Synthesis, Molecular Structure, and Olefin Polymerisation Activity of an Oxovanadium(V) Alkoxide with Unprecedented Chloride Bridging Ligands

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The reaction of 2-methoxyethanol or (2-methoxyethanolato)lithium with $VOCl_3$ yields the chloro-bridged dinuclear complex $[VOCl_2(OCH_2CH_2OCH_3)]_2$, which has been characterised spectroscopically and structurally by single-crystal X-ray diffraction analysis. This is the first reported structure of a neutral dinuclear oxovanadium complex connected by bridging chloro ligands. The orange complex is a precatalyst for the polymerisation of ethene and the oligomerisation of styrene.

Introduction

Oxovanadium complexes are known to act as catalysts for oxidation[1] and polymerisation reactions, for example.[2,3] As part of our investigations aimed at vanadium-based catalysts our interest is primarily concerned with the synthesis and characterisation of vanadium(V) compounds stabilised by alkoxyalkoxide ligands. While a significant number of oxovanadium(V) alkoxides and aryloxides derived from various alcohols have been synthesised,[4] the majority of (alkoxo- or aryloxo)chloro(oxo)vanadium compounds structurally characterised to date contain vanadium in the oxidation state +4.[5−10] The main feature of these complexes is that the alkoxide or aryloxide ligands predominantly act as bridging groups.[7−13] Monomeric derivatives have been reported with very bulky aryloxo groups,[14] intramolecular donor stabilisation[5,6,9,15] or additional donor ligands.[16−18] As far as we are aware, there are no examples of vanadium alkoxides in which chloro ligands appear as bridging units.

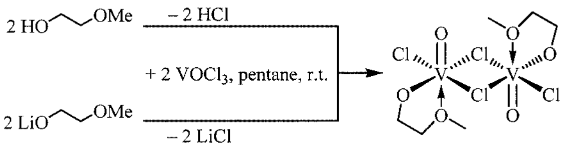
Previously we have reported the reaction of 2-phenoxyethanol with $VOCl_3$, which gives the mononuclear complex $[VOCl_2(OCH_2CH_2OPh)]$ and which is still the only structurally characterised dichlorooxovanadium(V) alkoxide.[19] The presence of the remaining chloro ligands in the complex makes the metal atom functionalisable, for example by the introduction of alkyl groups. Chloro ligands, either in the catalyst or in the co-catalyst, are essential for olefin polymerisation.[3]

Herein we show that in the field of vanadium alkoxides, the variation of substituents on the ligands can have large effects on the complex structure and possibly on their catalytic behaviour.

Results and Discussion

Synthesis and Structure

Bis[(μ-chloro)chloro(η^2-2-methoxyethanolato)oxovanadium(V)] was prepared by two different strategies: HCl elimination and a salt metathesis reaction. The equimolar reaction of $VOCl_3$ with 2-methoxyethanol in *n*-pentane gave the dinuclear vanadium(V) species only in very low yields due to significant quantities of reduction products. Such a reduction process has been observed previously when Hovnanian and co-workers obtained the vanadium(IV) complex $[VOCl\{OCH(CH_3)CH_2OCH_3\}]_2$ from a vanadium(V) starting material.[7] Employing the lithium salt instead of the pure alcohol minimised the amount of reduction. The reaction proceeds smoothly under ambient conditions in hydrocarbon solvents, which were chosen with the intention to obtain intramolecularly stabilised complexes instead of additional solvent coordination.



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The orange diamagnetic crystalline solid [$VOCl_2(OCH_2CH_2OCH_3)]_2$ slowly decomposes at ambient temperatures both in solution, where it forms blue vanadium(IV), and as a solid, where it forms a black crystalline material. Unfortunately, the black material contained no crystals suitable for X-ray diffraction; it is insoluble in inert solvents like hydrocarbons, dichloromethane or toluene and attempts to recrystallise it from pyridine led to [$VOCl_2(py)_2$],[20] which was identified by an X-ray structure determination. The title compound can be stored for weeks under an inert gas at −30 °C in the dark without any appreciable decomposition. It dissolves in dichloromethane and toluene and decomposes in water, tetrahydrofuran, diethyl ether, and alcohols. The compound has a ^{51}V NMR chemical shift of $\delta = -259$ ppm in C_6D_6 and $\delta = -262$ ppm in $CDCl_3$. A minor peak is observed at $\delta = -279$ ppm in C_6D_6 and $\delta = -282$ ppm in $CDCl_3$. As a decrease of the coordination number on going, for example, from an octahedral to a tetrahedral arrangement is usually accompanied by an increase of shielding, this signal may be ascribed to the presumably tetrahedral monomer. This chemical shift is also in good agreement with that of other tetrahedrally coordinated dichloro(oxo)vanadium alkoxides in solution.[19,21]

