Polyethers for biomedical applications

Polymerization of propylene oxide by organozinc/organotin catalysts

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SUMMARY:
    The polymerization of propylene oxide to obtain a high-molecular-weight polymer with an
atactic structure required for the application as artificial blood vessels was investigated using
combinations of organozinc and organotin compounds as catalyst. The composition of the
most active catalyst, resulting from the reaction of diphenyltin sulfide with bis(3-dimethyl-
aminopropyl)zinc, was found to be $R(C_6H_5)_2Sn(SZn)_2R$ with $R = (CH_2)_3N(CH_3)_2$. Using this
catalyst, an anionic coordination polymerization was observed with neither stereoselectivity nor
living type or cationic features. At low catalyst concentration (0,03 mol-% Zn) a high-molecu-
lar-weight poly(propylene oxide) (PPOX) was obtained in 80 – 90% yield ($\overline{M}_w$ = 500 000; 40%
isotactic). Lowering of the catalyst concentration and increasing the polymerization tempera-
ture changed the kinetics and the stereochemistry of the polymerization leading to polymers of
lower molecular weight and to a decrease in the isotactic PPOX fraction to 20%, probably due
to an association of the catalytic species.

Introduction

    Recently we reported on the applicability of atactic poly(propylene oxide) (PPOX)
as an elastomeric material for the manufacture of artificial blood vessels[1]. In our
research program we have also tried to reduce the catalyst residue content in the poly-
mer and to obtain high-molecular-weight atactic PPOX in a high yield. A reduction
of the content of catalyst residue is desirable because it is toxic and induces the degra-
dation of the polymer. Thus, a high molecular weight and an atactic structure of the
polymer are required for appropriate mechanical properties needed in artificial blood
vessels.

    Already in 1955 the first results were reported[2] about the polymerization of propylene oxide
(POX) with a ferric chloride-monomer complex as a catalyst, yielding high-molecular-weight
poly(propylene oxide) (PPOX). In the following years several authors explored this ring-
opening polymerization[3 – 6]. The initiation was proven to occur by coordination of the oxygen
of the monomer to a metal atom (e. g. Fe, Zn, Al) in the catalytic system, followed by an
opening of the methylene-oxygen and/or the methine-oxygen bond, depending on the catalyst.
The propagation was suggested to be catalyst site controlled[7, 8].

The stereochemistry of the polymerization was found to depend on the stereospecificity of the catalytic sites[3, 9, 10], which could lead to the formation of head-to-tail isotactic and atactic PPOX and atactic PPOX with head-to-head and tail-to-tail sequences. Head-to-tail polymerization results from an exclusive opening of the methine-oxygen bond and is associated with an anionic polymerization mechanism (e. g. KOH as a catalyst), whereas head-to-head and tail-to-tail sequences are formed in a cationic polymerization, which allows random opening of the carbon-oxygen bonds[11].

In a coordination polymerization reaction both anionic and cationic features can be present. Differences have been observed between organozinc and organoaluminium based catalysts: generally aluminium based catalysts are more cationic and zinc based catalysts are more anionic initiators[3, 12]. However, occasionally organozinc based catalysts also produce head-to-head and tail-to-tail sequences[11, 12].

The effect of cocatalysts was investigated with ferric chloride and organoaluminium catalysts[13], but also with organozinc compounds: water[14], alcohols[15, 16], nitromethane[17], sulfur and sulfides[18–20], DMSO[21], ketones[22], amines[21, 23] and metal oxides[24].

The activity of these catalytic systems was found to originate from the presence of Zn-O, Zn-S or Zn-N bonds. Comparison of the different organozinc based catalysts showed that in particular the sulfur and nitrogen[12] containing cocatalysts strongly contribute to the catalytic activity of the system. Results of Lal et al.[18–20] and Furukawa et al.[21] clearly illustrate this for the sulfur containing cocatalysts. The higher nucleophilicity of the Zn-S sequence present in these catalysts, compared to the Zn-O sequence in other catalysts, might be responsible for the observed increased initiation rate[25].

Recently Buys et al.[26] showed the high activity of catalysts based on organozinc compounds and organotin sulfides. Tin compounds have also been reported to yield active catalysts[27,28].

In view of the promising results of Buys et al.[26] we investigated the polymerization of propylene oxide with several combinations of organozinc and organotin compounds in order to obtain high-molecular-weight polymers with low residual catalyst contents and an improved stability against oxidative attack.

With the most active catalytic system the polymerization behaviour and the stereochemistry of the polymerization reaction was studied as a function of temperature and catalyst concentration.

Experimental part

General remarks: The preparation and handling of the catalyst systems were carried out in an atmosphere of purified nitrogen using Schlenk-type techniques. Solutions and solvents were transferred with syringes; all solvents used (pentane, benzene, toluene, and a mixture of *o*- and *p*-xylene) were carefully dried using the appropriate methods, and distilled under nitrogen directly before use.

Materials: The synthesis of bis(3-dimethylaminopropyl)zinc has already been described[29]. Diethylzinc (from Alfa-Ventron, Germany) was distilled prior to use. Triphenyltin hydroxide (from M & T Vlissingen, The Netherlands) was recrystallized from ethanol. Diphenyltin sulfide and 2-(triphenyltinthio)ethanol were synthesized according to Boersma[30].

