstrated in polymerization of ε-caprolactone to produce polycaprolactone possessing narrow molecular weight distribution. Complex **4** was found to exhibit highest efficiency of catalyst and reasonable polymerization rate at ambient temperature.

References and Notes

1 For a recent review, see: R. F. Jordan, *Advances in Organometallic Chemistry*, **32**, 325 (1991).
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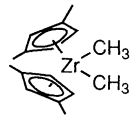
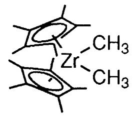
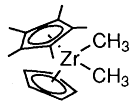
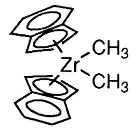
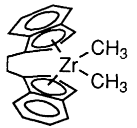
Table 2. Polymerization of ε-caprolactone with various zirconocene complexes

Entry[a]	Zirconcene complexes	Temperature / °C	Time / h	Conversion /%	Mn (Mw/Mn)[b]	E.C. /%[c]
1	$Cp_2Zr(CH_3)_2$ **1a**	RT	2	100	36000 (1.06)	30
2	 $Cp''_2Zr(CH_3)_2$ **2**	60°C	4	100	25000 (1.16)	45
3	 $Cp^*_2Zr(CH_3)_2$ **3**	RT	22	40	not determined	
4		60°C	6	88	9200 (1.31)	100
5	 $CpCp^*Zr(CH_3)_2$ **4**	RT	22	100	10000 (1.29)	100
6	 $Ind_2Zr(CH_3)_2$ **5**	RT	1.5	50	6200 (1.25)	88
7	 $Et(Ind)_2Zr(CH_3)_2$ **6**	RT	18	100	17000 (1.50)	66

[a] Reaction conditions; monomer / cat = 100. [b] Detemined by GPC analysis, detailed conditons were described in Ref. 8. [c] Efficiency of catalyst was calculated according to the equation in Ref. 6.

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6 Efficiency of the catalyst (E.C.) was defined as following equation; E.C. /% = Mn calcd./ Mn obs. "Mn calcd." means theoretical molecular weight, which can be simply calculated from the molecular weight of monomer, initial molar ratio of monomer / catalyst and conversion (see Ref. 12b). "Mn obs." is the molecular weight (Mn) determined by GPC analysis described in Ref. 8. According to this equation, E.C. in the polymerization reported in Ref. 5b were estimated to be 20 - 50%.

7 A typical polymerization was carried out as follows: Toluene was freshly distilled under nitrogen over sodium. ε-Caprolactone was distilled over potassium hydride and stored under argon atmosphere. Polymerization was carried out under argon atmosphere in a two necked round-bottomed flask equipped with a magnetic stirrer and a rubber septum. To a suspension of 62.6 mg (0.068 mmol) of triphenylmethyl tetra(pentafluorophenyl)borate in 2.7 ml toluene was added 0.72 ml ε-caprolactone (6.8 mmol) at room temperature. Then 0.68 ml of 0.1 M solution of **1a** (0.068 mmol) in toluene was injected. After stirring for 2 h, the reaction mixture was diluted with methylenechloride and the organic layer was washed with 1M HCl, sat. $NaHCO_3$, then brine. The organic layer was dried over Na_2SO_4, evaporated and dried under high vacuum.

8 GPC analysis: Waters, μStyragel columns 10^3 and 10^4 Å at 40 °C using THF as the solvent and calibrated with polystyrene standard samples. The observed molecular weight by GPC analysis, indicating not exactly absolute molecular weight, would closely correspond with absolute value. For the present purpose of discussing the tendency of E.C., molecular weight by GPC analysis would be valid as "observed molecular weight".

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