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New dialkylenetriamine zinc complexes as highly efficient ROP catalysts

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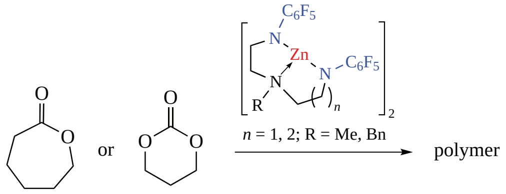
The reaction of $Zn[N(SiMe_3)_2]_2$ with *N*-alkyl-*N*-[ω-(pentafluorophenylamino)alkyl]-*N*-[2-(pentafluorophenylamino)ethyl]amines afforded new bicyclic zinc complexes. The complexes initiate ring-opening polymerization of ε-caprolactone and trimethylene carbonate to give the corresponding polymers with high molecular weight and satisfactory degree of polymerization.



highly active ROP initiators

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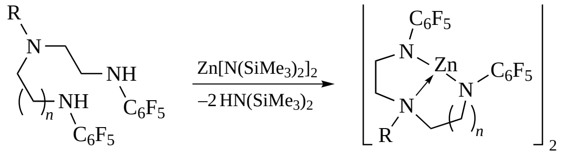
Preparation of biodegradable polymers (poly-ε-caprolactone, polylactide, polyglycolide and their copolymers) is an actual task of modern chemistry and chemical technology since these materials possess a broad range of useful properties.[1,2] One of the most suitable ways to synthesize the above polymers is ring-opening polymerization (ROP) with metal complexes as initiators.[3–12] Tin(II) 2-ethylhexanoate as a standard tin-based ROP initiator has disadvantages such as toxicity, the required temperature in technological processes, which is higher than 140 °C, or high degree of polymerization (DP) values of the resulting polymers.[13] Hence, search for new initiators free from these drawbacks is an actual task. Zinc complexes are among the most active ROP initiators and represent a good alternative because of their high Lewis acidity, low cost, accessibility and especially biocompatibility of zinc.[14,15]

The general requirement for ROP initiators with electron-deficient metal atoms is the presence of a ligand environment that, on the one hand, enables the initiator itself to be monomeric, since it is believed that it is this type of catalyst that provides controllable process together with the best polymer characteristics, and on the other hand, leaves a vacant space at the catalytic centre for the organic monomer molecule. Recent investigations revealed that sufficient conformational flexibility of the ligand was necessary for the efficient ROP.[14] On the contrary, excessive rigidity of the ligand retards the whole polymerization process.[16] Thus, the choice of appropriate ligand is crucial for the polymerization. For general structures of zinc complexes, which have shown promising results in the ROR,[14,17–21] *e.g.*, β-diketiminate type, see Online Supplementary Materials.

In our search of new active initiators we have chosen zinc derivatives based on dialkylenetriamines. These ligands allow variation of the Lewis acidity of the metal centre due to easy adjustment of substituents at nitrogen atoms, and are flexible enough to stabilize the convenient geometry for the polymerization of the monomer. The bulky C_6F_5 groups can provide both steric protection and increase the positive charge on zinc atom due to their acceptor properties. To the best of our knowledge, zinc complexes with diamido-amine ligands are scarce. Complex $[MeN(CH_2CH_2NSiMe_3)_2Zn]_2$ was studied in copolymerization of (D,L)-lactide with glycolide[18] and found to be active providing full conversion of the monomers at 180 °C for 3 h. For example, from 702 and 398 equivalents of lactide and glycolide, respectively, relative to catalyst, a polymer with $M_n = 39400$ and DP = 1.7 was obtained after 140 min. Nevertheless, a higher initiator activity is desirable for industry. Thus, zinc derivatives of diamido-amine ligands especially with electron-withdrawing groups represent promising catalytic systems for the ROP.

