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ORIGINAL PAPER

Novel triazole-based aluminum complex for ring-opening polymerization of lactones

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Abstract Novel triazole-based aluminum complex $\{O,O'$-[4,5-P(O)Ph$_2$tz]-AlMe$_2$ was studied as the catalyst for the ring-opening polymerization of caprolactone (ε-CL) in chlorobenzene. In the presence of methanol, isopropanol, and bifunctional poly(ethylene glycol), the catalytic system produced polymers with high conversion (81–85 %) but broader distribution ($M_w/M_n = 1.5$–1.8). The system of catalyst and benzyl alcohol produced relative monodisperse PCLs ($M_w/M_n \sim 1.2$) with defined molecular weight at 1/1ratio, 60 °C and an initial concentration of ε-CL equal to 0.5 mol/L.

Keywords Aluminum · Polycaprolactone · Ring-opening polymerization

Introduction

Biodegradable and biocompatible aliphatic polyesters have played a leading role in specialty biomedical and pharmaceutical polymer applications such as resorbable implant materials and drug delivery systems (DDS) namely since the control of their degradation rate through the composition and processing can be realized [1, 2]. From this point of view, the availability of suitable synthetic method producing polymers of the required molecular weight (according to monomer to initiator ratio) and defined chain end groups is of the utmost importance. Polymerization of di/lactones via ring-opening polyaddition (ROP) mechanism has been known as a

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synthetic strategy enabling fine tailoring the physico-chemical properties of polyester products [3]. Among important ROP initiators, aluminum alkoxides are particularly interesting especially because of their high selectivity, polymerization efficiency, and ability to produce the polyesters having both defined and predictable end groups. Besides classical coordination initiators based on aluminum isopropoxides [Al(O-i-Pr)$_3$] and bimetallic μ-oxo-alkoxides [4, 5] reported by Teyssié et al., a series of aluminum alkoxides (aryloxides) modified by ancillary ligands with various electronic and steric characteristics having a significant influence on the polymerization performance have been developed. Monodisperse polyesters were produced by monomeric [6] and dimeric Al complexes with O,O-bidentate ligands [7–9], (porfinato)aluminum alkoxides with N,N,N,N-donor atoms [10], Al complexes with O,N,N-tridentate [11], O,O,N-tridentate [12] or O,O,N,N-tetradentate ligands [13, 14], and phenoxyimine aluminum complexes with N,O-bidentate ligands [15–17].

The objective of our work was to study the polymerization behavior of a novel aluminum complex with O,O-bidentate ligand sphere; {O,O'-[4,5-P(O)Ph$_2$tz]-AlMe$_2$} denoted as **1** for ε-caprolactone polymerization.

Experimental

All manipulations were carried out under a dry nitrogen atmosphere (99.999%, Siad, CZ) using vacuum/inert manifold and standard Schlenk techniques. Chlorobenzene (p.a.) and ε-caprolactone (ε-CL) supplied by Lach-ner, CZ were purified with calcium hydride and freshly distilled prior to use. Anhydrous benzyl alcohol (BnOH, 99.8%), anhydrous methanol (MeOH, 99.8%), and anhydrous isopropanol (iPrOH, 99.5%) supplied by Aldrich, tetrahydrofuran (THF, p.a) supplied by Lach-ner, CZ, and deuterochloroform (CDCl$_3$, 99.8%) supplied by Isosar, CZ were used without further purification. Poly(ethylene glycol) 400 (PEG, bifunctional, $M_n = 400$, Fluka) was degassed at 130 °C for 8 h under vacuum prior to use.

{O,O'-[4,5-P(O)Ph$_2$tz]-AlMe$_2$} denoted as **1** was synthesized by Dr. Moya-Cabrera's group according to the published procedure [18].

