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Stereoregular polymerization of propylene oxide by bis-dimethylaluminium oxide

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Stereoregular polymerization of propylene oxide (PO) by bis-dimethylaluminum oxide (BMAO) was studied. It is found that at 80°C a relatively high initial rate of the process rapidly dies away. By measuring and identifying the evolved by-product gases of the polymerization it was concluded that the decay of the rate is due to the transfer of a proton from the methyl (Me) group of PO, to the Me-Al groups of BMAO, by forming an aluminium allylalkoxide bond and a methane molecule. However, this transformation (and also the alcoholysis of Me groups of BMAO with several alcohols) apparently increases the stereoregular yield of the process. The polymerization process as well as the ionization of BMAO and the transport properties of ions were studied in the presence and absence of solvents, additives and monomer. Although BMAO extensively ionizes in the polymerization solution, the stereoregular yield of process increases as the dielectric constant of the media decreases. On the basis of present data the mechanism of polymerization was discussed. © 1997 Elsevier Science Ltd.

(Keywords: bis-dimethylaluminium oxide; propylene oxide; stereoregular polymerization)

INTRODUCTION

BMAO ($Me_2AlOAlMe_2$) is a monomer of poly(methylaluminium oxide) ($Me_2Al(OAlMe)_xMe$)[1] (PMAO). PMAO has been employed in homogeneous Ziegler–Natta catalysis[2] as well as being used to catalyse stereoregular polymerization of aldehydes[3], cyclic ethers[4] and lactones[5,6]. Stereoregular polymerization of PO by BMAO has been studied to some extent[4,7]. The observed fast decay of the relatively high initial rate of the process was interpreted by the presence of two consecutive reactions with different products[4]. In the primary reaction a mainly atactic low molecular weight polymer was produced by a fast simple cationic mechanism. This stage was quickly terminated due to combination of the counter charges. The terminated species were formulated by replacing the oxygen atoms of BMAO with oxygen–polyether–oxygen groups. It was further postulated that due to rearrangement and further association of Al atoms with ether groups of these terminated species produced active species for the secondary slow stage, that yielded a stereoregular high polymer[4]. The observed catalytic efficiency of BMAO in stereoregular polymerization was extremely low (1/600–1/40 stereoregular chain/Al atom[1,4]). Öktem *et al.*[1] by using PMAO and BMAO observed no significant difference in the catalytical activity between BMAO and PMAO with a variety of degree of polymerization [$1 \leq DP$ ($= x$ in the general formula of PMAO) ≤ 7] and concluded that the methylaluminiumoxide repeat units are the active catalysts in the stereoregular polymerization. Thus activity cannot be assigned to the presence of an 'undetected impurity' or an 'unidentified unique structure of PMAO'. In the present paper we would like to report new experimental data for the purpose of providing a detailed description of the stereoregular polymerization of PO with BMAO and a greater understanding of the mechanism of the process.

EXPERIMENTAL

General procedure

All experiments were carried on a vacuum line that allowed storing, measurement and transfer of reagents, solvents and products *in vacuo* with the possibility of handling them (transfer of measured amounts of samples, filtrations, decantations etc.) *in vacuo*.

Materials

All reagents and solvents were purified by standard procedures prior to fractionation by distillation on a column with approximately 25 theoretical plates. Calcium hydride was used as a drying agent and once purified, all solvents and reagents were stored *in vacuo* over CaH_2.

BMAO

BMAO was prepared as described in Ref. [1], by mixing dilute dioxan solutions of H_2O and $AlMe_3$ in a 1/6 molar ratio. A dilute solution ($\approx 5 \times 10^{-5}$ mol Al ml^{-1}) of the product in dioxan was stored in a closed flask from which known quantities could be measured out via a burette fitted with greaseless taps. ^{1}H-n.m.r. examination and molar mass measurements by isopiestic distillations showed that BMAO forms stable, cyclic-trimeric aggregates in dilute dioxan solution (6.3 Al atoms mol^{-1} of BMAO[1]).

Polymerization of PO and characterization of poly(propylene oxide)

Polymerizations were carried out by mixing PO, solvent or additives with freeze-dried BMAO. The reaction conditions are described in detail in the appropriate tables. Reaction rates were studied either by dilatometry or

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sampling experiments. Dilatometers with 0.1 cm bore Veridia glass tube necks and 1.0 cm bore cylindrical bulbs were used. Percentage conversions (0–20%) that were calculated from the volume shrinkage were found to be in good agreement with that of the gravimetric measurements. In sampling experiments the initial polymerization mixture was rapidly distributed into several sampling tubes at about 0°C; then these were placed in constant temperature baths (either at 40 or 80°C). Polymerization was terminated by adding a mixture of benzene and methanol. Polymers were isolated by freeze-drying from filtered benzene solutions and they were stabilized by the addition (1%) of diphenylamine acting as an antioxidant. The products could be split into two contrasting fractions[8]:

(1) K-polymers—this fraction had the higher molecular weight and crystalline fraction;
(2) D-polymers—this fraction was of low molecular weight ($500 \leq \bar{M}_n \leq 1000$), non-crystallizable oily polymer that contained considerable amounts of cyclic ethers.