The ^{1}H and ^{13}C{^{1}H} NMR spectra of the title compound show the expected number of signals for the coordinated 2-methoxyethanolato ligand as well as the 1:1 relative intensity proton pattern for the methylene peaks in the ^{1}H NMR spectrum. The signals at lower field at $\delta \approx 4.6$ ppm in C_6D_6 and $\delta \approx 5.7$ ppm in $CDCl_3$ are due to the $VOCH_2$ protons while those at $\delta \approx 2.8$ ppm in C_6D_6 and $\delta \approx 3.9$ ppm in $CDCl_3$ are assigned to the CH_2OMe methylene protons. The ^{13}C{^{1}H} NMR resonance for the carbon atom adjacent to the alcohol moiety shifts approximately 30 ppm downfield upon vanadylation. As for the corresponding proton resonances this shift may be ascribed to the deshielding of this carbon atom due to transfer of electron density to the metal atom. The signals of all other carbon atoms shift very little.

The dimeric nature of the compound is supported by mass spectrometric data, which exhibit no molecular ion but [$VOCl(OCH_2CH_2OCH_3)]_2$, formed by loss of two chlorine atoms and containing two vanadium atoms, as the fragment with the highest molecular mass. The same is true for IR spectroscopy, which indicates both terminal and bridging V−Cl bonds. The intense bands at 464 and 434 cm^{-1} arise from terminal V−Cl and bridging V−Cl stretching vibrations, respectively. The sharp bands at 1028 cm^{-1} in nujol and 1024 cm^{-1} in CS_2, associated with the V=O moiety, are characteristic of $VOCl_2(OR)$ compounds.[9,19,21]

Single crystals of the complex, suitable for X-ray diffraction, were obtained from cold *n*-hexane solutions. An ORTEP drawing of the molecule is shown in Figure 1, and selected bond lengths and angles are given in the caption. The structural analysis revealed the (alkoxyalkoxo)vanadium compound to be a dimer with two bridging chlorine atoms. The two halves of the dimer are related by a centre of inversion. Thus, oxo groups and terminal chlorine atoms adopt an *anti* orientation while the V=O groups are orientated perpendicular and the chlorine atoms coplanar with respect to the bridging plane, which is spanned by the $V_2(\mu\text{-}Cl)_2$ core.[22] Each vanadium atom possesses a distorted octahedral geometry which is similar to that in other hexacoordinate vanadium(V) complexes.[23−25] The vanadium atom is displaced by 0.296(1) Å from the plane formed by the equatorial atoms Cl(1), Cl(2), O(2), and Cl(1′) towards the oxo oxygen atom. It is unusual, and we believe unique, in having the two VO_3Cl_3 octahedra joined by chlorine atoms. Hitherto structurally characterised examples of dimeric chloro(oxo)vanadium complexes containing an $[OV(\mu\text{-}Cl)_2VO]^{n+}$ (n = 2, 4) core have only been reported for the purely inorganic vanadium(IV) anions $[\{VOCl_2(OH_2)\}_2(\mu\text{-}Cl)_2]^{2-}$ and $[V_2O_2Cl_6]^{2-}$.[26,27] So far if alkoxo or aryloxo ligands are involved they function as bridging units instead of chlorine atoms.[7−13]