Preparation of catalysts: In a flask flushed with nitrogen the zinc and tin components (1 : 1 mole ratio) (Tab. 1) were dissolved in a freshly distilled solvent (benzene, toluene, *o*- and *p*-xylene). The mixture was gently heated to reflux, kept boiling for 45 or 60 min and allowed to cool to room temperature. For a detailed study of the catalytic activity of the 3,3-bis(dimethylaminopropyl)zinc/diphenyltin sulfide system (catalyst C4), stock solutions of both components in freshly distilled benzene were prepared, and for the catalyst preparation correct volumes were mixed applying a 1 : 1 mole ratio with nitrogen flushed syringes.

Catalyst C1: During the reaction of the components (s. Tab. 1) an insoluble product was formed, which proved to be catalytically acitve. The precipitate was isolated by filtration and washed with benzene to remove byproducts.

Tab. 1. Conditions for the syntheses of catalysts[a]

Catalyst code	Zn component	Sn component	Reaction time in min	Temp. in °C	Solvent
C1	Et_2Zn	$Ph_3SnSCH_2CH_2OH$	60	80	Benzene
C2A	Et_2Zn	Ph_3SnOH	60	80	Benzene
C2B	Et_2Zn	Ph_3SnOH	60	130	Toluene/ o- and p-xylene
C3	Et_2Zn	Ph_2SnS	60	80	Benzene
C4	$((CH_3)_2N(CH_2)_3)_2Zn$	Ph_2SnS	45	80	Benzene

[a] 1:1 mole ratio of Zn component/Sn component. Conc. of the solutions see Tab. 2.

Catalysts C2: Heating of the components in refluxing benzene (catalyst C2A) or in a toluene/o- and p-xylene mixture (vol. ratio 1:9) (catalyst C2B), and subsequent cooling to room temperature gave a yellow solution and a white crystalline precipitate of tetraphenyltin, which was separated by filtration. Evaporation of the solvent from the filtrate resulted in a catalytically active yellow solid, which was further purified by extraction with pentane.

Catalyst C3: In this case a precipitate was formed during the reaction of the components in refluxing benzene. This precipitate was not filtered, but from the whole reaction mixture the benzene was evaporated and the remaining solid was used as catalyst.

Catalyst C4: During the reaction of the components in boiling benzene and after cooling no precipitate was formed. Evaporation of the benzene resulted in a white oily residue, which was used as catalyst.

Polymerizations: Propylene oxide (from Merck; purity > 99%), freshly distilled from anhydrous calcium chloride in a nitrogen atmosphere, was added to the catalyst in glass tubes, and after sealing the tubes the polymerization proceeded at room temperature. After the polymerization, volatile compounds, if present in the reaction products, were evaporated (0,1 mbar; 20 °C) until constant weight of the tube contents. The amounts of zinc and tin in the polymerizing systems were determined indirectly by analysis of the Zn and Sn in the polymers (AAS). Polymer yields were not corrected for catalyst residues in the polymers. After evaporation until constant weight, the polymers were dissolved in monomer, filtered and precipitated in water. Samples of these precipitated polymers were used for molecular weight determinations.

Differential scanning calorimetry (DSC): In a temperature range from 0 to +100°C thermograms were recorded using a Dupont DSC 990 instrument at a heating rate of 10 °C/min. Indium was used to calibrate the temperature scale and to determine the heat of fusion of the PPOX batches. Transition temperatures were determined with samples weighing 10 ± 2 mg.

Zinc, tin and sulfur analysis: The Sn and Zn content in the polymers was determined using a Zeeman/5000 (Perkin-Elmer) atomic absorption spectrometer (AAS). Destruction was realized with a HNO_3/H_2SO_4 mixture according to Kjeldahl. Zinc was detected with a flame AAS, following standard methods; tin was measured with a flameless AAS with stabilized temperature platform and Zeeman correction, using $(NH_4)_2HPO_4$ (2,5%) and $Mg(NO_3)_2$ (0,2%) as a matrix modifier. Detection errors were 2 and 5% for Zn and Sn, respectively. The sulfur analysis was performed according to ref. [31] (error: 5%).

Low angle laser light scattering (LALLS): The refractive index increment of PPOX in dichloromethane was determined using a Brice Phoenix differential refractometer BP-2000-V (at 633 nm): $dn/dc = 0,035 \pm 0,001$. Dichloromethane was chosen, having the best combination

of good solubility for PPOX and a low refractive index of the solvent. The instrument was thermoset to 25 ± 0,1 °C by means of a water-circulating thermostat. The instrument was calibrated with KCl solutions of known concentration. The 0,5 wt.-% solutions of PPOX in dichloromethane were filtered through a Fluoropore filter (Millipore S. A.) FHLP (0,5 μm) prior to injection into the HPLC-LALLS system. (Laser Ne-He: 633 nm, pump: Waters, Solvent Delivery System 6000 A, Waters U6K Injector, detectors: Chromatix KMX-6 LALLS-photometer and a Waters differential refractometer R 403, columns: Waters micro-styragel 10^5 + 10^4 + 10^3 Å (serial). The dn/dc and LALLS signal were recorded simultaneously and calculation of the molecular weight distribution was accomplished using a computer program. The errors in the dn/dc value and in the LALLS signal resulted in a 10% error in the calculated molecular weights. For samples of polymerizations with low conversions (5 – 15%) the molecular weight determinations are less accurate due to microgel formation.

Viscometry: Using solutions of poly(propylene oxide) in toluene (0,1 g/dl) the intrinsic viscosity at 25 °C was determined.

^1H *and* ^{13}C *Nuclear magnetic resonance:* ^{1}H and ^{13}C NMR spectra were recorded in deuterated solvents (^{1}H: *d*-chloroform and ^{13}C: d_2-dichloromethane) using a Nicolet NT 200 (200 MHz) and a Bruker WP80 (80 MHz) instrument, respectively.