Fractionation of PPO and characterization of K-polymers by intrinsic viscometry have been described previously[8].

Measurement of evolved methane

The amounts of active methyl groups (i.e. methyl groups those are directly bound to Al atoms), were determined by collecting the methane (MeH) gas that formed in the hydrolysis of BMAO or BMAO residues of the polymerization mixtures. For this purpose a specially designed Hg manometer that could measure the pressure difference between a known volume sample compartment and a reference compartment was used. Before the measurement the evolved gas mixture was treated by alkaline $KMnO_4$ solution (in order to remove any PO) and dried by passing through concentrated H_2SO_4 and finally over P_2O_5. Following this chemical treatment the evolved gas was found to be pure MeH, using a Finnigan MAT model 3000 quadruple mass spectrometer. In some experiments instantaneous amounts of evolved MeH in the course of polymerization were also measured. In these measurements the reference compartment contained pure PO. The sample compartment consisted of two glass bulbs with known volumes; one of these bulbs served as the polymerization reactor, and it can be isolated from the rest of the sample compartment by a teflon plug stopcock, while the other contained only pure PO. The whole apparatus was immersed in a bath at 40 ± 0.1°C. In order the measure the total amount of evolved MeH at a given polymerization time, the stopcock of the polymerization flask was closed and the gas mixture in the remaining volume of the sample compartment was saturated with PO vapour by vigorous stirring of the apparatus for 20 min. Following the establishment of the phase equilibria the pressure difference between two compartments was recorded.

Hittorf electrolysis of BMAO and PO-treated BMAO

Ionic transport property of BMAO in acetonitrile solution was studied by Hittorf electrolysis under vacuum conditions. The description of the instrumentation and details of electrolysis has been reported in a previous work[9]. Two solutions were electrolysed: the first one was BMAO and the other one PO-treated BMAO. The latter was prepared by polymerizing PO with BMAO until the formation of an apparently viscous solution. At this stage the excess PO was removed by distillation and a solution of known volume was obtained by adding acetonitrile.

RESULTS AND DISCUSSION

The primary and secondary stage of polymerization

Colclough and Wilkinson[4] observed that the initial rate of polymerization quickly decays; however, in later stages it becomes almost steady. Hence they described the polymerization as a double-stage consecutive process that consists of primary and secondary stages. In the primary stage, where the rate decelerates, PO is polymerized by BMAO with a simple cationic mechanism producing mainly D-polymers. In the course of this stage low molecular weight poly(propylene oxide) chains (PPO) replace O atoms in BMAO forming bis-dimethylaluminium alkoxydes of PPO (Me_2Al-OPPO-$AlMe_2$). Lewis acid–base interactions between Al atoms and etheric oxygens give rise to the formation of inter- and intramolecular cyclic complexes. Due to the occupation of all the coordination sites of Al atoms in these complexes, the cationic process is quickly terminated. However, these cyclic structures may be partially broken by the competition between O atoms of PO and PPO. When this occurs K-polymers are formed by a coordinate cationic mechanism. Thus according to Colclough and Wilkinson[4] BMAO is not an active catalyst for the stereoregular polymerization of PO, but the active species are formed from BMAO in the primary stage of the polymerization. However, on the basis of the following experimental results we concluded that the polymerization cannot be described as a 'double-stage process'.

(1) Dilatometric measurements showed that deceleration of the rate takes place throughout the process, but does not occur exclusively in the initial stages of the process (*Figure 1*).
(2) Sampling experiments have shown that the D- and K-polymers are concurrently formed throughout the process (*Table 1* and *Table 2*). The relative rate of K-polymer production steadily increases not only after the initial stage, but throughout the process.
(3) In the experiment-P9 (*Table 2*) only 3 min was allowed for polymerization (see also experiment-P19 in *Table 3*). Even under this condition the isolated product contained considerable amounts of K-polymers.

The deceleration of the rate of the polymerization process and methane production

Although the process cannot be described as a 'double-stage process', neither is it a smooth single-stage process. In sampling experiments (*Tables 1* and *2*) it is observed that production of D-polymers occurs at faster rates in the initial stages of polymerization. On the other hand the rate of K-polymer formation increases at the later stages of polymerization as the overall rate of process becomes apparently slower. We found that methane gas was simultaneously produced during the polymerization process. However, the content of active methyl groups of the reaction mixture (i.e. Me groups of BMAO or of the residue of BMAO in the polymerization mixture that can be hydrolysed to methane by 0.5 M aqueous H_2SO_4) decreased with increasing reaction time (*Table 4*). The methane evaluation rate decelerated together with the polymerization rate. In order to show this two aliquot mixtures were studied under similar conditions, the first sample was polymerized in a dilatometer whilst the second was polymerized using methane measuring equipment. Thus both instantaneous rates of polymerization and methane evolution are compared and given in *Figure 2*.