Typical polymerization procedure

Polymerization reactions were carried out in a double-neck glass Schlenk flask (25 mL) with a magnetic stirring bar. To the flask containing the solution of aluminum complex **1** in chlorobenzene, the nucleophilic agent as benzyl alcohol (BnOH), methanol (MeOH), isopropanol (iPrOH), and poly(ethylene glycol) 400 (OH-PEG-OH) were added via microsyringe and the solution was stirred (600 rpm/min) for 30 min to form initiating species (I). The dosing for a particular run was as follows: **1** (31 μmol, 16 mg) and BnOH (31 μmol, 3.3 mg); **1** (42 μmol, 22 mg) and MeOH (42 μmol, 1.3 mg); **1** (23 μmol, 12 mg) and iPrOH (23 μmol, 1.4 mg), **1** (29 μmol, 15 mg) and OH-PEG-OH (29 μmol, 11.4 mg).

Afterward, a defined amount of ε-CL ([ε-CL]$_0$/[I]$_0$ = 200) was added keeping the ratio of solvent to monomer equal to 10 and the mixture was stirred at constant temperature (50, 60, and 70 °C). The polymerization reaction was quenched after the prescribed time (6, 8 h) by adding a few drops of an acetic acid solution. The polymerization mixture obtained was poured into cold methanol (−10 °C) and the white precipitate formed was collected by filtration and dried under vacuum until a constant weight was obtained. The crude product was purified three times by dissolving in THF and precipitating in cold methanol (−10 °C).

Polymer characterization

^{1}H NMR spectra of the polymers were measured in $CDCl_3$ on Bruker Avance 300 MHz equipment. The chemical shift was determined with respect to residual proton signals from $CDCl_3$. Gel permeation chromatography (GPC) was performed on Agilent Technologies 1100 Series instrument equipped with a refractive index (RI) detector, two PL gel Mixed columns 300 × 7.5 mm with particle size of 5 μm using THF as an eluent at a flow rate of 1 mL/min. Molecular weight and molecular weight distribution were calculated using a series of polystyrene standards ($M_p = 316500 - 162$).

Results and discussion

Within this work, we studied the catalytic efficiency of the novel triazole-based aluminum complex (**1**) for the ring-opening polymerization (ROP) of ε-caprolactone. A series of polymerization runs was carried out using **1** as the catalyst and different alcohols with well-known ROP initiator properties; methanol, isopropanol, benzyl alcohol, and the macroinitiator—bifunctional poly(ethylene glycol) at 60 °C in chlorobenzene. The ^{1}H NMR spectra of synthesized PCLs are presented in Figs. 1, 2, 3, 4.

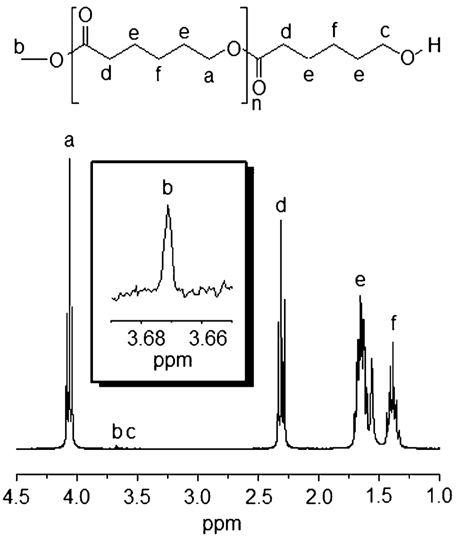


Fig. 1 ^{1}H NMR spectrum of PCL produced by **1**/MeOH in $CDCl_3$; polymerization conditions: 60 °C, chlorobenzene, 8 h. P(ε-CL) $\delta = 1.37$ ppm [m, 2H, ($-CH_2-$)], $\delta = 1.64$ ppm [m, 4H, ($-CH_2-$)], $\delta = 2.30$ ppm [t, 2H, ($-CH_2CO-$)], $\delta = 3.62$ ppm [t, 2H, ($-CH_2OH$)], $\delta = 3.67$ ppm [s, 2H, (CH_3O-)], $\delta = 4.05$ ppm [t, 2H, ($-CH_2O-$)]