Results and discussion

Introductory experiments

The results of a first attempt to obtain polymers of high molecular weight with low catalyst residue contents are given in Tab. 2. Although the polymerization with the various catalytic systems has not been investigated in detail by varying parameters like catalyst concentration, reaction time or temperature, it can be seen that, depending on the type of catalyst, poly(propylene oxide)s with high molecular weight and low $\bar{M}_w/\bar{M}_n$ values could be obtained.

Polymerizations of propylene oxide with organozinc based catalysts have been reported[13–28] to result in conversions of 50 – 100% with catalyst concentrations of 0,5 to 5 mol-% and viscosity-average molecular weights of 0,1 to 4,5 · 10^5. Comparison of these results with the data shown in Tab. 2 shows that the catalysts, used in our study, have similar activities.

It can also be seen from Tab. 2 that polymers P-C4A and P-C4B have lower molecular weights than the other polymers. However, using catalyst C4 polymers with the lowest Zn and Sn contents were obtained, and for that reason the polymerization conditions leading to high-molecular-weight polymers were studied in more detail.

Characterization of catalyst C4

The formation of the catalyst by reaction of bis(3-dimethylaminopropyl)zinc with diphenyltin sulfide was studied in benzene at 80 °C using ^{1}H and ^{13}C NMR. During the reaction and after cooling no precipitate was formed. Samples were taken from the solution after different reaction times and ^{1}H NMR spectra (at 80 MHz) of the reaction mixture showed that the triplet, originating from Zn-CH$_2$—C$\lesssim$ (δ = 0,27), slowly disappeared indicating a transfer of a 3-dimethylaminopropyl group from the zinc to the tin atom. Simultaneously, in the phenyl group region a new multiplet

Tab. 2. Results of the polymerization of propylene oxide (POX) with various catalysts [a]

Polymer code	Catalyst [b] conc. in mol-%	Pentane [c] extraction	Conversion [d] in %	$10^{-3} \cdot \bar{M}_n$ [e]	$10^{-3} \cdot \bar{M}_w$ [e]	$\bar{M}_w/\bar{M}_n$	Crystallinity [f] in %	Mole ratio Zn/Sn	Wt.-% of [g] Zn + Sn
P-C1	1,05	−	90	450	510	1,3	6	8	1,61
P-C2A	1,07	+	95	413	442	1,1	9	4,2	1,80
P-C2B	0,92	+	95	415	442	1,1	9	2,4	1,48
P-C3	0,80	−	90	218	322	1,5	8	1	2,68
P-C4A	0,10	−	100	140	515	3,7	15	1	0,32
P-C4B	0,03	−	80	171	308	1,8	15	1	0,10

[a] Catalyst and 20 ml of monomer (0,28 mol) mixed at 20°C; polymerization time: 20 h; polymerization time for P-C4B: 120 h.

[b] ±2%, based on the initial amount of Zn-component.

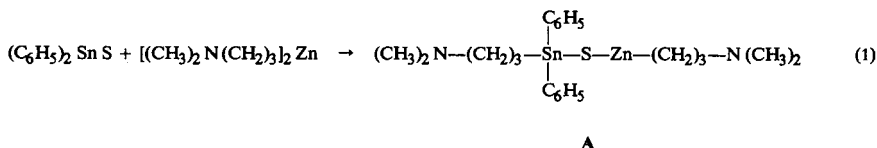[c] Extraction of the catalyst with pentane prior to polymerization.

[d] ±5%; after evaporation of volatile compounds; time: 12 h, pressure: 0,1 mbar, temp.: 20°C.

[e] ±10%.

[f] ±5% (DSC), compared to ref. [32]; ΔH_f = 8,4 kJ/mol (= 100%).
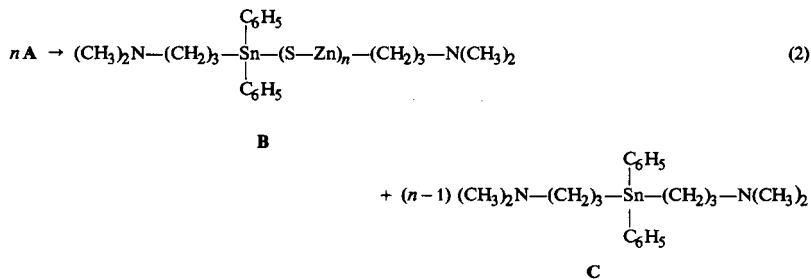
[g] ±7%, determined in the polymer.

centered at $\delta = 7,3$ appeared and the intensity of the original diphenyltin sulfide multiplet, centered at $\delta = 7,7$, decreased. Complete conversion of the initial zinc and tin component was indicated by the total disappearance of the signals at $\delta = 0,27$ and 7,7. The observations indicate the reaction as shown in Eq. (1).

$$(C_6H_5)_2 \, Sn \, S + [(CH_3)_2 \, N(CH_2)_3]_2 \, Zn \quad \rightarrow \quad (CH_3)_2 \, N\!-\!(CH_2)_3\!-\!\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{\overset{|}{\underset{|}{Sn}}}}\!-\!S\!-\!Zn\!-\!(CH_2)_3\!-\!N(CH_3)_2 \qquad (1)$$