Herein, we present synthesis and characterization of new zinc-based ROP initiators with bulky substituted dialkylenetriamine ligands and their application as initiators of the ROP. Two dialkylenetriamine ligands **1a** and **1b** were synthesized according to known procedures,[22,23] whereas the new ones **1c** and **1d** were obtained in two steps similar to those reported for **1a** and **1b** (Scheme 1). To synthesize compounds **2a–d**, we used reaction between free ligands **1a–d** and zinc bis(trimethylsilylamide) to furnish the desired compounds in moderate to excellent yields (58–90%). The reaction was performed with heating except for compound **2a**. Complexes **2a–d** have low solubility in common organic solvents, and their ^1H, ^{13}C and ^{19}F NMR spectra were recorded in DMSO-d_6. We believe according to X-ray data for compex **2d** that compounds **2a–d** are



1a–d **2a–d**

a n = 1, R = Me (90%)
b n = 1, R = Bn (84%)
c n = 2, R = Me (67%)
d n = 2, R = Bn (58%)

Scheme 1 *Reagents and conditions*: PhMe, room temperature (for **2a**) or Δ (for **2b–d**).

dimeric, however, additional studies to prove this have not been performed.

To obtain a single crystal of compound **2d** for X-ray study, crystallization was performed from hot toluene. The structure comprises three crystallographically independent dimeric molecules, one on general position and two on two-fold axis, with close geometric parameters. We suggested that bulky C_6F_5 groups could prevent dimerization, but it was not the case. In all the independent dimeric molecules both zinc atoms are four-coordinated and each surrounded by four nitrogen atoms (Figure 1).† Analogous dimerization was observed for the reported zinc complex $[MeN(CH_2CH_2NSiMe_3)_2Zn]_2$ where the authors supposed its origin from the geometry enforced by the diamido-amine ligand.[18] In a similar manner, complex **2d** has a central rectangular $(Zn–N)_2$ four-membered ring. Note, that dimerization for this unsymmetrical complex occurs due to the binding of the nitrogen atom of the ligand longer arm to the zinc atom of another monomer unit. This correlates well with the greater stability of six-membered cycles compared with five-membered ones. Three types of Zn–N bonds are present in structure **2d**: for each zinc atom, they include the covalent bond with the tri-coordinated nitrogen atom N(12), the dative bond with the internal nitrogen atom of the ligand N(13), and two bonds in the fragment $(Zn–N)_2$, namely to N(11) and N(21), one formally dative and one formally covalent. The covalent Zn(1)–N(12) bond is the shortest of all those present in the three independent molecules (1.937–1.956 Å). Of interest, this bond is slightly longer than the Zn–N covalent bond in the zinc complex described (1.907 Å),[18] although according to Bent's rule this bond in structure **2d** should be shorter due to more electronegative character of nitrogen atom in the NC_6F_5 group compared with that in the $NSiMe_3$ one (see, for example, ref. 25). The dative bond Zn–N(13) is somewhat shorter (2.167–2.193 Å) than the analogous dative bond in the complex described (2.238 Å).[18] However, note the different nature of substituent at the internal nitrogen atom of the ligand, namely Bn one in complex **2d** and Me one in the previously described zinc complex. Other two Zn–N bonds are essentially the same and lie in the typical range for mixed dative and covalent bonds (2.061–2.120 Å). In addition to these bonds, each zinc atom has two weak interactions with fluorine atoms at the *ortho*-positions with *ca*. 2.8 Å distance. Probably, these contacts are the reason for bond lengths inconsistency to the Bent's rule pointed above. Coordination polyhedron of the zinc atoms is thus distorted octahedron (4 + 2). In general, Zn–N distances fall in the typical range for Zn–N bonds in complexes with an N_4 environment.[19,26–39] Some of these N_4-complexes turned out to be active in the ROP.[18,19,27,28]