Fig. 2 ^{1}H NMR spectrum of PCL produced by **1**/iPrOH in $CDCl_3$; polymerization conditions: 60 °C, chlorobenzene, 8 h. P(ε-CL) $\delta = 1.15$ and 1.17 ppm [s, 6H, (CH_3–)], $\delta = 1.31$ ppm [m, 2H, (–CH_2–)], $\delta = 1.58$ ppm [m, 4H, (–CH_2–)], $\delta = 2.24$ ppm [t, 2H, (–CH_2CO–)], $\delta = 3.58$ ppm [t, 2H, (–CH_2OH)], $\delta = 4.00$ ppm [t, 2H, (–CH_2O–)]

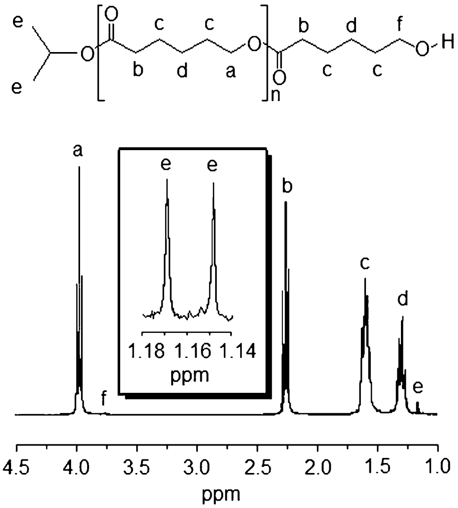
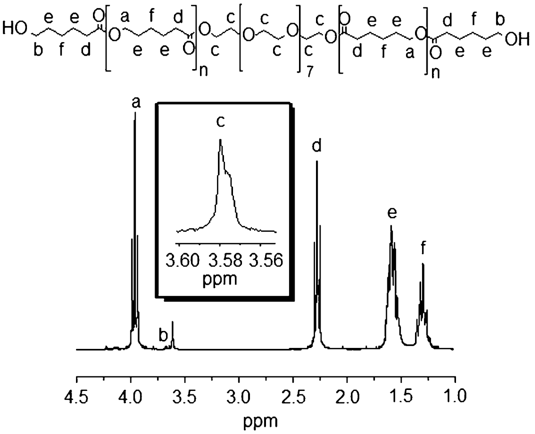


Fig. 3 ^{1}H NMR spectrum of PCL produced by **1**/PEG(400) in $CDCl_3$; polymerization conditions: 60 °C, chlorobenzene, 8 h. P(ε-CL) $\delta = 1.31$ ppm [m, 2H, (–CH_2–)], $\delta = 1.58$ ppm [m, 4H, (–CH_2–)], $\delta = 2.23$ ppm [t, 2H, (–CH_2CO–)], $\delta = 3.57$–3.59 ppm [4H, (–CH_2O–)], $\delta = 3.74$ ppm [t, 2H, (–CH_2OH)], $\delta = 4.00$ ppm [t, 2H, (–CH_2O–)]



Based on the results obtained (Table 1), one can suggest that the influence of the steric hindrance of a particular alkoxide ligand, has a significant impact on the activity of catalytic species, compared to its electronic contribution as a Lewis acidic center. Thus, both **1**/MeOH and **1**/iPrOH formed effective ROP catalytic systems with the monomer conversion of 81–88% after a polymerization period of 8 h. For **1**/OH-PEG-OH, a prolonged period of 20 h was necessary to reach a comparable conversion of 85 %. Based on well correlation between theoretical and experimental molecular weight, we can suggest the participation of both hydroxylic end groups of PEG during the initiation of ROP. The presence of the phenyl ring close to the polymerization active center of the **1**/BnOH probably led to poorer access of monomer molecules resulting in both the decrease of the polymerization rate as well as the inhibition of side reactions.