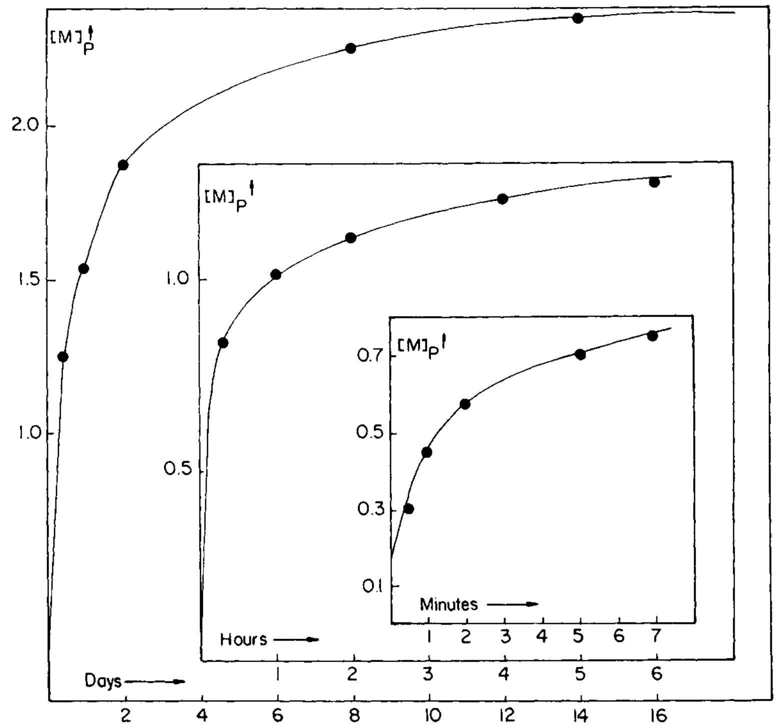


Figure 1 Deceleration of polymerization rate; where $[M]_p$ is the moles of PO polymerized in 1 l of reaction mixture. Reaction conditions: [Al] = 1.5×10^{-2} mol Al l^{-1}, $T = 80°C$

Table 1 The sampling experiment of the polymerization PO by BMAO. Reaction conditions—molarity of Al atoms = 1.72×10^{-2} mol kg^{-1}, temperature 80°C)

Experiment	Time	P_T[a]	P_K[a]	$100 \times P_K/P_T$	$\bar{M}_v \times 10^{-4}$[b]
P1	1 h	12.00	0.67	5.6	5.7
P2	5 h	16.20	1.20	7.4	9.3
P3	22 h	19.70	1.70	8.6	10.7
P4	3 days	23.80	2.32	9.7	12.4
P5	5 days	26.90	2.60	9.7	15.3
P6	15 days	31.60	3.16	10.0	16.3
P7	45 days	39.30	4.44	11.3	20.9
P8	130 days	59.80	11.45	19.2	29.8

[a] P_T and P_K are per cent conversions into total (i.e. K + D), K-polymers, respectively
[b] $\bar{M}_v$ of K-polymer

Table 2 The sampling experiment of the polymerization PO by BMAO. Reaction conditions—molarity of Al atoms = 1.80×10^{-2} mol kg^{-1}, temperature 40°C)

Experiment	Time	P_T[a]	P_K[a]	$100 \times P_K/P_T$	$\bar{M}_v \times 10^{-4}$[b]
P9	3 min	6.8	0.2	2.9	4.3
P10	30 min	12.6	0.6	4.8	6.3
P11	2 h	14.2	0.8	5.6	11.2
P12	8 h	16.0	0.9	5.6	12.5
P13	2 days	17.9	1.7	9.5	18.0
P14	30 days	24.4	3.7	15.2	35.6

[a,b] For an explanation of abbreviations see *Table 1*

No unsaturation on the K- or D-polymers could be detected by i.r.[8]. However, the almost oily product obtained from experiment M1 in *Table 4*, where a relatively low monomer/catalyst ratio was employed by allowing relatively short polymerization time, did show characteristic double bond absorption in the i.r. region. The double bond absorption vanished by treating the sample by iodine. Thus it appears that during the process methyl groups on Al atoms abstract a proton from the monomer yielding an aluminium-allyl alkoxide group together with a methane molecule. It is important to note that these result are insufficient to distinguish the location of double bonds. Double bonds might be on the chain terminals of PPO and/or might be attached to Al atoms as allyl alkoxide groups. We observed that removing the Al residue from the polymeric product was rather difficult[9] and the Al-PPO bond is almost stable even for prolonged storage under open conditions. In order to not to lose possible volatile and soluble fractions of the product of experiment M1 no attempt was made to remove the Al residues prior to the i.r. examination. Hence the question of whether or not the alkoxide or (allyl alkoxide) groups on the Al atom are added into growing chain remains unanswered.

