A mechanistic study on the stereoregular polymerization of propylene oxide by the Pruitt–Baggett catalyst

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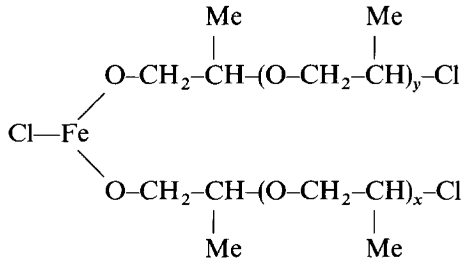
The structures of the Pruitt–Baggett adduct (PBA) and the Pruitt–Baggett catalyst (PBC) were studied in some detail. PBC extensively ionizes in acetonitrile ($K_d = 3.48 \times 10^{-3}$ mol l^{-1} at 25°C) producing an anionic fragment composed of seven Fe atoms and a cationic fragment with two Fe atoms. Hittorf electrolysis showed that the anionic fragments exclusively bore the high molecular weight stereoregular poly(propylene oxide)s (K-polymers). However, study of the polymerization in the presence of anion and cation scavengers and in different dielectric media supported a previous conclusion that neither free anions nor cations were solely responsible for the stereoregular polymerization, but together with a monomer molecule they combine to yield catalytically active monomer-bound ion pairs. The study of the product showed that K-polymers were connected to each other with Fe atoms. However, these chains could be freed by extracting the Fe residues with hydrochloric acid. A mechanism for the stereoregular polymerization of propylene oxide that is consistent with the present and already published data was suggested.

(Keywords: Pruitt–Baggett catalyst; propylene oxide; Hittorf electrolysis)

INTRODUCTION

The Pruitt–Baggett catalyst (PBC), as a catalyst for the stereoregular polymerization of propylene oxide (PO), attracted considerable interest in the 1960s[1]. However, owing to imprecise terminology, where different authors referred to different compounds as PBC or the 'iron catalyst', the chemical identity and physical properties (such as solubility) of this catalyst have been described rather differently[2–6]. Çolak and Alyürük[7] and Aksoy *et al.*[8] used different terms to refer to the compounds or intermediates formed during the synthesis of PBC.

The Pruitt–Baggett adduct (*PBA*). The adduct that forms between PO and $FeCl_3$ is the precursor of PBC and is soluble in ethereal solvents, yielding a yellow–green colour at extreme dilutions. The following formula[3,4] has been suggested for PBA, but this formula is revised and corrected in the present text:



$(y+x \simeq 5)$

Aksoy *et al*[8] found that PBA was monomeric in ether solutions.

The Pruitt–Baggett hydrolysate (*PBH*/r). PBH/r (where r is the hydrolysis ratio = mol H_2O added/Fe) is formed as a brown precipitate insoluble in ether, by mixing dilute ethereal PBA solutions with molar quantities of H_2O. At $r = 0.67$ the reaction is complete[7] in 48 h at 40°C.

The Pruitt–Baggett catalyst (*PBC*/r). PBH/r is converted into PBC/r by heating at 80°C for 3 h *in vacuo*. If $r \leqslant 1$, PBC/r is soluble in ethereal solvents, cyclohexane, pyridine and acetonitrile, giving red coloured electrically conductive solutions. PBA is almost inactive as a catalyst in the stereoregular polymerization of PO[7]; however, PBC/r becomes progressively more active as r increases from 0 to 0.5, but its activity slowly decreases with further increase of r, and it is almost inactive[7] at $r = 4$. PBC/r also produces low molecular weight mainly cyclic by-product polyethers (D-polymers), together with high molecular weight stereoregular poly(propylene oxide)s (PPOs, K-polymers). However, the maximum stereoregular yield (i.e. maximum yield of K-polymers and minimum yield of D-polymers) was obtained at $r = 0.67$. Çolak[9], by fractionating K-polymers on the basis of molecular weight, has shown that 1 ∼ 5 mol of K-polymer chains are formed per mole of PBC/0.67. This value is ∼ 500–50 times larger than that of the catalysts derived from Al or Zn[10,11]. Hence, this compound appears to be a suitable catalyst for the mechanistic studies on the stereoregular polymerization of PO. In the present research only PBC/0.67 was studied and it was simply referred to as PBC.