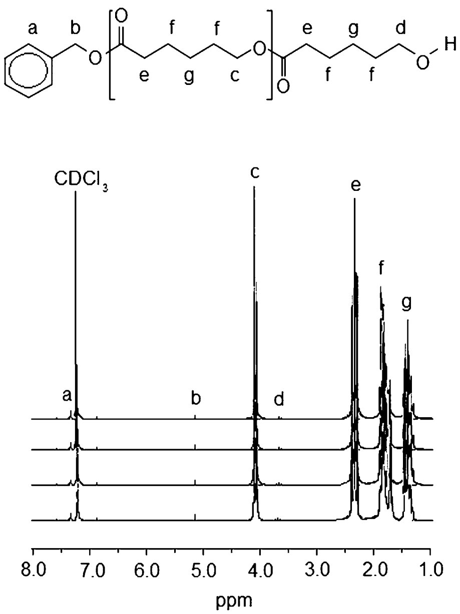


Fig. 4 ^{1}H NMR spectrum of PCL produced by **1**/BnOH in CDCl$_3$; polymerization conditions: 60 °C, chlorobenzene, 8 h. P(ε-Cl) $\delta = 1.27$ ppm [m, 2H, (–CH$_2$–)], $\delta = 1.63$ ppm [m, 4H, (–CH$_2$–)], $\delta = 2.29$ ppm [t, 2H, (–CH$_2$CO–)], $\delta = 4.05$ ppm [t, 2H, (–CH$_2$O–)], $\delta = 3.63$ ppm [t, 2H, (–CH$_2$OH)], $\delta = 5.10$ ppm [s, 2H, (–CH$_2$OBn)], $\delta = 7.25$ ppm [s, CDCl$_3$]

Moreover, the triazole-based aluminum complex **1** produced the polymer ($M_n = 25{,}000$, $M_w/M_n = 1.5$) in 6 h of polymerization performed under identical conditions even in absence of alcohol initiator. However, the yields were very low (of about 3–5%) with poor reproducibility, hence chain end-group NMR analysis was not carried out. Most probably, the monomer insertion took place either in a small portion of the aluminum-carbon(methyl) bonds or in Al–O bond of the ligand sphere, which has been already reported for some complexes [19].

Furthermore, polymerization study focused on the promising system of benzyl alcohol along with **1** as catalyst was performed in order to find the best conditions for producing polymers with the well-defined molecular weight (consistent with monomer to initiator ratio), predicted end groups, and a relative narrow polydispersity ($M_w/M_n \leq 1.2$).

The ^{1}H NMR spectra of the PCLs (Fig. 4) synthesized using ratio of **1**/BnOH = 1/1 (Table 1) confirmed the presence of the methylene signals from both benzylalkoxyl ($\delta = 5.1$ ppm) and hydroxyl ($\delta = 3.63$ ppm) chain ends, which correlate well with the expected character of active species. Thus, we assumed that the initiation step proceeds through a monomer insertion into the Al–O bond of the aluminum benzylalkoxide intermediate, which is formed "in situ" with the concomitant evolution of methane (Fig. 5). Monomer molecules are subsequently cleaved in a way that maintains the growing chains having benzylalkoxide dead end attached to the aluminum atom through an alkoxide bond. Consequently, the quenching of these aluminum active bonds by hydrolysis results in the hydroxyl end group.

Regarding the discrepancy between the actual values of molecular weights of the polyesters and those determined by GPC using polystyrene standards, ^{1}H NMR

Table 1 Screening of ROP efficiency of **1**

Run	ROH	*t* (h)	Yield[a] (%)	M_n[b] (GPC)	M_n[c] (NMR)	M_n[d] (Theor.)	M_w/M_n (GPC)
1	MeOH	8	88	53,000	25,000	20,000	1.8
2	iPrOH	8	81	42,000	16,000	18,000	1.7
3	OH-PEG-OH	20	85	37,000	25,000	20,000	1.5
4[e]	BnOH	8	60	26,000	11,000	14,000	1.3
5[e]	BnOH	8	66	24,000	11,000	15,000	1.2
6[e]	BnOH	8	67	25,000	15,000	15,000	1.2
7[e]	BnOH	8	67	24,000	9,000	15,000	1.2