<div align="center">A</div>

The formation of a species like **A** was also proposed by Buys et al. [26] for the system triphenyltin hydroxide and diphenylzinc. Due to the large number of different methylene and methyl groups present in the reaction mixture the interpretation of the splitting patterns was difficult. Therefore, bis(3-dimethylaminopropyl)zinc was reacted with elementary sulfur and tin sulfide in benzene at 65 °C, using a 1:1 or a higher mole ratio. From the ^{1}H NMR spectra of the reaction mixtures the shifts of the protons attached to the α-carbon could be determined. Comparison of these spectra with the ^{1}H NMR spectrum of the catalyst showed that thiolate moieties $\geqslant$C—Sn—S—C$\leqslant$ or $\geqslant$C—Zn—S—C$\leqslant$ ($\delta = 2,4-2,6$) were absent and that S—Mt—CH$_2$CH$_2$CH$_2$N(CH$_3$)$_2$ groups were present (for Mt = Zn and Sn). In addition, triplets were observed from the —S—Sn(Ph)$_2$—CH$_2$—($\delta = 1,2$) and —S—Zn—CH$_2$—groups ($\delta = 0,8$) and a multiplet system ranging from $\delta = 2,1$ to 1,0 for the —CH$_2$CH$_2$N(CH$_3$)$_2$ groups.

In order to get more information about the structure of the catalyst, the benzene was evaporated from the solution and the oily residue was extracted with pentane [26]. This resulted in an insoluble white solid **B** and a soluble part **C**. ^{1}H analysis of **B** and **C** gave spectra with about the same aromatic/aliphatic proton ratio (10/24 and 10/22), indicating in both cases a 1:1 ratio of phenyl groups to 3-dimethylaminopropyl groups. A zinc and tin analysis of **B** and **C** showed a Zn/Sn ratio of 2 in **B** and the presence of only tin in **C**.

These data point to the occurrence of a subsequent reaction of **A** leading to **B** and **C**.

$$n\,\mathbf{A} \;\rightarrow\; (CH_3)_2N\!-\!(CH_2)_3\!-\!\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{\overset{|}{\underset{|}{Sn}}}}\!-\!(S\!-\!Zn)_n\!-\!(CH_2)_3\!-\!N(CH_3)_2 \qquad (2)$$

<div align="center">B</div>

$$+\; (n-1)\,(CH_3)_2N\!-\!(CH_2)_3\!-\!\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{\overset{|}{\underset{|}{Sn}}}}\!-\!(CH_2)_3\!-\!N(CH_3)_2$$

<div align="center">C</div>

A reaction leading to species like **B** and **C** has also been reported for the system triphenyltin hydroxide/diphenylzinc [26]. Compound **B** showed catalytic activity, where-

as polymerization did not occur in the presence of compound **C**. Product **B** was found by elemental analysis to contain 10,5% sulfur, which means $n = 2$ (calc. 10,0% S).

Analysis of the catalyst by ^{13}C NMR spectroscopy revealed the presence of phenyl groups attached to tin (two multiplets at $\delta = 126 - 128$ and $135 - 137$) and also signals for the 3-dimethylaminopropyl group were found: $Mt-C_\alpha-C_\beta-C_\gamma-N-C_\delta$, $\delta\,C_\alpha = 14,3$, $\delta\,C_\beta = 23,6$, $\delta\,C_\gamma = 62$ and $\delta\,C_\delta = 45,7$. However, no peaks could be assigned to distinguish between $-S-Zn-C\xi$ and $-S-Sn-C\xi$.

From these results we suggest the catalytically active species in the polymerization of propylene oxide to be **B** with $n = 2$.

Studies on organozinc complexes used for the polymerization of propylene sulfide[25, 33 - 35] indicate a strong coordination of nitrogen leading to 5-membered rings (like $Zn-S-CH_2-CH_2CH_2-N-$) which were stable during the polymerization of propylene sulfide. It is very suggestive that the coordination of a tertiary amine to zinc in these complexes increases the rate of the polymerization of propylene sulfide. The coordinative interaction between zinc and nitrogen was also observed[29, 36, 37] in bis(3-dimethylaminopropyl)zinc. It may, therefore, be assumed that this coordination is also present in catalyst **B**, possibly affecting the rate of the polymerization of propylene oxide.

Polymerization of propylene oxide (POX)

In Tab. 3 the results of the polymerizations of POX with different concentrations of **B** are presented. When the monomer was brought into the glass tubes a white suspension was formed. At catalyst concentrations lower than 0,045 mol-% Zn a transparent viscous solution was formed during the polymerization, which at completion of the polymerization turned into a white solid. Polymerizations with higher catalyst concentrations lacked this transparent phase. Tab. 3 shows that high conversions of POX could be realized with Zn concentrations of 0,030 mol-% or higher. Whereas only small fluctuations in the $\bar{M}_w$ values were observed, the $\bar{M}_n$ value initially increased with the catalyst concentration. It is interesting to note that most of the $\bar{M}_w/\bar{M}_n$ values of the polymers in Tab. 3 and also in Tab. 2 are lower than generally observed in coordination polymerizations[12] ($\bar{M}_w/\bar{M}_n > 3$).

No relationship between catalyst concentration and molecular weight was observed; obviously, the number of active sites and the activity are not proportional to the catalyst concentration. Several authors[6, 11, 33] mentioned the inefficiency of the catalysts for epoxy polymerization in comparison with the very low transition metal content used for olefin polymerizations. Only a few tenth of per cent or a few per cent of the catalytic species is active in epoxy polymerization[11]. The inactivity of the catalysts is attributed to the formation of less active species, which may result from association of monomeric catalyst molecules[12]. This association is favoured in heterogenic monomer/catalyst systems and is often still present in apparently homogenic systems[33, 38].

