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In summary, the results of the measurements and the simulations demonstrate that orientation selection affects the DEER response. For az-1 it suggests that in solution more conformations are accessible than in the crystal, an aspect which is currently undergoing detailed analysis. With respect to the determination of distances in other systems, usually enough information about the relative g tensor orientation is known to allow the distances to be determined with sufficient accuracy. If the relative orientation is not known, the dipolar frequency v_{dip} will differ by a factor of 2 between the two extreme angles $\theta_{\rm AB}\,{=}\,0^{\rm o}$ and 90°. The resulting difference in r_{AB} of 25% is therefore the maximum uncertainty expected from orientation effects. Finally, the study demonstrates that DEER can be applied to the determination of structures of compounds which contain paramagnetic transition-metal ions, and thus provides an additional method for structural investigations on biological systems. This is particularly important given the physiological significance of metal ions.

Experimental Section

Spectra were measured on a Bruker Elexsys E680 spectrometer with modifications to the microwave bridge to introduce the second microwave frequency analogous to those described by Pannier et al.^[3] using a HP synthesizer HP 83752B and a microwave amplifier (Microwave Amplifiers AL 16-9-10-15). The four-pulse DEER sequence^[3] with pulse lengths of 16 ns for $\pi/2$, 32 ns for π pulses, and $\tau = 896$ ns was employed. Pulse powers were adjusted to equal intensity at $\nu_{\rm obs}$ and $\nu_{\rm pump}$. The maximum frequency separation of $\nu_{\rm obs}$ and ν_{pump} was estimated by detuning the measurement frequency from the resonator frequency. At offsets of $\pm 37.5 \,\text{MHz}$ attenuation of the signal was observed, leading to the choice of $\nu_{\rm obs} - \nu_{\rm pump}$ of 75 MHz. At that separation, the echo is reduced by less than a factor of 2. The excitation bandwidth of the pulses is smaller than in the experiments described by Pannier et al., where a maximum of 25 MHz is given.^[3] In the Fourier transformation (by using the Origin program (Microcal(TM) Northhampton, USA) of the modulation, a Gaussian background was subtracted from the experimental data, the resulting curve was filtered with a Hamming window, and filled with zeros to 1024 points to a total time of 3.2 µs.

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Propylene Oxide Polymerization

An Efficient Method for Controlled Propylene Oxide Polymerization: The Significance of Bimetallic Activation in Aluminum Lewis Acids**

Wigand Braune and Jun Okuda*

Propylene oxide (PO) is with a worldwide production of 4.5 million tons a significant intermediate of the petrochemical industry. Two-thirds of the propylene oxide is converted by ring-opening polymerization into polypropylene glycols and propoxylated products of polyurethane.^[1] The classical initiator for this reaction is KOH, whose high basicity leads to deprotonation of the methyl group, resulting in side reactions.^[2] Rapid and controlled PO polymerization has recently become possible through so-called double-metal cvanide compounds (DMC), whose structure and mechanism is, however, still unclear.^[3] Only a small number of structurally characterized initiators for living coordination PO polymerization has been published so far: aluminum complexes with tri- or tetradentate ligands (porphyrins, phthalocyanine, tetraazaannulene, salen-type ligands, diethylenetriamine) polymerize PO by a mechanism based on chain growth at a single metal center by reaction of the monomer with the coordinated alkoxo ligand (in addition, cis migration, rear attack, and participation of two metal centers are also assumed).^[4] The sterically demanding Lewis acidic organoaluminum complexes accelerate the coordination ring-opening polymerization.^[5] We report here the targeted synthesis of new aluminate complexes and their polymerization properties in combination with their neutral Lewis acid precursors. Our results prove for the first time that PO polymerization does not occur at a single Lewis acidic metal center and confirm the earlier proposal of bimetallic activation by Price and Vandenberg.^[6,7]

[{Al(L)Cl}₂] (1: L = mbmp, 2: mmcp), easily obtained by reaction of AlEt₂Cl with 2,2'-methylenebis(6-*tert*-butyl-4methylphenol) (mbmpH₂) or 2,2'-methylenebis(4-methyl-6-(1-methylcyclohexyl)phenol) (mmcpH₂), as well as the isopropanolato complexes [{Al(L)(μ -O*i*Pr)}₂] (3: L = mbmp, 4: mmcp), obtainable from trimethylaluminum in a two-step procedure, did at first appear to be suitable for ring-opening polymerization of PO (Scheme 1).^[8,9] With these initiators we could, however, only observe slow (> 24 h) and regioirregular oligomerization of PO.^[10,11] We suspect that the ring opening

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 ^[*] Prof. Dr. J. Okuda, Dipl.-Chem. W. Braune
 Institut für Anorganische Chemie und Analytische Chemie
 Johannes Gutenberg-Universität Mainz
 Duesbergweg 10–14, 55099 Mainz (Germany)
 Fax: (+49) 6131–39–25605
 E-mail: okuda@mail.uni-mainz.de



Scheme 1. Compounds 1-8.

is, at least partly, induced by the chelating bisphenolato ligands.