Polymerization conditions: $T = 60$ °C, chlorobenzene, $[\varepsilon\text{-CL}]_0 = 0.7$ mol/L, $[1]_0/[\text{ROH}]_0/[\varepsilon\text{-CL}]_0 = 1/1/200$

[a] Isolated yield

[b] GPC values according PS standards

[c] M_n value was estimated by the ^{1}H NMR spectrum based on the intensity of the methylene protons at the PCL chain ($\delta = 4.05$ ppm) and that of protons derived from BnOH ($\delta = 5.10$ ppm) according to the equation: $M_n(\text{PCL}) = [(c/b + 1) \times M(\varepsilon\text{-CL})] + M(\text{BnOH})$, where *c* and *b* are the integral intensities of peaks at 4.05 ppm and 5.1 ppm, respectively. In case of $\text{PCL}_n/\text{PEG}_9/\text{PCL}_n$ copolymer, the presence of one PEG molecule per one copolymer molecule was assumed. In one PEG monomer unit ($–\text{CH}_2–\text{CH}_2–\text{O}–$), there are four hydrogens, so the total number of hydrogens per one PEG molecule with polymerization degree equal to 9 was calculated to be 36. Consequently, the signal integral for methylene protons of PEG ($\delta = 3.58$ ppm) was set to represent 36 hydrogens. The intensity of the methylene protons at the PCL chain ($\delta = 4.00$ ppm) was used to calculate relative number of PCL protons (2n) per one $\text{PCL}_n/\text{PEG}_9/\text{PCL}_n$ copolymer molecule. Since the intensity signal at $\delta = 4.00$ ppm is related to only two hydrogens, the ratio of signal integrals should be multiplied by 18 instead of 36. Molecular weight of the copolymer was calculated according to the equation $M_n(\text{PCL/PEG/PCL}) = [(a/c \times 18) \times M(\varepsilon\text{-CL})] + M(\text{PEG})$, where *a* and *c* are the integral intensities of peaks at 4.00 and 3.58 ppm, respectively

[d] Calculated from initial molar ratio $[\varepsilon\text{-CL}]_0/[\text{ROH}]_0 \times 114.15 \times$ conversion yield, considering one active alkoxide (RO-) group per Al complex. In case of OH-PEG-OH, the theoretical molecular weight of triblock copolymer was calculated using the same equation, since the composition at quantitative conversion is expected to be $\text{PCL}_{100}/\text{PEG}_9/\text{PCL}_{100}$

[e] $[\varepsilon\text{-CL}]_0 = 0.5$ mol/L

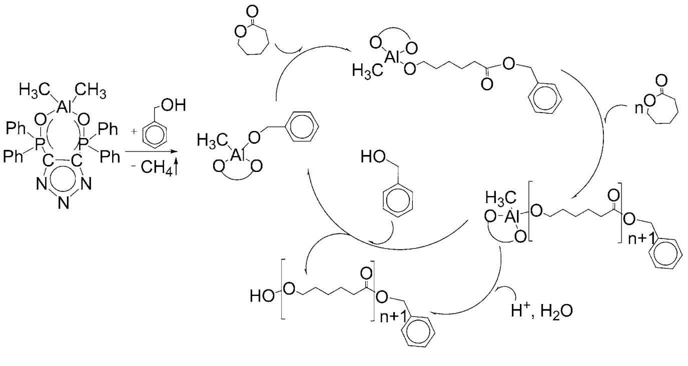


Fig. 5 Suggested mechanism for the ROP initiated by **1**/BnOH system

spectra of the PCLs synthesized under identical conditions (60 °C, chlorobenzene, 8 h, $[\varepsilon\text{-CL}]_0 = 0.5$ mol/L) were used as well to determine their actual chain lengths (Fig. 4). By comparison of M_n values obtained using GPC and those calculated from certain intensities of the proton signals of PCL in NMR spectra [19], the correction factor of 0.58 was estimated. Consequently, the values of M_n (GPC) of the PCLs produced were multiplied by this factor to give the actual values denoted as M_n (corr).