Association of monomeric organozinc catalyst molecules, even in solution and in the presence of monomer, has been observed by Tsuruta et al.[39] and Kageyama et

Tab. 3. Results of the polymerization of propylene oxide (POX) with catalyst **B**[a]

Polymer code	Conc. of[b] Zn in mol-%	Conc. of[c] Sn in mol-%	Mole ratio Zn/Sn	Conversion[d] in %	$10^{-3} \cdot \bar{M}_n$[e]	$10^{-3} \cdot \bar{M}_w$[e]	$\bar{M}_w/\bar{M}_n$	Wt.-% of[f] Zn + Sn
3.1	0,081	0,041	1,98	100	182	433	2,4	0,18
3.2	0,074	0,036	2,06	99	261	484	1,9	0,16
3.3	0,045	0,023	1,96	99	330	463	1,5	0,10
3.4	0,030	0,015	2,00	88	308	483	1,6	0,07
3.5	0,015	0,007	2,14	25	308	486	1,6	0,12
3.6	0,010	0,005	2,00	4	297	434	1,5	0,77

a) Polymerization of 60 ml POX (0,84 mol) in sealed glass tubes at 20°C during 120 h.
b) ±2%.
c) ±5%.
d) ±2% (after 12 h; pressure: 0,1 mbar; temp.: 20°C).
e) ±10%.
f) ±7%, determined in the polymer.

al. [40]. Therefore, in our study, the initial heterogeneity of the monomer/catalyst mixture might also lead to association, owing to the presence of ZnS sequences and electrondonating tertiary amine moieties.

From Tab. 3 it is obvious that high molecular weights could be obtained applying catalysts with low contents of residues. The Zn/Sn mole ratio of about 2, as determined in the polymers, agrees with the ratio found in the catalyst **B**. Comparison of the properties of polymer P-C4B (Tab. 2) with those of polymer 3.4 (Tab. 3) shows that extraction of the catalyst with pentane resulted in the formation of polymers with higher molecular weights as well as a lower catalyst residue contents. Tab. 3 also shows that the yield does not vary substantially changing from a concentration of 0,08 to 0,03 mol-% Zn, an effect only been found by Lal[20] with a diethylzinc/sulfur system (0,1 to 0,4 mol-% Zn) and by Furukawa et al. [21] with a diethylzinc/DMSO catalyst (0,01 to 0,2 mol-% Zn). With these zinc and sulfur containing catalysts they report molecular weights ($\overline{M}_v$) of 0,4 to $2 \cdot 10^5$ and yields up to 100%.

Fig. 1 shows the conversion vs. time curve for the polymerization of propylene oxide with catalyst **B**. Polymerizations were carried out during different times using in each experiment the same amount of monomer and catalyst. An initial low polymerization rate was found, also observed by Lal[19] for zinc containing catalysts for the polymerization of POX which he explained by suggesting an initiation proceeding over an extended period of time. Nomura et al. [28] observed an induction period using organotin based catalysts for the polymerization of POX and tentatively attributed this induction period to a cleavage of the tin component into active catalyst species.
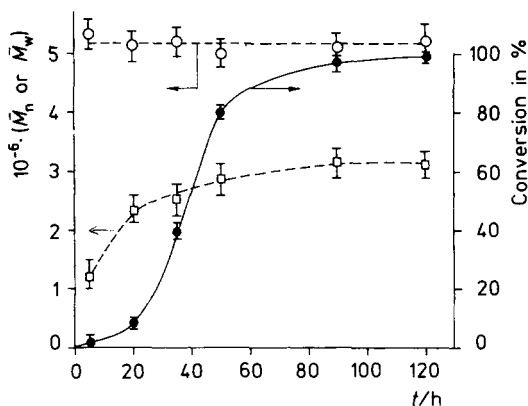

Fig. 1. Conversion (●), $\overline{M}_n$ (□) and $\overline{M}_w$ (○) as functions of time for the polymerization of 10 ml (0,14 mol) of propylene oxide at 20 °C with catalyst **B** (0,051 mol-% Zn)

As mentioned before the results presented in Tab. 3 do not indicate a relationship between molecular weight and catalyst concentration. On the other hand, the polymerization rate increases with increasing catalyst concentration: The conversion of POX with a catalyst concentration of 0,015 mol-% Zn was 25% after 120 h (Tab. 3, Exp. 3.5), whereas a 25% conversion was already obtained after 30 h with a catalyst concentration of 0,051 mol-% Zn (Fig. 1).

Fig. 1 also shows that during the polymerization $\bar{M}_n$ initially increases, whereas at higher conversions a constant value is observed. Since $\bar{M}_w$ is constant during the polymerization this results in a narrowing of $\bar{M}_w/\bar{M}_n$ to 1,6, which is attributed to a uniformity in the conformation and reactivity of the catalytic sites[11]. Upon introduction of a second batch of monomer (10 ml; 0,14 mol) to a catalyst/polymer/monomer mixture (10 ml POX, 0,14 mol, 0,03 mol-% Zn; 120 h; 20 °C; conversion: 95%) polymerization was re-initiated. After another 120 h of polymerization a conversion of 90% was observed (based on 20 ml of POX) and the intrinsic viscosity of the polymer before and after the second introduction of monomer was the same [η] = 14,5 dl/g (120 h) and 14,7 dl/g (240 h). The observation of identical molecular weights suggests that the re-initiation of the polymerization is caused by new catalytic sites and a living type polymerization, as observed by Booth et al.[14], can, therefore, be excluded.