Table 3 Effect of the catalyst concentration upon the K-polymer formation (polymerization temperature = 80°C)

Experiment	Time	m_{Al} (mol Al kg^{-1}) × 10^3	P_T^{a}	P_K^{a}	100 × P_K/P_T	$\bar{M}_v$ × 10$^{-4\,b}$
P15	5 days	4.0	7.8	1.2	15.3	34.2
P16	5 days	8.1	14.0	1.7	12.1	27.1
P17	5 days	17.2	25.9	2.6	10.0	15.7
P18	5 days	81.4	71.5	7.1	9.9	11.3
P19	5 min	81.4	21.2	0.8	3.8	5.9

^{a,b} For an explanation of abbreviations see *Table 1*

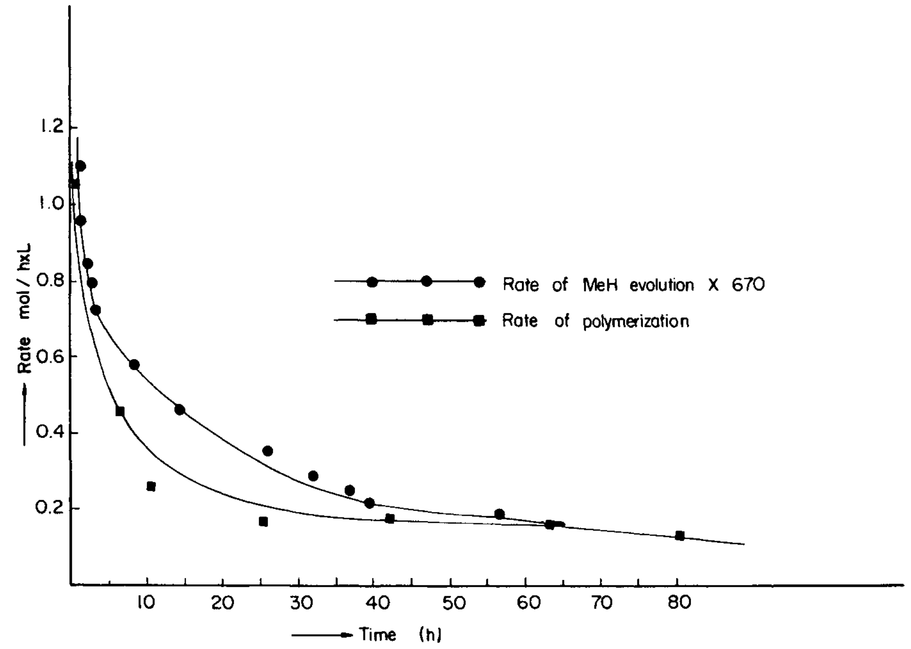
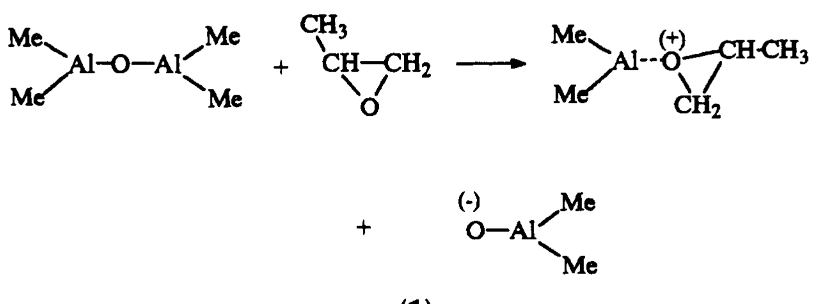


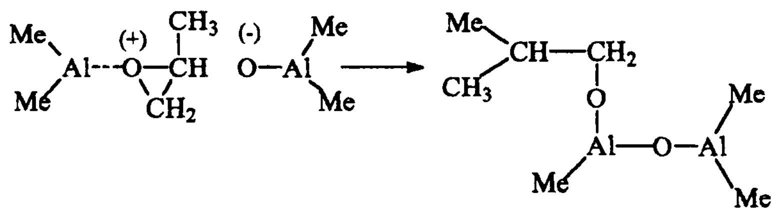
Figure 2 Deceleration of MeH evolution and polymerization rates. Reaction conditions: [Al] = 3.1 × 10^{-2} mol Al l^{-1}, T = 50°C

The sum of instantaneous amount of active methyl groups and evolved moles of methane gas was less then the initially present active methyl groups. In *Table 4* it appears that a considerable amount of active methyl groups are consumed without yielding methane gas. This likely indicates the presence of another path for the formation of Al-alkoxide groups which is described in the following steps (see *Schemes 1* and *2*) (in fact dissociation of



(1)

Scheme 1



(2)

Scheme 2

Table 4 Consumption of active methyl groups through the polymerization. Reaction conditions—temperature: M1~M3 = 20°C, M5 = 50°C; monomer/BMAO ratio, PO/Al (mol/mol): M1~M3 = 25, M5 = 460