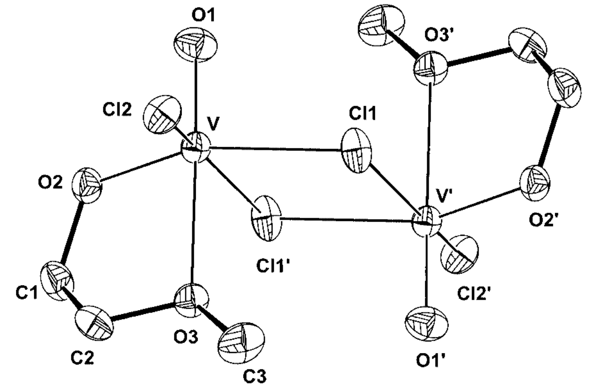

Figure 1. ORTEP view of $[VOCl_2(OCH_2CH_2OMe)]_2$; displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: V−Cl(1) 2.4321(6), V−Cl(1′) 2.4172(6), V−Cl(2) 2.2581(6), V−O(1) 1.5827(16), V−O(2) 1.7697(15), V−O(3) 2.3120(15); Cl(1)−V−Cl(1′) 79.33(2), V−Cl(1)−V′ 100.67(2), Cl(1)−V−O(1) 97.15(7), Cl(1′)−V−O(1) 95.23(6), Cl(2)−V−O(1) 99.40(6), O(1)−V−O(2) 99.08(8), O(1)−V−O(3) 175.88(7)

As in $[\{VOCl_2(OH_2)\}_2(\mu\text{-}Cl)_2]^{2-}$, both vanadium atoms are part of a planar $V_2(\mu\text{-}Cl)_2$ four-membered ring,[26] in which the angles at the vanadium atom are 79.33(2)° and those at μ-Cl are 100.67(2)°. The two chlorine atoms bridge the two vanadium atoms in an almost symmetric fashion: both bonds have approximately the same length [2.4321(6) Å and 2.4172(6) Å for V−Cl(1) and V−Cl(1′), respectively] and are similar to those in the $[V_2O_2Cl_6]^{2-}$ ion.[27] The distances of the vanadium atom to the terminal chlorine atoms are 2.2581(6) Å, which are very similar to those observed for [{$HB(pz)_3$}VOCl(O*i*Pr)][18] and [$VOCl\{OC(CH_3)_2C(CH_3)_2O\}]_2$.[12]

Three different vanadium−oxygen bonds are present. The vanadium−oxo distance is in the normal range for such a bond [V−O(1) = 1.5827(16) Å].[5−15,17−21,23−27] The V−O distance for the alkoxide oxygen atom O(2) is only about 0.2 Å longer, which is in agreement with some degree of π-donation from O(2) to the metal atom and is typical for vanadium alkoxide moieties.[5,9,13,15,17−19,21,23] Owing to the fact that the oxygen atom O(3) of the methoxy group encounters the *trans* influence of the doubly bonded oxygen atom O(1), its distance to the vanadium atom is, as expected, the longest [2.3120(15) Å].

In contrast to the monomeric vanadium(V) complex [$VOCl_2(OCH_2CH_2OPh)$] and the dimeric vanadium(IV) complexes [$VOCl\{OCH(CH_3)CH_2OCH_3\}]_2$ and [$VOCl\{OCH_2(C_4H_7O)\}]_2$, where the aryloxy- and alkoxyalkoxides are pendant or bridging, respectively,[7,8,19] both groups in the compound reported here coordinate directly to a single vanadium centre. Although [$VOCl_2(OCH_2CH_2OPh)$] was obtained by the corresponding reactions with 2-phenoxyethanol, both dichloro(oxo)vanadium compounds differ completely in their structures.[19] As there are no steric reasons for this phenomenon the origin of this difference is probably due to the lower Lewis basicity of the phenyl ether than the methyl one.

Catalytic Activity

The catalytic activity of the title compound for the polymerisation of styrene, 1-decene, and ethene was examined. Polymerisation studies were conducted employing a polymerisation catalyst prepared by adding the vanadium compound to a toluene solution of methylaluminoxane (MAO) as the co-catalyst. The low molecular masses given in Table 1 show that only oligomers are obtained for styrene with methyl trichloroacetate (MTCA) as promoter. The catalytic activity decreases with rising temperatures and is highest at room temperature, with quantitative conversion of styrene, while the polydispersity (*D*) has values of around 2.

Under the same conditions the activity for styrene oligomerisation is ten times higher than that for 1-decene conversion and is independent of the nuclearity of the precatalyst employed (Table 2). The molecular mass and polydispersity of styrene oligomers are in the same range as for the mononuclear (M_n = 2700 g/mol, M_w = 4100 g/mol, D = 1.8) and the dinuclear complex (M_n = 3200 g/mol, M_w = 5000 g/mol, D = 1.5).