The influence of heterogeneity, possibly due to association, was investigated by adding benzene, which dissolves both the monomer and the catalyst, to the polymerization mixture. However, the transparent solution turned opaque during the initiation phase. The results of these experiments are shown in Tab. 4 and it is obvious that no conclusions can be drawn.

The influence of the temperature on the polymerization was studied by polymerizing at 20 and 65 °C, using different catalyst concentrations (Tab. 5). In these experiments a benzene stock solution of the catalyst was used to obtain catalyst/monomer/solvent mixtures of known catalyst concentration.

It is obvious that the polymerizations at 20 °C give higher-molecular-weight polymers than those at 65 °C. With the same catalyst concentration lower molecular weights are obtained at 65 °C than at 20 °C (0,050, 0,020 or 0,010 mol-% Zn). Furthermore, broader molecular weight distributions are observed at 65 °C. In contrast with the room temperature experiments, the polymerization mixtures kept at 65 °C remained transparent until conversions higher than 55% were reached. From Exps. 5.1 and 5.2 it can be seen that higher catalyst concentrations lead to molecular weights which are higher than those obtained with other catalysts (see Tab. 2). The apparent change in the catalytic activity by increasing the temperature might be caused by dissociation of di-, tri- or tetramers of catalyst molecules at higher temperatures. This hypothesis will be verified by ebulliometric analysis of the catalyst species in benzene (25 – 80 °C).

Polymer characterization

Stability of PPOX

Poly(propylene oxide) is known to be susceptable to degradation[41,42] on exposure to air, moisture and daylight; its stability is strongly influenced by the amount of residual catalyst in the polymer. In an attempt to remove the catalyst residue the crude polymer was dissolved in propylene oxide or dichloromethane and precipitated in water or hexane, respectively. In case of the solvent/non-solvent system propylene oxide/water, apart from de-ionized water 0,1 N HCl and 0,1 N NaOH solutions were used as non-solvents for removal of the tin and zinc residues. However, these purifications resulted only in a decrease of the tin contents in the polymer.

Tab. 4. Results of polymerization of propylene oxide (POX) with and without benzene as solvent [a]

Polymer code	Conc. of [b] Zn in mol-%	Conc. of [c] Sn in mol-%	Conversion [d] in %	Vol. of benzene in ml	$10^{-3} \cdot \bar{M}_n$ [e]	$10^{-3} \cdot \bar{M}_w$ [e]	$\bar{M}_w/\bar{M}_n$
4.1	0,150	0,075	98	0	221	585	2,6
4.2	0,153	0,075	97	8	230	636	2,8
4.3	0,074	0,036	95	0	217	377	1,7
4.4	0,070	0,037	97	8	207	369	1,8

[a] Polymerization of 8 ml POX (0,11 mol) at 20°C during 120 h, using catalyst **B**.
[b] ±2%.
[c] ±5%.
[d] ±2% (after 12 h, pressure: 0,1 mbar, temp.: 20°C).
[e] ±10%.

J. G. F. Bots, L. van der Does, A. Bantjes, J. Boersma

Tab. 5. Results of the polymerizations of propylene oxide (POX) at 20 and 65 °C[a]

Polymer code	Conc. of[b] Zn in mol-%	Conc. of[c] Sn in mol-%	Conversion[d] in %	Temp. in °C	$10^{-3} \cdot \bar{M}_n$[e]	$10^{-3} \cdot \bar{M}_w$[e]	$\bar{M}_w/\bar{M}_n$
5.1	0,200	0,098	100	20	627	768	1,2
5.2	0,100	0,047	100	20	432	562	1,3
5.3	0,050	0,025	78	20	299	462	1,5
5.4	0,020	0,009	50	20	209	387	1,9
5.5	0,010	0,005	11	20	189	343	1,8
5.6	0,050	0,026	80	65	97	272	2,8
5.7	0,020	0,009	55	65	67	200	3,0
5.8	0,010	0,005	6	65	56	171	3,1

a) Polymerization of 8 ml of POX (0,11 mol) in 8 ml of benzene during 120 h with catalyst **B**, prepared by mixing of exact volumes of a catalyst stock solution with benzene and monomer.

b) ± 2%.

c) ± 5%.

d) ± 2% (after 12 h, pressure: 0,1 mbar, temp.: 20°C).

e) ± 10%.

Another method to decrease the metal contents was used by dissolving the polymer in toluene followed by steam distillation. By removing the toluene the polymer precipitated and the catalyst residues remained in the aqueous phase. The metal contents decreased, but polymer degradation was also induced. Therefore, all the polymers listed in Tab. 2 were only purified by a propylene oxide/water precipitation. However, they lost their elastomeric properties within a few months, except for P-C4B (Tab. 2) which did not show any degradation after one year, possibly due to the low metal content.

Stereochemistry of PPOX

Analysis of the amount of crystallinity in the different polymer batches by DSC (Tab. 2) showed that amorphous polymers were obtained and that only little influence of a variation in the zinc and tin components on the crystallinity was observed.

To obtain more information about the stereochemistry of the polymerization, two polymerization products were analyzed (4.3 and 4.4, Tab. 4). Both polymers could be separated in an atactic and an isotactic fraction by precipitation of the isotactic polymer at $-30\,°C$ in $0,5$ weight-% acetone solutions. The fractions were analyzed by determination of their optical rotations (in a 5% dichloromethane solution) and no optical rotation was observed. Therefore, it could be concluded that equal amounts of active sites polymerizing only $(-)$-propylene oxide and only $(+)$-propylene oxide were present in the catalyst. GPC-LALLS measurements (Tab. 6) showed that different molecular weights for the atactic and isotactic fraction were obtained. Obviously, the stereospecific catalytic sites yielding isotactic poly(propylene oxide) are more active than the atactic polymer yielding sites[12].