Experiment	Time (h)	$A^0_{Me} \times 10^3$ moles	$A_{Me}/A^0_{Me} \times 100$	MeH/$A^0_{Me} \times 100$	Miss. MeH/ $A^0_{Me} \times 100$	P_T
M1	0.2	1.07	72.6	–	–	27.3
M2	1.0	1.06	60.2	–	–	43.6
M3	102	1.06	28.5	51.9	19.6	57.9
M5	113	0.75	10.5	52.5	34.7	26.6

A^0_{Me} = initial moles of active methyl groups; A_{Me}/A^0_{Me} = the molar ratio of instantaneous amount of active methyl groups to the initial; MeH = evolved moles of methane gas, Miss. MeH/A^0_{Me} = molar ratio of missing active methyl groups (= $A^0_{Me} - A_{Me}$) to the initial; P_T = percentage (total) conversion of polymerization

Table 5 Polymerization of PO with BMAO and alcoholized BMAO catalysts. Reaction conditions—polymerization time = 48 h, temperature = 40°C, molar ratio of PO/Al = 952, molar concentration of Al in the reaction mixture = 1.81×10^{-2} mol kg^{-1}

Experiment	Alcohol	Alcohol/Al (mol/mol)	$P_T{}^a$	$P_K{}^a$	$P_K/P_T \times 10^2$	$\bar{M}_v \times 10^{-4\,b}$
P20	Nil	0	18.5	1.5	8.1	21.9
P21	Nil	0	17.9	1.3	7.3	29.4
P22	Allylalcohol	0.5	18.1	1.3	7.2	24.4
P23	Allylalcohol	1.0	11.9	1.2	10.1	16.3
P24	Allylalcohol	2.1	6.0	0.7	11.7	21.7
P25	2-d-octanol	0.5	12.7	1.7	13.4	30.7
P26	2-d-octanol	1.0	7.5	2.0	26.7	40.3
P27	2-d-octanol	2.1	3.6	1.5	41.7	84.7

[a,b] For an explanation of abbreviations see *Table 1*

BMAO into free ions in etheric solvents has been already reported[1]).

Thus it is clear that the structure of BMAO and its residue change gradually throughout the reaction, by the conversion of a large majority of Me-Al bonds into RO-Al bonds. We have prepared several derivatives of BMAO by partially or completely alcoholysing it either with allyl alcohol or d-octane-2-ol. Alcoholysis reactions were carried out by mixing dilute alcohol and BMAO solutions in dioxan on a vacuum line and the completion of the reaction (about 3 days at 40°C) was monitored by volumetric measurement of the evolved methane. Polymerization results with BMAO and alcoholized BMAO catalysts are given and compared with each other in *Table 5*. Increasing the extent of the alcoholysis of BMAO drastically decreases the overall rate of process and production of D-polymers. Therefore, although the yield of K-polymers remains almost constant or slightly decreases, the stereoregular yield of the process markedly increases with alcoholysis. These results show that in the polymerization Me-Al bonds of BMAO are gradually transformed into Al-alkoxide bonds. This transformation steadily decreases the overall rate, but increases the stereoregular yield of process. Alcoholysis with 2-d-octanol instead of ally alcohol has considerable effect on the $\bar{M}_v$ of the K-polymers (*Table 5*), possibly indicating that Al-alkoxide bonds, which are formed through proton abstraction from PO or simply synthesized by alcoholysis, have important effects on the reactivity of active centres, but they are not consumed (i.e. are not added to PO) in the process. This explanation is based on the reasoning that if the alkoxide groups on the Al atoms are consumed in the initial stages of the polymerization the properties of the products would not be affected by the chemical nature of alkoxides. In fact Colclough and Wilkinson[4] reported that aluminium tri-isopropoxide is inactive in the PO polymerization. It is also important to note that, with 2-d-octanol alcoholized BMAO, we have not detected any optical activity either in the K-polymer or in the recovered unreacted monomer.

The stereoregular yield of the process

By changing the reaction conditions the characteristic features of the process and hence the stereoregular yield can be varied.

Temperature. As expected, a decrease in temperature causes the rate of the process to also decrease. However, only a slight increase in the stereoregular yield was observed with decreasing temperature (cf. P4 with P13 and P7 with P14 in *Tables 1* and *2*).

BMAO concentration. The overall rate of the process can be markedly increased by increasing the BMAO concentration; however, both stereoregular yield and viscosity average molar mass of K-polymers drastically decrease with increased BMAO concentration[9] (*Table 3*).