The evaluation of data from the runs performed simultaneously at the same conditions (runs 4–7 in Table 1) confirmed a high reproducibility of PCL yields, which was estimated to be of about 3%. However, the deviations of values of molecular weight and polydispersity index determined by GPC method could be ascribed to its accuracy.

To understand better the role of BnOH in the polymerization system, the different ratios to **1** (0.5 and 2 equiv. to Al) were examined (see in Table 2). In the case of the 0.5/1.0 ratio of BnOH/**1**, PCLs were obtained in high yield (92–93 %) after 6 and 8 h of polymerization (runs 4 and 5, respectively, in Table 2). The increase in polydispersity ($M_w/M_n \geq 1.6$) can be ascribed both to the occurrence of side reactions at high monomer conversions and to the participation of different active species in the polymerization process. The aluminum complex **1** which was in excess, could participate on the polymer chain growth along with the **1**/BnOH initiating system.

On the other hand, the polymerization with two equivalents of BnOH to **1** (Run 5 in Table 2) produced PCL in a low yield of only 21%. Taking into account the good correlation between the theoretical and experimental molecular weights (calculated according to the ratio of $[\varepsilon\text{-Cl}]_0/[\text{BnOH}]_0$), we can suggest the benzyl alcohol functions as a chain transfer agent. Reversible exchange of growing polymer chain between BnOH and active aluminum-alkoxide center resulted in participation of all

Table 2 Effect of the Al-complex (**1**) to BnOH ratio

Run	$[1]_0/[\text{BnOH}]_0/[\varepsilon\text{-CL}]_0$	t (h)	Yield[a] (%)	M_n[b] (GPC-corr)	M_n (NMR)	M_n[c] (Theor.)	M_w/M_n (GPC)
1	1/0/200	6	3	15,000	n.a.	–	1.5
2	1/1/200	6	45	11,000	9,000	10,000	1.2
3	1/1/200	8	67	15,000	14,000	15,000	1.2
4	2/1/200	6	92	12,000	17,000	21,000	1.6
5	2/1/200	8	93	15,000	n.a.	21,000	1.7
6	1/2/400	6	37	6,000	n.a.	8,000	1.1
7	1/2/400	8	21	3,000	4,000	5,000	1.4

Polymerization conditions: $T = 60$ °C, chlorobenzene, $[\mathbf{1}]_0 = 0.003$ mol/L, $[\varepsilon\text{-CL}]_0 = 0.5$ mol/L

[a] Isolated yield

[b] Corrected values in the brackets obtained according to the equation $M_n(\text{Corr}) = 0.58 \times M_n$ (GPC)

[c] Calculated from initial molar ratio $[\varepsilon\text{-CL}]_0/[\text{BnOH}]_0 \times 114.15 \times$ conversion yield, considering one active benzoxide group per Al complex

Table 3 Effect of polymerization temperature and initial concentration of ε-caprolactone

Run	T (°C)	[ε-CL]$_0$[a]	Yield[b] (%)	Mn[c] (GPC-corr)	M_n (NMR)	M_n[d] (Theor.)	M_w/M_n (GPC)
1	40	0.5	5	3,000	n.a.	1,000	1.1
2	50	0.5	23	6,000	8,000	5,000	1.2
3	60	0.5	45	11,000	9,000	10,000	1.2
4	60	0.7	72	16,000	12,000	17,000	1.4
5	60	1.4	99	23,000	n.a.	23,000	1.8
6	70	0.5	95	16,000	17,000	22,000	1.8

Polymerization conditions: initial molar ratio [ε-CL]$_0$/[Al]$_0$/[BnOH]$_0$ = 200/1/1, chlorobenzene, activation period 30 min, [**1**]$_0$ = 0.003 mol/L, t = 6 h

[a] Initial molar concentration of ε-caprolactone [mol/L]

[b] Isolated yield

[c] Corrected values in the brackets obtained according to the equation M_n(Corr) = 0.58 × M_n (GPC)

[d] Calculated from initial molar ratio [ε-CL]$_0$/[BnOH]$_0$ × 114.15 × conversion yield, considering one active benzyl alkoxide group per Al complex

BnOH molecules in ROP initiation. Furthermore, the overall polymerization rate decreased since the chain transfer reaction competed with the propagation step.