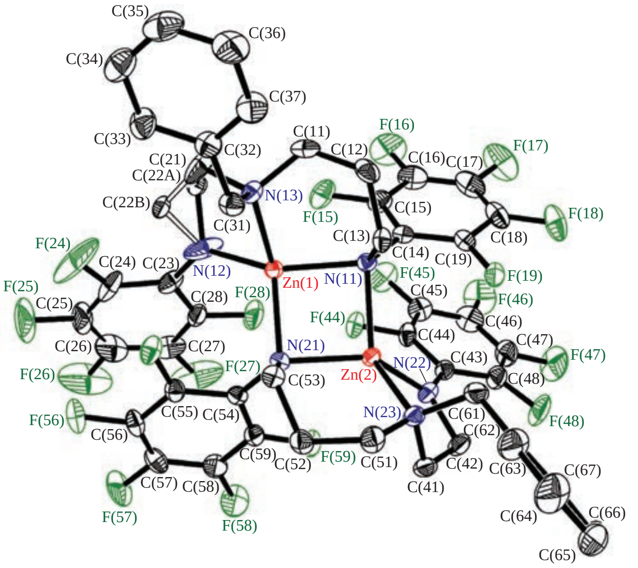


Figure 1 Molecular structure of complex **2d**. Only the molecule occupying general position is shown. Disordered CH_2 group is drawn by open lines. Hydrogen atoms are omitted for clarity.

To determine the potential application of prepared complexes in the ROP we tested compounds **2b** and **2d**, having different lengths of carbon chains in the ligand structure, in the ε-caprolactone (ε-CL) and trimethylene carbonate (TMC) polymerizations (Table 1). We have chosen the bulk conditions as the closest to the ones used in the industry and obtained encouraging results, namely conversion of > 99% was achieved at organic monomer–complex ratio of 105 : 1 at 95 °C after 0.5 h, the time of polymerization was not optimized. The initiators are highly active in the absence of co-initiators and chain-transfer agents such as alcohols. Possible mechanism of this type of process, namely polymerization without alcohols, has been discussed.[40] Polycaprolactone with high M_n and satisfactory DP values was obtained using compounds **2b** and **2d**. Further increase in the monomer–initiator ratio gave polymers with high molecular weight with retention of satisfactory DP < 2. The polymerization results suggest that there is no significant difference in activity between complexes **2b** and **2d** and therefore no influence of extra carbon atom in the ligand chain. Polymerization of TMC in the presence of complex **2d** at 1080 : 1 ratio was completed after 60 min resulting in polymer with molecular weight 26 000 and broad DP (2.46). These data allow us to consider the compounds synthesized as effective initiators for further synthesis of copolymers.

In conclusion, we have synthesized and characterized by NMR and XRD data four new zinc complexes containing diamido-amine ligands with acceptor substituents on terminal nitrogen atoms. To evaluate the potential of their use in ROP, we have performed polymerization of some monomers in bulk and found the zinc complexes essentially active.

Table 1 Polymerization of ε-CL and TMC using complexes **2b** and **2d** in bulk at 95 °C.

Complex	Organic monomer	Organic monomer to complex ratio	Time /min	Conversion (%)[a]	M_n[b]	DP
2b	ε-CL	105 : 1	30	> 99	16 900	1.82
2d	ε-CL	105 : 1	30	> 99	31 800	1.67
2b	ε-CL	320 : 1	30	> 99	50 500	1.75
2d	ε-CL	320 : 1	30	> 99	44 700	1.80
2d	TMC	1080 : 1	60	> 99	26 000	2.46

[a] Determined using NMR spectroscopy. [b] Determined by GPC with PMMA standards.

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† *Crystal data for* **2d**. $C_{55}H_{42}F_{20}N_6Zn_2$, M = 1297.69, monoclinic, space group $C2/c$, a = 45.7841(16), b = 18.6643(6) and c = 27.6537(9) Å, β = 118.2203(5)°, V = 20822.0(12) Å^3, Z = 16, d_{calc} = 1.656 g cm^{-3}, $F(000)$ = 10464, μ(MoKα) = 1.039 mm^{-1}, colourless plate with dimensions of *ca*. 0.40 × 0.22 × 0.04 mm. Total of 101359 reflections (22749 unique, R_{int} = 0.0380) were measured on a Bruker SMART APEX II diffractometer (graphite monochromatized MoKα radiation, λ = 0.71073 Å) using ω-scan mode at 150 K. The structure was solved by direct methods and refined by full matrix least squares using F^2 with anisotropic thermal parameters for all non-hydrogen atoms.[24] Methylene group $C(22)H_2$ was found to be disordered over to positions with occupancy ratio 0.57/0.43. The structure contains as well two disordered toluene solvent molecules lying on general positions with occupancies 0.56/0.44 and 0.60/0.40. All the H atoms were placed in calculated positions and refined using a riding model. The final residuals were: R_1 = 0.0378, wR_2 = 0.0857 for 15583 reflections with $I > 2\sigma(I)$ and 0.0680, 0.1001, respectively, for all data, 1589 parameters, GOOF = 1.007, max/min $\Delta\rho$ = 0.994/–0.965 e Å^{-3}.