Table 1. Oligomerisation of styrene with [$VOCl(OCH_2CH_2OCH_3)]_2$[a]

T [°C]	Yield [%]	M_w [g/mol]	M_n [g/mol]	M_w/M_n
20	99.6	2900	1200	2.3
40	85.3	3000	1500	2.0
50	71.1	2700	1600	1.7

[a] Reaction conditions: V catalyst/styrene/MAO/MTCA = 0.01:13:1:1, 20 h; solvent: toluene.

Table 2. Activity (kg per mol vanadium atom per h) of olefin conversions with vanadium(V) compounds[a]

Precatalyst	Styrene	1-Decene
[$VOCl_2(OCH_2CH_2OMe)]_2$	27.7	2.5
[$VOCl_2(OCH_2CH_2OPh)$]	27.9	2.7

[a] Reaction conditions: V catalyst/monomer/MAO/MTCA = 0.01:17:1:1, 90 min at 23 °C; solvent: toluene.

The ethene polymerisation catalysts were prepared by treating the vanadium compound either with MAO or chlorodiethylaluminium as the co-catalyst. The results of ethene polymerisation are shown in Table 3. Even at atmospheric pressure and room temperature the title compound displays a reasonable activity (100 kg PE/mol[V] h) for ethene polymerisation with MTCA as promoter in the presence of MAO; without MTCA the activities are negligible. The conditions have been optimised for MAO to give highest activities at an Al/V ratio of 400 (300 kg PE/mol[V] h bar). Et_2AlCl, with almost double the activity (560 kg PE/mol[V] h bar), is the best co-catalyst for the system, as has been found previously for other vanadium procatalysts.[3] For comparison, under similar conditions, the best result for a catalyst based on $VOCl_3$ was 360 kg PE/mol[V] h bar after activation with Et_2AlCl. In the range investigated the activities drop if the Al/V ratio is lowered. During the polymerisation reaction the catalyst is stable and the activities decrease only after 30 min. GPC analyses showed that the product molecular mass distribution is very broad. With MAO as co-catalyst the system forms polyethene with a higher molecular mass than with Et_2AlCl. The molecular mass distribution of all polymers formed is bimodal.

Table 3. Data for polymerisation of ethene

Entry	Precatalyst	Co-catalyst	$[V]_0$ [a]	[Al]/[V] [*n*/*n*]	Activity[a]	10^{-3} M_w [g/mol]	10^{-3} M_n [g/mol]	M_w/M_n
1[b]	[$VOCl_2(OCH_2CH_2OMe)]_2$	MAO	0.2	80	100	954	87	11.0
2[c]	[$VOCl_2(OCH_2CH_2OMe)]_2$	MAO	0.1	100	6	1084	119	9.9
3[c]	[$VOCl_2(OCH_2CH_2OMe)]_2$	MAO	0.02	400	300	1414	168	8.4
4[c]	[$VOCl_2(OCH_2CH_2OMe)]_2$	MAO	0.02	1000	15	1169	155	8.5
5[c]	$VOCl_3$	MAO	0.02	400	3	[d]	[d]	[d]
6[c]	[$VOCl_2(OCH_2CH_2OMe)]_2$	Et_2AlCl	0.1	100	560	586	66	8.9
7[c]	[$VOCl_2(OCH_2CH_2OMe)]_2$	Et_2AlCl	0.1	20	320	696	110	6.3
8[c]	$VOCl_3$	Et_2AlCl	0.1	100	360	390	34	11.4

[a] $[V]_0$ [mmol/L]; activity [kg PE/mol[V] h bar]. [b] Schlenk tube; *p*(ethene) = 1 bar, 30 min at 22 °C; solvent: toluene. [c] Glass autoclave; *p*(ethene) = 2 bar, 30 min at 30 °C; solvent: toluene. [d] Entry 5 contained a substantial amount of insoluble material resulting in very poor data detection.

Conclusion

In summary, the synthesis of $[VOCl_2(OCH_2CH_2OCH_3)]_2$ has resulted in the first dinuclear chloride-bridged oxovanadium alkoxide to be structurally characterised. The two bridging chloro ligands build the sharing edge of two VO_3Cl_3 octahedra, which incorporate a five-membered chelate ring. This structural feature may give rise to altered reactivities as polymerisation catalyst or oxidation reagent compared to mononuclear or alkoxide-bridged oxovanadium sites. The title compound shows catalytic activity in ethene polymerisation and styrene oligomerisation. Further catalytic studies besides polymerisation, including the oxidation properties, as well as comparative synthetic investigations concerning other alkoxyalkoxides are currently underway.