By reaction of $[NEt_4][OiPr]$ with **3** or **4** at -20 °C, the aluminate $[NEt_4][Al(L)(OiPr)_2]$ (**5**: L = mbmp; **6**: mmcp) could be isolated in yields from 63 to 74% (Scheme 1). The ¹H NMR spectra of these complexes in CDCl₃ at room temperature showed the presence of C_s symmetry, with two sharp doublets for the methyl protons for each of the *syn*- and *anti*-isopropoxy ligands (**5**: $\delta = 1.07$, 1.15 ppm with ³J_{H,H} = 5.9 Hz; **6**: $\delta = 1.15$, 1.12 ppm with ³J_{H,H} = 5.9 Hz). A crystal structure determination of the alu-

shucture determination of the andminate (ate) complexes confirmed the expected tetrahedral coordination of the aluminum centers within the anion, which has merely an electrostatic interaction with the cation.^[12] To exclude the possibility of participation of the cation in the polymerization, the cesium aluminate Cs[Al(mbmp)(O*i*Pr)₂] (**7**) was prepared by reaction of **3** with CsO*i*Pr. We obtained the related dichloroaluminate [NEt₄][Al(L)Cl₂] (**8**) quantitatively by direct reaction between **1** and NEt₄Cl. Like the neutral compounds **1–4**, aluminates



Figure 1. Polymerization of PO (0.21 mL) initiated by **3** and **5** ($[3]_0/[5]_0/[PO]_0 = 1:1:200$) in CDCl₃ (0.45 mL) at room temperature.

5–8 were not reactive towards ring-opening polymerization of PO.

When neutral complexes 1, 3, and 4 were combined with ate complexes 5–8 to form initiator systems $[Al(L)(X)]_2/$ $[Al(L)(X)_2]^-$ (L = mbmp, mmcp; X = Cl, O*i*Pr), ring-opening polymerization of PO occurred with pronounced speed and control at room temperature. Figure 1 shows the ¹H NMR spectroscopically observed conversion of PO (0.21 mL) in CDCl₃ (0.45 mL) at room temperature with the initiator system formed from equimolar quantities of 3 and 5, and with a monomer/initiator ratio of 50:1 in accordance to the mechanism discussed below. In Table 1, the polymerization conversions at room temperature obtained with Lewis acid precursor (LA) to aluminate (AT) ratios of 1.0 and 1.5 are compared.

Polymerization initiated by the isopropanolato systems is clearly faster than that initiated by the corresponding chloro systems. The most active initiator system was the combination of **4** and **6** (Experiment 3, Table 1) with a conversion of 77 % after 180 min. The 1-methylcyclohexyl substituent of the bisphenolato ligand mmcp in **4** may cause a significant shift of the monomer–dimer equilibrium in favor of the Lewis acidic monomeric species.^[8a] The cesium aluminate **7** in combination with **3** did not initiate polymerization, addition of crown ether ([18]crown-6), however, allowed an activity comparable to

Table 1: Polymerization of PO (2 mL) in CH_2Cl_2 (2 mL) with various systems composed of neutral Lewis acid precursors (LA) and ate complexes (AT).

Exp.	LA	AT	[LA]/[AT]	t [min]	Ratio PO/active centers ^[a]	Conversion [%]	<i>M</i> _n [g mol ⁻¹]	M _{theor.} [g mol ⁻¹]	$M_{\rm w}/M_{\rm n}$
1	1	8	1.0	180	100	22	1190	1280	1.09
2	3	5	1.0	180	100	49	2500	2850	1.18
3	4	6	1.0	180	100	77	3580	4470	1.22
4	3	7	1.0	180	100	0	-	-	-
5	3	7 ^[b]	1.0	180	100	42	2270	2440	1.19
6	3	7 ^[c]	1.0	180	100	33	1680	1920	1.12
7	3	5	1.5	180	100	49	2320	2850	1.20
8	4	6	1.5	180	100	65	3090	3780	1.22

[a] The active centers are the alkoxo and chloro ligands of the initiator system. [b] With addition of two molar equivalents of [18]crown-6. [c] With addition of one molar equivalent of [18]crown-6.