Presence of additives. Pyridine was used an additive to probe the effect of a cation scavenger in the process. Although pyridine is added only in molar quantities (0.5–0.1 mol pyridine mol^{-1} of Al) it markedly depressed both K- and D-polymer production. However, $\bar{M}_v$ of the K-polymers increased in the presence of pyridine (*Table 6*). Tsuruta[10] suggested that catalysts in the stereoregular polymerization of PO were inherently asymmetric and they were racemic mixtures. In order to test this possibility 1.3 moles of 1-brucine for 2 moles of BMAO was added and the adduct used in the polymerization. It might be expected that 1-brucine would preferentially block the stereochemically suitable antipode to lead a stereoelective polymerization. However, neither the polymer obtained nor the recovered unreacted polymer from experiment P30 (*Table 6*) displayed any optical activity. 1-Brucine markedly depressed D-polymer production without any noticeable effect on K-polymers. It should be also noted that although 1-brucine bears a tertiary amine group, which would act as a cation scavenger, it also has a carbonyl group that would readily react with active methyl groups of BMAO. Thus the

Table 6 Polymerization of PO with BMAO in the presence of additives. Reaction conditions—polymerization time = 48 h, temperature = 40°C, molar ratio of PO/Al = 952, molar concentration of Al in the reaction mixture = 1.81×10^{-2} mol kg^{-1}

Experiment	Additive	Additive/Al (mol/mol)	P_T[a]	P_K[a]	$P_K/P_T \times 100$	$\bar{M}_v \times 10^{-4}$[b]
P20	Nil	0	18.5	1.5	8.1	21.9
P28	Pyridine	0.5	0.5	0.15	30	–
P29	Pyridine	1.0	0.4	0.16	40	34.1
P30	1-Brucine	0.1	8.7	1.8	21	122
P31	TCNE	0.5	9.9	1.8	18	40.2
P32	TCNE	1.0	7.5	1.9	25	26.5

[a,b] For an explanation of abbreviations see *Table 1*

Table 7 Polymerization of PO with BMAO in different solvents. Reaction conditions—polymerization time = 48 h, temperature = 40°C, molar ratio of PO/Al = 952

Experiment	Composition[a]	$m(\mathrm{Al}) \times 10^3$[b]	ε[c]	P_T[d]	P_K[d]	$P_K/P_T \times 100$	$\bar{M}_v \times 10^{-4}$[e]
P20	10/0	18.1	13.1	18.5	1.5	8.1	21.9
P33	1/10 (Dx)	7.3	7.7	3.4	1.0	29.4	77.9
P34	1/10 (Dx)	7.2	7.7	3.9	1.1	28.2	84.2
P35	10/1 (Dx)	15.9	12.1	9.4	1.4	14.9	46.5
P36	1/10 (Et)	8.0	8.5	6.3	1.7	27.0	98.1
P37	1/10 (Et)	8.0	8.5	6.2	1.7	27.4	96.3
P38	10/1 (Et)	16.2	12.2	13.9	1.5	10.8	44.1
P40	1/10 (CHx)	8.2	7.5	7.4	2.3	31.1	104.1
P41	10/1 (CHx)	16.0	12.1	13.6	1.7	18.6	50.7

[a] Mol ratio of monomer to solvent, Dx = dioxane, Et = diethyiether, CHx = cyclohexane
[b] Moles of Al atoms in 1 kg polymerization mixture
[c] Estimated dielectric constant of the polymerization mixture
[d,e] See *Table 1*

effect of 1-brucine on the polymerization cannot be directly compared with that of the pyridine. Tetracyanoethylene (TCNE), which would possibly act as an anion scavenger was also tested as an additive. It depressed D-polymer production and slightly increased K-polymer yield and $\bar{M}_v$ (*Table 6*). We also tested the effect of TCNE on the electrical conductivity of BMAO solutions. TCNE in 0.5 TCNE/Al mol ratio was added to a diethyl ether solution of BMAO that had an equilibrium[1] conductivity of 9.5×10^{-2} S cm^{-2} mol^{-1} BMAO. Upon addition the conductivity suddenly increased to 11.1×10^{-2} S cm^{-2} mol^{-1} BMAO. This sudden jump cannot be explained by the change of dielectric constant since only $8.2 \mathrm{x} 10^{-5}$ moles of TCNE in 1 cm^3 ether solution were added under high vacuum conditions into 24 cm^3 ether solution of BMAO. However, the conductivity of this solution decayed slowly and steadily: in 30 min at 0°C the conductivity decreased to 8.0×10^{-2} and 4.0×10^{-2} S cm^{-2} mol^{-1} BMAO in 24 h, and it almost vanished in few days. In addition during this ageing process the initial faint yellow colour of the solution became deeper and turned pink. Ether of the BMAO/TCNE solution was evaporated and PO was destilled (molarity of BMAO = 2.7×10^{-3} mol L^{-1}). This mixture was allowed to polymerize. At the beginning of the polymerization at 0°C, the conductivity of the polymerization mixture steadily increased up to a maximum value of 892×10^{-2} S cm^{-2} mol^{-1} BMAO in 25 min and then slowly decayed. Conductivity of the mixture at 15 h of polymerization was measured as 570×10^{-2} S cm^{-2} mol^{-1} BMAO. In the absence of any additive the maximum conductivity observed during polymerization was 311×10^{-2} S cm^{-2} mol^{-1} BMAO. When pyridine is added in a 0.5 mol ratio, the observed maximum conductivity was only 75×10^{-2} S cm^{-2} mol^{-1} BMAO.