CCDC 1944539 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.09.014.

References

1 V. Siracusa, P. Rocculi, S. Romani and M. Dalla Rosa, *Trends Food Sci. Technol*., 2008, **19**, 634.

2 F. Asghari, M. Samiei, K. Adibkia, A. Akbarzadeh and S. Davaran, *Artif. Cells, Nanomed.*, *Biotechnol*., 2017, **45**, 185.

3 B.-H. Huang, C.-Y. Tsai, C.-T. Chen and B.-T. Ko, *Dalton Trans*., 2016, **45**, 17557.

4 J. Wu, T.-L. Yu, C.-T. Chen and C.-C. Lin, *Coord. Chem. Rev*., 2006, **250**, 602.

5 Y. Sarazin and J.-F. Carpentier, *Chem. Rev*., 2015, **115**, 3564.

6 J. Kiriratnikom, S. Chotchatchawankul, S. Haesuwannakij, S. Kiatisevi and K. Phomphrai, *New J. Chem.*, 2018, **42**, 8374.

7 W.-J. Chuang, Y.-T. Huang, Y.-H. Chen, Y.-S. Lin, W.-Y. Lu, Y.-C. Lai, M. Y. Chiang, S. C. N. Hsu and H.-Y. Chen, *RSC Adv.*, 2016, **6**, 33014.

8 P. Wang, X. Hao, J. Cheng, J. Chao and X. Chen, *Dalton Trans.*, 2016, **45**, 9088.

9 I. E. Nifant’ev, A. V. Shlyakhtin, V. V. Bagrov, R. N. Ezhov, B. A. Lozhkin, A. V. Churakov and P. V. Ivchenko, *Mendeleev Commun.*, 2018, **28**, 629.

10 T. A. Egiazaryan, V. M. Makarov, M. V. Moskalev, D. A. Razborov and I. L. Fedushkin, *Mendeleev Commun*., 2019, **29**, 648.

11 S. S. Karlov, G. S. Zaitseva and M. P. Egorov, *Russ. Chem. Bull., Int. Ed.*, 2019, **68**, 1129 (*Izv. Akad. Nauk, Ser. Khim*., 2019, 1129).

12 I. I. Stoikov, P. L. Padnya, O. A. Mostovaya, A. A. Vavilova, V. V. Gorbachuk, D. N. Shurpik and G. A. Evtugin, *Russ. Chem. Bull., Int. Ed*., 2019, **68**, 1962 (*Izv. Akad. Nauk, Ser. Khim*., 2019, 1962).

13 S. P. Dubey, H. A. Abhyankar, V. Marchante, J. L. Brighton and K. Blackburn, *Int. Res. J. Pure Appl. Chem*., 2016, **12**, 27469.

14 A. Thevenon, C. Romain, M. S. Bennington, A. J. P. White, H. J. Davidson, S. Brooker and C. K. Williams, *Angew. Chem., Int. Ed*., 2016, **55**, 8680.

15 C. A. Wheaton, P. G. Hayes and B. J. Ireland, *Dalton Trans*., 2009, 4832.

16 D. E. Stasiw, M. Mandal, B. D. Neisen, L. A. Mitchell, C. J. Cramer and W. B. Tolman, *Inorg. Chem*., 2017, **56**, 725.

17 M. Cheng, A. B. Attygalle, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc*., 1999, **121**, 11583.

18 A. Dumitrescu, B. Martin-Vaca, H. Gornitzka, J.-B. Cazaux, D. Bourissou and G. Bertrand, *Eur. J. Inorg. Chem*., 2002, 1948.