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Figure 2. ¹³C NMR spectrum (CDCl₃) of the polyether obtained with initiators **3** and **5** $([3]_0/[5]_0/[PO]_0=1:1:400, 49\%$ conversion).

that of Experiment 2 to be achieved. GPC measurements of the polyether showed polydispersities between 1.09 and 1.22. To examine the polymer end groups more closely, we separated the initiators obtained from equimolar combinations of either **1** with **8** or **3** with **5** from their polymers with molecular weights of 2.4×10^3 gmol⁻¹ and 2.5×10^3 gmol⁻¹, respectively, by column chromatography. Figure 2 shows the ¹³C NMR spectrum of the polyether obtained with isopropanolato complexes **3** and **5** in CDCl₃.

The signals of the CH₃- (a), CH₂- (b), and CH groups (c) appeared at $\delta = 17.2, 17.4$ (a), 72.8, 73.2 (b), and 75.0, 75.2, 75.4 (c) ppm, and showed a chiral polymer with exclusive head-totail bonding, with the four possible head-to-tail triads appearing with the same frequencies in a purely statistical distribution.^[13,7a] The weak signals arose from the end groups: the isopropoxy group appeared at $\delta = 21.9, 22.0$ (CH(CH₃)₂) (d)), and 71.8 ppm ($CH(CH_3)_2$ (e)), and the terminal methine carbon atom CHOH (f) appeared at $\delta = 65.4$ and 67.1 ppm.^[5b,14] The resonance signal of the terminal methylene carbon atom CH₂OiPr (g) was found at $\delta = 72.0$ ppm.^[15] The relatively strong resonance signals at $\delta = 18$ ppm therefore stem not only from the methyl groups CH_3 (h) at the ends of the regularly obtained polymer, but also from those at the ends of the very low-molecular-weight oligomers ($M_{\rm p}$ < 600 g mol⁻¹) resulting from the bisphenolato ligands.^[16] The ¹³C NMR spectrum of the polyether obtained with chloro complexes 1 and 8 gave the same statistical distribution of triads and the same resonance signals corresponding to the end groups (CH₂Cl: $\delta = 47.4$ ppm; CHOH: $\delta = 65.4$, 67.1 ppm). The MALDI-TOF mass spectra (dithranol, K, THF) of the polymers examined showed a monomodal weight distribution. The mass difference was 58 in each case, and the detected masses confirmed the end groups determined from the ¹³C NMR spectra.^[17]

We propose that the ring-opening polymerization proceeds as shown in Scheme 2 under the synergic interaction of a phenolatoaluminum complex with the corresponding ate complex. The first step consists of the reaction of the dimeric neutral complex with PO to form a labile adduct (step 1 in Scheme 2).^[8a,c, 18] Ring opening of the epoxide activated by the monomeric complex proceeds by transfer of an alkoxy group from the corresponding ate complex; this is accompanied by simultaneous regeneration of the aluminate (steps 2 and 3 in Scheme 2). The activity of the initiator system based on the cesium alkoxide with added crown ether shows that separa-



Scheme 2. The concept of coordination anionic polymerization with chain transfer.

tion of the ion pairs is a requirement for efficient transfer of the alkoxy group. When the initiator consisted of a combination of **1** and **8**, the chloro complexes underwent a prior reaction with PO to form the corresponding 1-chloro-2propanolato complexes. During polymerization, the neutral phenolato aluminum complexes bear one growing polymer chain, and the aluminate two (step 3 in Scheme 2). The average initiator efficiency (number of polymer chains initiated per aluminum atom) should therefore depend on the ratio of neutral to anionic complexes. To check the proposed mechanism, we carried out the polymerization of PO with four different initiator efficiencies until complete conversion had taken place (Figure 3).