Both K- and D-polymers obtained from TCNE/BMAO had a dark red–brown colour. The colour of the product in benzene solution could not be removed even after several extractions with 2 M HCl.

Dielectric constant. A decrease in the dielectric constant of the polymerization mixtures by using several solvents depresses D-polymer production. Although K-polymer production is not noticeably effected, viscosity average molecular weights of K-polymers markedly decrease with an increase in the dielectric constant (*Table 7*).

The order of mixing of BMAO with PO. The possibility of stereoelective polymerization was tested by performing a two-step polymerization: in the first step ℓ-PO and BMAO were mixed in PO/Al = 10.3 mol ratio. Following the completion of the fast polymerization (50 min at 40°C) racemic PO was added to make a (total) PO/Al mole ratio of 968, which is the usual mole ratio used in the other polymerizations reported in this study. Neither the isolated K- and D-polymers nor the recovered unreacted monomer exhibited any optical activity. However, the stereoregular yield of the process and $\bar{M}_v$ of the K-polymers were markedly increased (*Table 8*). The same two-step polymerization was repeated, but this time only racemic PO was employed in both of the steps (exp 42 in *Table 8*). It is obvious that the increase in the stereoregular yield in the two-step process cannot be explained by the chirality of monomer, but rather is the result of the order of mixing PO with BMAO.

Hittorf electrolysis of BMAO and PO-treated BMAO

Assuming that both anionic and cationic fragments contain Al atoms and the number of Al atoms in anionic (f_a) and cationic (f_c) fragments is constant (i.e. there is only one type of anion and cation present in the BMAO solution) and all the ions are univalent, the change in the Al mol number in the anode branch ($\Delta n_{\mathrm{Al,A}}$) after transferring n_e moles of electrons in Hittorf electrolysis, is given by equation (1)[9]:

$$\Delta n_{\mathrm{Al,A}}/n_{\mathrm{e}} = f_{\mathrm{a}}t_{-} - f_{\mathrm{c}}t_{+} \qquad (1)$$

(where t_- and t_+ are transference numbers of the anion and cation, respectively).

Table 8 Two-step polymerization of PO with BMAO. Reaction conditions—polymerization time, first step 50 min, second step 48 h; temperature = 40°C, molarity of Al atoms = 1.8×10^{-2} mol kg^{-1}

Experiment	PO/Al (first step)	PO/Al (second step)	P_T[a]	P_K[a]	$P_K/P_T \times 100$	$\bar{M}_v \times 10^{-4}$[b]
P20	Single-step polymerization (for comparison)	952 (recamic PO)	18.1	1.5	8.1	21.9
P41	10.34 (laevarotary PO)	958 (recamic PO)	9.6	1.9	19.8	37.5
P42	10.31 (recamic PO)	950 (recamic PO)	9.5	1.7	18.0	34.8

[a,b] For an explanation of abbreviations see *Table 1*

Table 9 Hittorf electrolysis of BMAO

	Al (mol) in the anode compartment	Al (mol) in the cathode compartment
Before electrolysis	2.0156×10^{-4}	2.0958×10^{-4}
After electrolysis	2.0751×10^{-4}	1.9950×10^{-4}

The change of Al in the anode compartment ($\Delta n_{\mathrm{Al,A}}$) = 8.01×10^{-6} mol, moles of electrons transferred (n_e) = 1.498×10^{-5} mol. $\Delta n_{\mathrm{Al,A}}/n_e = 0.53$ mol

Table 10 Hittorf electrolysis of PO-treated BMAO

	Al (mol) in the anode compartment	Al (mol) in the cathode compartment
Before electrolysis	2.4292×10^{-4}	2.6698×10^{-4}
After electrolysis	2.4091×10^{-4}	2.6898×10^{-4}

The change of Al in the anode compartment ($\Delta n_{\mathrm{Al,A}}$) = -2.0×10^{-6} mol, moles of electrons transferred (n_e) = 1.1747×10^{-5} mol. $\Delta n_{\mathrm{Al,A}}/n_e = -0.17$

If polymer chains exclusively grow on the anionic fragments and they are strongly bound on these ions, then the value of t_- should be close to zero in the PO-treated BMAO. Under this condition measuring the value of $\Delta n_{\mathrm{Al,A}}/n_e$ should yield the f_c value[9]. The value of f_a can be determined from the known (average) number of Al atoms in BMAO[1] (= 6.3). Hittorf electrolysis of PO-treated BMAO did not yield clear cut results, i.e. the f_c value turned out to be a fraction rather than a whole number (*Table 10*). Nevertheless it did not contradict the electrolysis results of the PO-treated Pruitt–Baggett catalyst (PBC) as regards the fact that the anionic fragments bore the growing PPO chains[9]: i.e. the $\Delta n_{\mathrm{Al,A}}/n_e$ value was positive in the electrolysis of BMAO, but became negative after PO treatment (*Table 9* and *Table 10*).

