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Ring-Opening Polymerization of ε-Caprolactone Catalyzed by Titanocene and Zirconocene Alkyne Complexes

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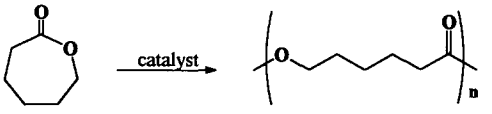
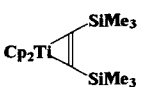
Abstract: Various zirconocene and titanocene complexes **1 - 8** effectively catalyze the polymerization of ε-caprolactone in a nearly living fashion at ambient temperature to afford poly-ε-caprolactone. The highest T.O.N. of 8000 was obtained at 70 - 75°C with the agostic complex **8**. © 1997 Elsevier Science Ltd.

Ring-opening polymerizations of lactones provide a convenient route to polyesters which are of interest for a variety of practical applications. ε-Caprolactone is one substrate that is currently under investigation in this regard, and recently group 4 transition-metal and lanthanoide complexes containing one or two cyclopentadienyl ligands (metallocenes) have emerged as a new class of initiators of these processes.[1] We report here, that crystalline and well defined zirconocene and titanocene alkyne complexes are capable of polymerizing ε-caprolactone in toluene with turn over numbers T.O.N. in the range of 2000 to 8000 (table).



Catalysts:



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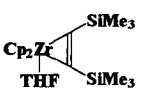

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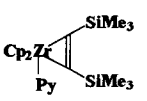

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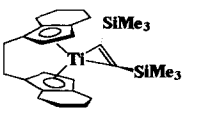
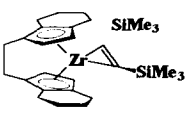
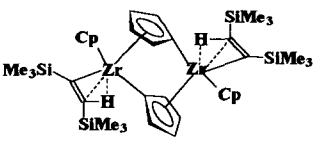


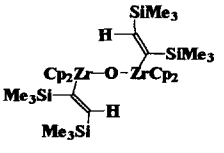
4[3]



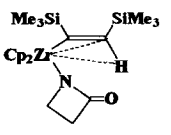
5[3]



6[2]



7[2]



8[4]

Polymerizations were carried out in an argon atmosphere with the complexes **1 - 8** (0.02 -0.04 mmol) in a 1:1 mixture of toluene and lactone (5 ml) with stirring for 10 min at 70 -75 °C; then further lactone (20 ml)

was added and after the reaction time (1 - 2 h), poly-ε-caprolactone was isolated as a white solid in a good yield by usual work up[5] (table).

Table. Polymerization of ε-caprolactone with various metallocene alkyne complexes

catalyst	reaction time (h)	yield (%)	T.O.N.
1	1	86	4400
2	1	10	280
3	1	82	4200
4	2	0	0
5	1	56	1800
6	1	84	3800
7	1	20	1500
8	1	88	8200

The polymer produced with catalyst **3** was shown to possess a very high molecular weight (M_w = 73 000) and a narrow molecular weight distribution (M_w/M_n = 1.4) by GPC analysis. The white solid becomes in the range of 80 - 100 °C clear and highly viscous.

The highest number of 8000 catalytic cycles per mol catalyst per hour showed the zirconocene lactam complex **8** which has an agostic H atom.
Good activities were also obtained with **3** and the analogous *ansa*-metallocene complex **5**.
In the reaction of **3** or **5** with ε-caprolactone as the first step a coupling of the alkyne with the lactone is observed. **3** forms a coupling product which is not stable at room temperature and reacts with further lactone under ring-opening polymerization. In the case of the analogous *ansa*-metallocene complex **5** at room temperature a stable complex was isolated and characterized by spectral methods and crystal structure analysis.[6]
The corresponding titanocene complexes **1** and **4** show great differences, while **1** turns over 4400 cycles, in the case of the *ansa*-metallocene complex **4** no catalytic activity was obtained and no polymer could be isolated.

The work is in progress to expand the polymerization capability of metallocene alkyne complexes to other heterocyclic substrates as well as substituted olefins.

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