Moreover, the overall polymerization rate increased with the temperature (Table 3). Every temperature increase by 10 °C in the range of 50–70 °C resulted in almost a double increment with regard to the previous polymer yield. However, the polydispersity increase at 70 °C ($M_w/M_n = 1.8$) indicated possible occurring undesired transfer reactions. In the same manner, the increase on the original monomer concentration in the polymer mixture caused higher yields accompanied with lower control over the propagation step as expressed by a rise in the polydispersity (Runs 3–5 in Table 3).

The conditions during which relative monodisperse PCLs ($\sim$1.2) were synthesized were considered as 60 °C, initial concentration of ε-CL equal to 0.5 mol/L, and equivalent ratio of **1**/BnOH = 1/1. The subsequent polymerization experiments performed at selected conditions confirmed a living character of the process due to both a linear dependency of M_n on conversion and a relative narrow polydispersity of PCLs prepared (M_w/M_n = 1.2–1.3) (Fig. 6).

Regarding the synthesis of PCL with the lowest polydispersity index ($M_w/M_n = 1.1$) at 40 °C, we can expect the proceeding of polymerization process at 30 °C in the living manner as well. However, the polymerization period should be prolonged over 24 h to obtain yields comparable with those produced at higher temperatures.

On the basis of the results, ROP of ε-CL catalyzed by the novel aluminum complex **1** proceeded in a controlled manner with high catalytic efficiency under optimized conditions producing PCLs with defined molecular weight. The catalytic efficiency of **1**/BnOH for ROP of ε-CL at 60 °C and the excess of monomer of 200 to **1** estimated on the bases of [Mn(Theor.)/(Mn(NMR)] is close to 1, which is comparable with the efficiencies of aluminum amine bis(phenolates)/BnOH under similar conditions [12].

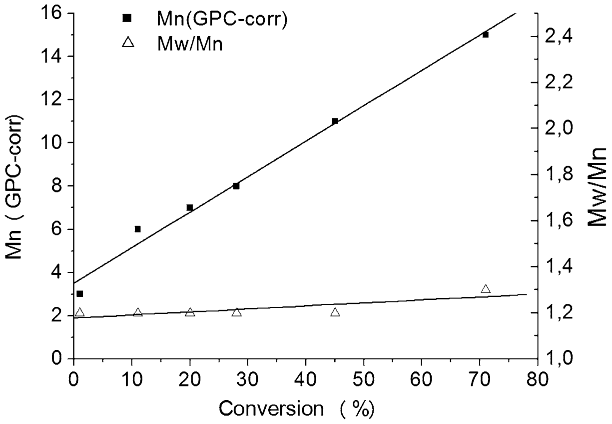


Fig. 6 The relationship between M_n (GPC-corr (*filled square*)) and its distribution (M_w/M_n) (*open triangle*) and the conversion for **1**/BnOH/ε-Cl = 1/1/200 system. Polymerization conditions: $[\varepsilon\text{-CL}]_0 = 0.5$ mol/L, chlorobenzene, 60 °C

Conclusions

In conclusion, an efficient system based on novel aluminum complex **1** and benzyl alcohol for ROP of ε-caprolactone was obtained. The living character of the polymerization process was supported by the low polydispersity index ($M_w/M_n = 1.2$) of the PCL at certain conditions. Further details of the character of active species and the relationship between the alkylgroup attached to the Al-complex and the alcohol are under investigation.

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