A comparison of the stereoregular polymerizations of PO catalysed by PMAO and PBC

Catalytic activities of BMAO and the PBC in the stereoregular polymerization of PO show striking similarities. A mechanism for the stereoregular polymerization of PO with PBC has already been suggested[9]. With the aim of discussing how satisfactorily this mechanism fits in BMAO catalysed polymerization, we would like to conclude this paper with a brief comparison of these two processes.

The ionic nature of catalysts. Both catalysts dissociate into free ions; however, in etheric solutions the ionic fragments bind onto each other with an ether (or PO) to form ether (or monomer) bound ion pairs[1,11]. The initial free ions can be regenerated by removing the binding ether molecule by simply pumping off the solution or by insertion of the PO onto the growing polymer chain[9,11]. Hittorf electrolysis showed that K-polymers grow on the anionic fragment of PBC residue. The marked decrease of the ionic mobility of anionic fragments during the polymerization possibly indicates that the anionic fragments are also the site on which K-polymers grow in BMAO system.

Solvent and additive effects. In spite of the ionic nature of catalysts the increase in the dielectric constant of the polymerization mixtures decreases the total conversion. However, this decrease is mainly due to the depression of D-polymer production in BMAO, whereas it is essentially due to the depression of K-polymers in PBC. Additives that used a 1/2000–1/1000 molar ratio (additive/PO) have a marked effect on the polymerization. Pyridine, which plausibly acts as a cation scavenger, effectively depresses both K- and D-polymer production in both of the systems (see *Table 6* and Ref. [11]). TCNE has a marked adverse effect on both K- and D-polymerization in PBC[1] on the other hand as it only depresses D-polymer production in BMAO (*Table 6*). It should be pointed out that the dielectric constant and additive effects on the BMAO system is probably much more complicated than that of the PBC system, since in the former there is an additional competitive reaction in which a methane by-product is formed. The study of polymerizations in different dielectric media has shown that in both systems K-polymer production is not enhanced by increasing the dielectric constant. These observations indicate that niether free anions nor cations are solely responsible for the stereoregular polymerization, but togather with a monomer molecule they combine to yield catalytically active monomer-bound ion pairs[9].

D-polymer production. K- and D-polymers in both systems are concurrently produced throughout the process. D-polymers are produced at higher rates at the initial stages of polymerization, and increasing catalyst concentrations D-polymer production is enhanced, whereas K-polymer production and the average molar mass of K-polymers falls (*Table 3* and Ref. [8]). Comparison of the polymerization experiments carried out with using fractionally purified poly(methylaluminium oxide) catalysts[1] showed that formation of K- and D-polymers cannot be attributed to different kind of catalytic species. In addition to such results, the high cycloether content of D-polymers shows that these polymers are formed via a transfer process. This view is strengthened from the observation that any change in the reaction conditions which enhance D-polymer production decreases the $\bar{M}_v$ of the K-polymers (*Tables 3, 5–8*). A ^{13}C-n.m.r. study of fractionated PPO samples has shown that K-polymers contain a considerable amount of configurational and structural irregularities. The amount of these irregularities increases as $\bar{M}_v$ of the fraction decreases, and it is maximized in D-polymers. This might indicate that an irregular addition of the incoming monomer onto the growing K-polymer increases the probability of D-polymer production. In contrast to the high cyclicether content, which is a typical by-product of cationic polymerization of epoxides, formation of D-polymers can be effectively depressed by an anionic scavenger as well as a cationic one (*Table 6*). This result is in accordance with the conclusion that both the anion and the cation together may be responsible for D-polymerization[9].

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REFERENCES

1. Öktem, Z., Sari , A. and Alyürük, K., *European Polymer Journal*, 1993, **29**, 637.
2. Giannetti, E., Nicoletti, G.M. and Mazzocchi, R., *Journal of Polymer Science Part A*, 1985, **23**, 2117.
3. Araki, T., Aoyagi, T., Ueyama, N., Aoyama, T. and Tani, H., *Journal of Polymer Science Part A*, 1973, **11**, 699.
4. Colclough, R.O. and Wilkinson, K., *Journal of Polymer Science Part C*, 1964, **4**, 699.
5. Iada, M., Araki, T., Teranishi, K. and Tani, H., *Macromolecules*, 1977, **10**, 275.
6. Zhang, Y., Gross, R.A. and Lenz, R.W., *Macromolecules*, 1990, **23**, 3206.
7. Ueyama, N., Araki, T. and Tani, H., *Inorganic Chemistry*, 1973, **12**, 2218.
8. Alyürük, K., Özden, T. and Çolak, N., *Polymer*, 1986, **27**, 2009.
9. Takrouri, F. and Alyürük, K., *Polymer*, 1994, **35**, 1518.
10. Tsuruta, T., *Journal of Polymer Science Part C*, 1980, **67**, 73.
11. Aksoy, S., Altinok, H., Tümtürk, H. and Alyürük, K., *Polymer*, 1990, **31**, 1142.