19 Y. Han, Q. Feng, Y. Zhang, Y. Zhang and W. Yao, *Polyhedron*, 2017, **121**, 206.

20 W.-J. Chuang, H.-Y. Chen, W.-T. Chen, H.-Y. Chang, M. Y. Chiang, H.-Y. Chen and S. C. N. Hsu, *RSC Adv*., 2016, **6**, 36705.

21 S. Ghosh, P. M. Shäfer, D. Dittrich, C. Scheiper, P. Steiniger, G. Fink, A. N. Ksiazkiewicz, A. Tjaberings, C. Wölper, A. H. Gröschel, A. Pich, S. Herres-Pawlis and S. Schulz, *ChemistryOpen*, 2019, **8**, 951.

22 E. Kh. Lermontova, M. M. Huan, A. V. Churakov, J. A. K. Howard, M. V. Zabalov, S. S. Karlov and G. S. Zaitseva, *Dalton Trans*., 2009, 4695.

23 F. V. Cochran, P. J. Bonitatebus, Jr. and R. R. Schrock, *Organometallics*, 2000, **19**, 2414.

24 G. M. Sheldrick, *Acta. Crystallogr., Sect. A: Found. Adv*., 2008, **64**, 112.

25 J. E. Huheey, *J. Phys. Chem*., 1965, **69**, 3284.

26 S. J. Birch, S. R. Boss, S. C. Cole, M. P. Coles, R. Haigh, P. B. Hitchcock and A. E. H. Wheatley, *Dalton Trans*., 2004, 3568.

27 A. Caovilla, J. S. Penning, A. C. Pinheiro, F. Hild, R. Stieler, S. Dagorne, O. L. Casagrande, Jr. and M. P. Gil, *J. Organomet. Chem*., 2018, **863**, 95.

28 C.-S. Hsiao, T.-Y. Wang, A. Datta, F.-X. Liao, C.-H. Hu, C.-H. Lin, J.-H. Huang and T.-Y. Lee, *J. Organomet. Chem*., 2012, **718**, 82.

29 T. Kloubert, H. Görls and M. Westerhausen, *Z. Anorg. Allg. Chem*., 2010, **636**, 2405.

30 T. Kloubert, H. Görls and M. Westerhausen, *Z. Naturforsch*., 2012, **67b**, 519.

31 N. Komine, R. W. Buell, C.-H. Chen, A. K. Hui, M. Pink and K. G. Caulton, *Inorg. Chem.*, 2014, **53**, 1361.

32 I. B. Lozada, T. Murray and D. E. Herbert, *Polyhedron*, 2019, **161**, 261.

33 A. Malassa, C. Koch, B. Stein-Schaller, H. Görls, M. Friedrich and M. Westerhausen, *Inorg. Chim. Acta*, 2008, **361**, 1405.

34 D. L. Miller and C. C. Lu, *Dalton Trans*., 2012, **41**, 7464.

35 C. Neuhäuser, M. Reinmuth, E. Kaifer and H.-J. Himmel, *Eur. J. Inorg. Chem*., 2012, 1250.

36 S. D. Reid, A. J. Blake, C. Wilson and J. B. Love, *Inorg. Chem*., 2006, **45**, 636.

37 Y. Wang, H. Fu, F. Shen, X. Sheng, A. Peng, Z. Gu, H. Ma, J. S. Ma and J. Yao, *Inorg. Chem*., 2007, **46**, 3548.

38 Q.-Q. Xu, D.-H. Wang, S.-M. Chi, X. Gan and W.-F. Fu, *Inorg. Chim. Acta*, 2009, **362**, 2529.

39 L.-Y. Yang, Q.-Q. Chen, G.-Q. Yang and J.-S. Ma, *Tetrahedron*, 2003, **59**, 10037.

40 S. Praban, S. Yimthachote, J. Kiriratnikom, S. Chotchatchawankul, J. Tantirungrotechai and K. Phomphrai, *J. Polym. Sci., Part A: Polym. Chem*., 2019, **57**, 2104.

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