The ratio of monomer to the total number of centers active for polymerization was deliberately kept constant (a: 50; b: 100). In good agreement with the hypothesis, the molecular weights obtained in the experimental series hardly



Figure 3. Polymerization of with PO (2 mL) a) variable ratios $[1]_0/[8]_0$ and constant ratio $[PO]_0/[active centers]_0 = 50:1$ (calculated according to a coordination anionic mechanism with chain transfer) in CH₂Cl₂ (1 mL) at room temperature and b) variable ratios $[3]_0/[5]_0$ and constant ratio $[PO]_0/[active centers]_0 = 100:1$ in CH₂Cl₂ (2 mL) at room temperature. Plotted are M_n (\bullet), M_w/M_n (\odot), the theoretical course when a coordination anionic mechanism with chain transfer is assumed (----), and the theoretical course when a simple anionic mechanism is assumed (----).

differed from each other. With a simple anionic mechanism without simultaneous chain growth at all metal centers, the molecular weight would have been linearly dependent on the number of ate complexes or neutral phenolatoaluminum complexes used.

In summary, we have confirmed here that ring-opening polymerization of PO cannot occur at simple Lewis acidic centers, but that nucleophilic ate complexes must be present at the same time. The fundamentally new mechanism reported herein should have far-reaching consequences for understanding PO polymerization, and should allow the design of new, structurally characterized initiators, also for the stereoselective polymerization of PO.^[19]

Experimental Section

5: At 70 °C, sodium (46 mg, 2.0 mmol) was dissolved with generation of hydrogen gas in isopropyl alcohol (10 mL). This solution was added dropwise at -20 °C to a solution of NEt₄Cl (331 mg, 2.0 mmol) in isopropyl alcohol (3 mL); this resulted in precipitation of NaCl. To reduce the solubility of the NaCl, diethyl ether (20 mL) was added at -20 °C. In another reaction flask, **3** (849 mg, 1.0 mmol) was suspended in diethyl ether (5 mL) cooled to -20 °C, and isopropyl alcohol (5 mL) was added. The precooled solution of the tetraethylammonium isopropoxide was added dropwise to this suspension; the reaction mixture dissolved as a result. The solution was stirred at below 0 °C for 45 min, and then the solvent was removed in vacuo. The residue was dissolved in dichloromethane (3 mL) and filtered. After the addition of diethyl ether (15 mL), the aluminate was recrystallized at -30 °C. Yield: 910 mg (74%) of **5** as colorless crystals. Complex **6** was prepared similarly.

¹H NMR (400 MHz, CDCl₃, 25 °C): $\delta = 0.85$ (t, ${}^{3}J_{\text{H,H}} = 7.4$ Hz, 12 H; NCH₂CH₃), 1.07 (d, ${}^{3}J_{\text{H,H}} = 5.9$ Hz, 6H; CH(CH₃)₂), 1.15 (d, ${}^{3}J_{\text{H,H}} = 5.9$ Hz, 6H; CH(CH₃)₂), 1.37 (s, 18 H; 6-C(CH₃)₃), 2.13 (s, 6 H; 4-CH₃), 2.46 (q, ${}^{3}J_{\text{H,H}} = 7.4$ Hz; NCH₂CH₃), 3.00 (d, ${}^{2}J_{\text{H,H}} = 13.7$ Hz, 1H; 2-CH₂), 4.19 (septet, ${}^{3}J_{\text{H,H}} = 5.9$ Hz; CH(CH₃)₂), 4.36 (septet, ${}^{3}J_{\text{H,H}} = 5.9$ Hz; CH(CH₃)₂), 3.75 (d, ${}^{2}J_{\text{H,H}} = 13.7$ Hz, 1 H; 2-CH₂), 6.72 (d, ${}^{4}J_{\text{H,H}} = 2.0$ Hz, 2 H; 5-H), 6.83 ppm (d, ${}^{4}J_{\text{H,H}} = 2.0$ Hz, 2 H; 3-H); 1³C NMR (100.6 MHz, CDCl₃, 25 °C): $\delta = 7.3$ (NCH₂CH₃), 20.9 (4-CH₃), 28.0 (CH(CH₃)₂), 28.2 (CH(CH₃)₂), 30.1 (6-C(CH₃)₃), 33.8 (6-C(CH₃)₃), 34.9 (2-CH₂), 52.0 (NCH₂CH₃), 62.4 (CH(CH₃)₂), 62.6 (CH(CH₃)₂), 122.7, 125.1, 128.6, 131.4, 138.0 (phenyl 2-C to 6-C), 156.2 ppm (*ipso*-phenyl-C); elemental analysis (%) calcd for C₃₇H₆₄AlNO₄ (613.91): C 72.39, H 10.51, N 2.28; found: C 72.30 H 10.64 N 2.71.

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