Experimental Section

General Remarks: All experiments were performed under nitrogen using standard Schlenk techniques in dry, oxygen-free solvents. Commercial $VOCl_3$ (Aldrich) was used as received. 2-Methoxyethanol, MTCA and styrene were dried with molecular sieves (4 Å). 1-Decene was distilled from CaH_2 followed by treatment with molecular sieves. The ethene gas (Messer Griesheim, 99.995%) was passed through an Oxiclear gas purifier before being passed into the reactor. The IR spectrum was recorded using a Nicolet Magna IR spectrometer 750. NMR spectra were recorded at ambient temperatures with a Bruker ARX 200 or ARX 400 spectrometer. All chemical shifts are reported in ppm relative to the ^1H and ^{13}C residue of the deuterated solvents. For ^{51}V NMR $VOCl_3/CDCl_3$ (2:1) was used as external standard. The mass spectrum (EI) was obtained using a Varian MAT 311 A instrument. Elemental analyses were performed with a Perkin−Elmer Series II CHNS/O Analyzer 2400. GPC data of styrene oligomers were obtained with a Waters model 150 LC/GPC in THF solvent running at ambient temperature and were calibrated using polystyrene standards. GPC measurements of polyethene samples were carried out by high-temperature GPC at 140 °C, using 1,2,4-trichlorobenzene as solvent and narrow polystyrene standard sample as reference. The measurements were performed with a PL-GPC210 with 4 PL-Gel Mixed A columns, with triple detection: RALLS detector (Precision Detector, PD2040 at 800 nm), H502 viscometer (Viscotek), refractive detector and DM400 datamanager (Viscotek).

$[VOCl_2(OCH_2CH_2OCH_3)]_2$. Method A: $VOCl_3$ (3.0 mL, 32 mmol) was added to a colourless mixture of $HOCH_2CH_2OCH_3$ (2.5 mL, 32 mmol) in *n*-pentane (150 mL). The reaction mixture turned brown immediately and was stirred at room temperature for 1 h. In order to complete the evolution of HCl gas, the mixture was heated in a warm-water bath. The resulting orange solution was concentrated and stored at 0 °C. Orange crystals separated overnight. Yield: 0.82 g (12%). M.p. 65 °C. **Method B:** *n*-Hexane (100 mL) and a 1 M solution of $VOCl_3$ (10 mL, 1.73 g, 10 mmol) in *n*-pentane were added to $LiOCH_2CH_2OCH_3$ (0.83 g, 10 mmol). The reaction mixture was stirred at room temperature for 12 h. The orange solution was decanted from the brown residue and stored at −30 °C. Orange crystals separated. Yield: 0.83 g (39%). IR (KBr, nujol mull): $\tilde{\nu}$ = 1255 m, 1224 m, 1192 m, 1156 w, 1102 s (V−O−C), 1081 vs (C−O), 1028 vs (V=O), 994 vs, 897 vs (C−O−C), 825 s, 629 s (V−OR), 577 w, 464 vs (V−Cl), 434 s (V−Cl−V) cm^{-1}. IR (KBr, CS_2): $\tilde{\nu}$ = 1127 s (V−O−C), 1108 w, 1090 w, 1047 vs (C−O), 1024 vs (V=O), 1001 m, 919 m (C−O−C), 644 w (V−OR), 484 s (V−Cl), 439 m (V−Cl−V) cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ = 4.61 (br. s, 4 H, $VOCH_2$), 2.94 (s, 6 H, CH_3), 2.81 (br. s, 4 H, CH_2OMe) ppm. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.71 (t, $^3J_{H,H}$ = 4.5 Hz, 4 H, $VOCH_2$), 3.86 (t, $^3J_{H,H}$ = 4.5 Hz, 4 H, CH_2OMe), 3.50 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.64 MHz, C_6D_6): δ = 90.6 ($VOCH_2$), 71.3 (CH_2OMe), 58.8 (CH_3) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ = 90.7 ($VOCH_2$), 71.7 (CH_2OMe), 59.2 (CH_3) ppm. ^{51}V NMR (105.19 MHz, C_6D_6): δ = −259 (> 99%), −279 (< 1%) ppm. ^{51}V NMR (105.19 MHz, $CDCl_3$): δ = −262 (> 98%), −282 (< 2%) ppm. MS (70 eV, 150 °C): *m/z* (%) = 354 (25) $[M^+ - 2\ Cl]$, 319 (5) $[M^+ - 3\ Cl]$, 318 (7) $[M^+ - 2\ Cl - HCl]$, 279 (11) $[M^+ - 2\ Cl - OCH_2CH_2OCH_3]$, 274 (10), 217 (39), 45 (100) $[CH_2OCH_3]^+$. $C_6H_{14}Cl_4O_6V_2$ (425.86): calcd. C 16.92, H 3.31; found C 16.93, H 3.49.