Separation of the atactic and isotactic fraction from the polymers, obtained with high and low catalyst concentration, showed that a decrease in the catalyst concentration results in a lower fraction of isotactic poly(propylene oxide) (Tab. 7). These results can be explained by a lower association degree of the catalytic species with decreasing catalyst concentration. A lower association degree can lead to a more stereorandom polymerization[12]. Thus, since stereorandom catalytic sites are less active than the stereospecific analogues, this might explain the increase in atactic polymer with a lower molecular weight with decreasing catalyst concentration.

From the analysis of the polymer samples obtained by polymerization at $65\,°C$ (Tab. 7) it is obvious that with increasing temperature a decrease in isotacticity is found, which points to a catalyst dissociation resulting from a higher temperature.

Apart from the tacticity also the presence of head-to-head and tail-to-tail linkages in the polymers was studied (Fig. 2). Comparison of the signals of methine and methylene groups in the ^{13}C NMR spectra with the data from the literature[9, 12] shows that only head-to-tail linkages are present in the polymers. As stated before this points to an anionic polymerization mechanism for this organozinc/tin based catalyst. Obviously, the absence of cationic features in this polymerization also prevents the formation of low-molecular-weight linear and cyclic products[11].

J. G. F. Bots, L. van der Does, A. Bantjes, J. Boersma

Tab. 6. Molecular weights of isotactic and atactic poly(propylene oxide)s [a]

Polymer code	Conc. of [b] Zn in mol-%	Conc. of [c] Sn in mol-%	Polymer fraction	Quantity in wt.-%	$10^{-3} \cdot \bar{M}_n$ [d]	$10^{-3} \cdot \bar{M}_w$ [d]	$\bar{M}_w/\bar{M}_n$
4.3	0,074	0,036	crude	100	217	377	1,7
			atact.	56	55	122	2,2
			isotact.	44	302	401	1,3
4.4	0,070	0,037	crude	100	207	369	1,8
			atact.	52	72	146	2,0
			isotact.	48	359	470	1,3

[a] Polymerization with catalyst **B** (see Tab. 4).
[b] ±2%.
[c] ±5%.
[d] ±10%.

Tab. 7.   Isotacticity of poly(propylene oxide)s

Polymer code	Conc. of [a] Zn in mol-%	Conc. of [b] Sn in mol-%	Temp. in °C	Conversion [c] in %	Isotactic [d] fraction in %
3.1	0,081	0,041	20	100	44
3.3	0,045	0,023	20	99	40
3.5	0,015	0,007	20	25	34
5.3	0,050	0,025	20	78	45
5.4	0,020	0,009	20	50	35
5.6	0,050	0,026	65	80	18
5.7	0,020	0,009	65	55	17

[a] $\pm 2\%$.
[b] $\pm 5\%$.
[c] $\pm 2\%$ (after 12 h, pressure: 0,1 mbar, temp.: 20 °C).
[d]   Separation by acetone precipitation at -30 °C.

Fig. 2.   ^{13}C NMR signals of methylene and methine groups in poly(propylene oxide)s. (A): Isotactic, (B): atactic poly(propylene oxide)
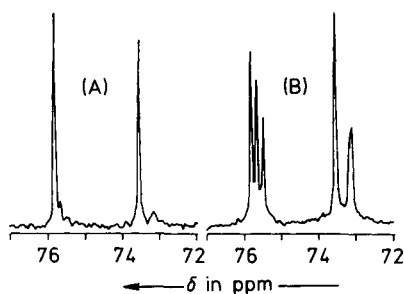
Conclusions

The most active organozinc/tin based catalyst **B** for the polymerization of propylene oxide is obtained by reacting bis(3-dimethylaminopropyl)zinc with diphenyltin sulfide and removing the byproducts by pentane extraction.

Association of catalyst **B** is indicated by several polymerization experiments. The polymerization is believed to be an anionic coordination polymerization without cationic features and without stereoselectivity. The ratio of isotactic/atactic PPOX, supposed to be determined by the association degree of the catalyst "monomers", increased with higher catalyst concentration and decreasing temperature. Re-initiation of the polymerization was observed by adding a second batch of monomer. The molecular weight and also the $\overline{M}_w/\overline{M}_n$ values remained the same. In most of the polymerization reactions the $\overline{M}_w/\overline{M}_n$ values were lower (1,5 − 2,0) than generally observed in coordination polymerizations ($\overline{M}_w/\overline{M}_n > 3$). With low concentrations of catalyst **B** high molecular weights could be obtained ($\overline{M}_w = 400\,000 - 500\,000$) substantially higher than those found by Lal[20] ($\overline{M}_v = 140\,000$) and Furukawa et al.[21] ($\overline{M}_v = 200\,000$). However, in our study no relationship between catalyst concentration and molecular weight was observed. Some preliminary data indicate an effect of the catalyst residue content in poly(propylene oxide)s on the stability against oxidative

attack. The presented results have shown that high yields of high-molecular-weight poly(propylene oxide) can be obtained using low concentrations of catalyst **B**, which is of considerable importance for our study on the use of these polymers for the manufacture of blood vessel prostheses.

[1] J. G. F. Bots, L. Van der Does, A. Bantjes, *Biomaterials* **7**, 393 (1986)
[2] U. S. 2 706 189 (1955), invs.: E. M. Pruit, L. Jackson, J. M. Baggett; *Chem. Abstr.* **49**, P9326a (1955)
[3] C. C. Price, R. Spector, *J. Am. Chem. Soc.* **87**, 2069 (1965)
[4] E. J. Vandenberg, *J. Polym. Sci., Part A-1*, **7**, 525 (1969)
[5] C. C. Price, M. Osgan, *J. Am. Chem. Soc.* **78**, 4787 (1956)
[6] E. J. Vandenberg, in *"Coordination Polymerization"*, vol. 19 of "Polymer Science and Technology", edited by C. C. Price and E. J. Vandenberg, Plenum Press, New York 1982, p. 11
[7] W. Kuran, A. Rokicki, J. Pienowsky, *J. Polym. Sci., Polym. Chem. Ed.* **17**, 1235 (1979)
[8] T. Tsuruta, *J. Polym. Sci., Part D* **6**, 179 (1972)
[9] J. Kasperczyk, A. Dworak, Z. Jedlinsky, *Makromol. Chem., Rapid Commun.* **2**, 663 (1981)
[10] C. C. Price, M. K. Akkepeddi, B. T. DeBona, B. C. Furie, *J. Am. Chem. Soc.*, **94**, 3964 (1972)
[11] S. Inoue, T. Aida, in *"Ring-opening Polymerization"*, vol. 1, edited by K. J. Ivin, T. Seagusa, Elsevier, London 1985, p. 187
[12] Y. Ishii, S. Sakai, in *"Ring-opening Polymerization"*, vol. 2, edited by K. C. Frisch, S. L. Reegen, Dekker, London 1965, p. 14 – 111
[13] E. J. Vandenberg, *J. Polym. Sci., Part A – 1*, **10**, 329 (1972)
[14] C. Booth, W. C. E. Higginson, E. Powell, *Polymer* **5**, 479 (1964)
[15] R. J. Harold, S. L. Aggerwal, V. Neff, *Can. J. Chem.* **41**, 1368 (1963)
[16] M. Nakaniwa, I. Kameoka, I. Hiria, J. Furukawa, *Makromol. Chem.* **155**, 197 (1972)
[17] M. Nakaniwa, I. Kameoka, K. Ozaki, N. Kabawata, J. Furakawa, *Makromol. Chem.* **155**, 185 (1972)
[18] J. Lal, *J. Polym. Sci., Polym. Lett. Ed.* **5**, 793 (1967)
[19] J. Lal, E. F. Devlin, *J. Polym. Sci.* **11**, 119 (1973)
[20] J. Lal, *J. Polym. Sci., Part A – 1*, **4**, 1163 (1966)
[21] J. Furukawa, N. Kabawata, A. Kato, *J. Polym. Sci., Part A – 1*, **5**, 3139 (1967)
[22] R. Sakata, K. Takeuchi, H. Yoskii, A. Onishi, *Makromol. Chem.* **98**, 253 (1966)
[23] D. R. Morgan, R. T. Wragg, *Makromol. Chem.* **125**, 220 (1969)
[24] K. Okazaki, *Makromol. Chem.* **43**, 84 (1961)
[25] P. Sigwalt, N. Spassky, in *"Ring-opening Polymerization"*, vol. 2, edited by K. J. Ivin, T. Seagusa, Elsevier, London 1985, p. 604
[26] H. C. W. M. Buys, H. G. J. Overmars, J. G. Noltes, in ref. [6], p. 75
[27] T. Nakata, in ref. [6], p. 55
[28] R. Nomura, Y. Shiomura, A. Ninagawa, H. Matsuda, *Makromol. Chem.* **184**, 1163 (1983)
[29] H. K. Hofstee, J. Boersma, J. D. van der Meulen, G. J. M. van der Kerk, *J. Organomet. Chem.* **153**, 245 (1978)
[30] J. Boersma, private communication
[31] H. T. Weber, J. H. H. G. Van Willigen, W. E. van der Linden, *Anal. Chim. Acta.* **160**, 271 (1984)
[32] *Polymer Handbook*, J. Brandup, E. H. Immergut, Wiley-Interscience, New York 1975
[33] J. Furukawa, Y. Kumata, K. Yamada, T. Fueno, *J. Polym. Sci., Part C* **23**, 711 (1968)

[34] W. Cooper, D. R. Morgan, *Eur. Polym. J.* **6**, 363 (1970), W. Cooper, D. R. Morgan. R. T. Wragg, *Eur. Polym. J.* **5**, 71 (1969)

[35] R. T. Wragg, *J. Chem. Soc. C:* **1969**, 2087

[36] J. Boersma, L. Fernholt, A. Haaland, *Acta Chem. Scand., Ser.* **A 38**, 523 (1984)

[37] J. Dekker, *Ph. D. Thesis*, Utrecht, The Netherlands, 1986

[38] J. Furukawa, T. Tsuruta, R. Sakata, T. Seagusa, A. Kawasaki, *Makromol. Chem.* **32**, 90 (1959)

[39] T. Tsuruta, T. Hagiwara, M. Ishimori, ref. [6], p. 45

[40] H. Kageyama, K. Miki, N. Tanaka, N. Kasai, *Makromol. Chem., Rapid Commun.* **3**, 947 (1982)

[41] S. L. Madorsky, S. Straus, *J. Polym. Sci.* **36**, 183 (1959)

[42] G. P. Roberts, M. Budzol, M. Dole, *J. Polym. Sci., Part A-2,* **9**, 1729 (1971)