X-ray Crystallographic Study: $C_6H_{14}Cl_4O_6V_2$, $M = 425.86$, orange plate, 0.46 × 0.36 × 0.08 mm, monoclinic, space group $P2_1/n$ (no. 14), $a = 6.9487(2)$, $b = 17.6924(5)$, $c = 6.9663(2)$ Å, $\beta = 117.514(1)°$, $V = 759.57(4)$ Å^3, $d = 1.862$ g/cm^3, $T = 173(2)$ K, $Z = 2$, $\mu = 1.944$ mm^{-1}, $2.30° < \theta < 27.50°$, 5617 measured reflections, 1731 independent reflections, $R_{int} = 0.0372$, $R1$ $[I > 2\sigma(I)] = 0.0288$, $wR2$ (all data) = 0.0688. X-ray data were collected with a Siemens SMART CCD diffractometer (graphite-monochromated Mo-K_α radiation, $\lambda = 0.71073$ Å) fitted with an area-detector by use of ω scans. The structure was solved by direct methods using SHELXS-97[28] and refined on F^2 using all reflections with SHELXL-97.[29] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned an isotropic displacement parameter of 0.08 Å^2. SADABS[30] was used to perform area-detector scaling and absorption corrections (max./min. transmission factors: 0.8911/0.6151). CCDC-232374 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Polymerisation Studies: Styrene and 1-decene polymerisation reactions were performed in a 50-mL Schlenk flask and an external temperature-controlled bath on a Schlenk line. In a typical procedure, toluene (10 mL) and MAO (2 mmol) were loaded into the Schlenk flask. The vanadium compound (0.05 mmol based on vanadium atoms) was then added as a toluene solution (0.01 M) and the mixture was stirred at room temperature for 5 min. After the external bath temperature had stabilised, MTCA (2 mmol) and the monomer were added with a syringe. The polymerisation was terminated by addition of acidic methanol (MeOH/HCl = 10:1; 3 mL). The product was precipitated into ethanol (200 mL), filtered off, and dried under vacuum. The molecular mass and the molecular mass distribution were determined by GPC. The polymerisation of ethene was carried out either in a Schlenk tube or in a glass autoclave (1 L) equipped with a stirrer. For Schlenk tube polymerisation, toluene (50 mL), MAO (0.8 mmol), $[VOCl_2(OCH_2CH_2OCH_3)]_2$ (5 μmol), and MTCA (0.8 mmol) were stirred for 10 min. Afterwards, ethene was polymerised at room temperature at an ethene pressure of 1 bar. Toluene (200 mL), MAO, and MTCA (MAO/MTCA = 1:1) were injected sequentially into the autoclave at 30 °C, and the mixture stirred for 15 min. The vanadium precatalyst was then injected into the reactor and allowed to interact with MAO for 10 min. In the case of Et_2AlCl the co-catalyst solution was divided into two parts: one half was injected into the autoclave together with MTCA (MTCA/$Et_2AlCl \geq 1{:}1$) and the other half was used to activate the sample of precatalyst solution for 15 min prior to injection into the reactor. The ethene pressure in the autoclave was kept at 2 bar during all polymerisations. Polymerisations were quenched with a 5% solution of HCl in ethanol (150 mL). The mixtures were poured into water (150 mL) and stirred for 30 min. The white precipitate was collected by filtration, washed with ethanol and dried at 60 °C to a constant weight. Molecular masses and polydispersities were determined by GPC.

Acknowledgments

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