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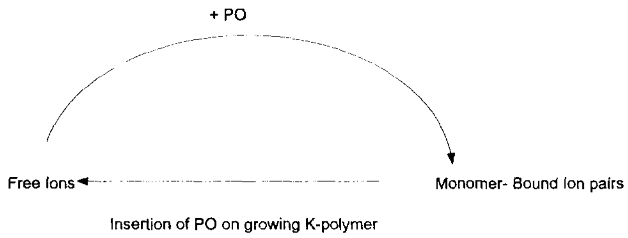


Figure 1 Cycle proposed in reference 8 for the stereoregular polymerization of PO

Aksoy *et al.*[8] reported that in ethereal solvents (as well as in PO), PBC ionizes, but as a result of a series of subsequent processes the free ions formed were bound together with an ether (or PO) molecule yielding ether (or monomer)-bound ion pairs. *Figure 1* shows the cycle they proposed for the stereoregular polymerization of PO.

With the aim of testing and improving their model, we studied the nature of the free ions as well as the identity of the ionic fragment on which the K-polymer grows. In this paper, we report our experimental results and discuss our ideas on the mechanism of the stereoregular polymerization of PO by PBC.

EXPERIMENTAL

Materials

The general procedure adopted for the purification of reagents and solvents, preparation of reaction mixtures, and for carrying out reactions in a high vacuum line with rigorous exclusion of air, moisture, etc., has already been described[7].

$FeCl_3$ was obtained by burning pure Fe powder in a rigorously dried Cl_2 atmosphere. PBA was prepared by reacting $FeCl_3$ and PO[7]. A diethylether solution of PBA was transferred in a storage vessel. Known quantities of samples from this stock solution could be measured out using a burette fitted with greaseless taps, without any exposure to atmosphere. PBH was prepared by adding a measured amount of water into an ether–PBA solution. The mixture was placed in a bath regulated at 40°C for 24 h. PBC was obtained by heating the brown precipitate formed at 80°C for 3 h with continuous pumping in the high vacuum line (hereafter, this thermal treatment will be referred to as 'baking').

Polymerizations

PO in the presence or absence of solvents and additives was polymerized by mixing PBC or PBA, at 80°C for 24 h. The molality of the catalyst used was kept constant at 2.06×10^{-2} mol of Fe atoms per kg of PO (or per kg of PO + solvent). The procedures followed for the isolation of polymers, stabilization with antioxidant (diphenylamine) and fractionating them into K- and D-polymers by thermal crystallization from dilute iso-octane solution and the determination of the viscosity-average molecular weights of K-polymers have been described previously[7,8].

Conductimetric measurements and Hittorf electrolysis

Electrical conductance measurements of PBC solutions were carried out as described in reference 8. The classical Hittorf electrolysis cell was slightly modified (*Figure 2*) to study the transport properties of PBC ions in organic solvents with rigorous exclusion of atmospheric gas. The following modifications were carried out: in order to decrease the electrical resistance the buffer compartment of the classical Hittorf cell was removed; and the vapour pressures of the two compartments were equalized with a gas-phase connection through a Teflon plug tap (*Figure 2*, P_2).

Two solutions were electrolysed: the first was PBC in acetonitrile and the other one was 'PO-treated PBC' in acetonitrile. The latter was prepared by polymerizing PO with PBC in acetonitrile. Polymerization was continued 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.

The sample to be electrolysed was put in a flask (*Figure 2*, S), under high vacuum conditions and the cell pumped off before sealing the constriction (*Figure 2*, C). The sample was transferred into the two compartments of the cell through P_1 and the whole apparatus was placed in a thermally insulated water bath. The compartments had been calibrated volumetrically and so by measuring the liquid level the Fe content (before electrolysis) in each compartment could be determined. Electrolysis was carried out by applying 500 V (d.c.) to the electrodes. The number of moles of electrons exchanged was determined from a plot of current *versus* time. In the first sample, the initial current was 1.5 mA and it decreased gradually down to 0.6 mA in 90 min. At this stage, the following changes could be observed visually, and the electrolysis

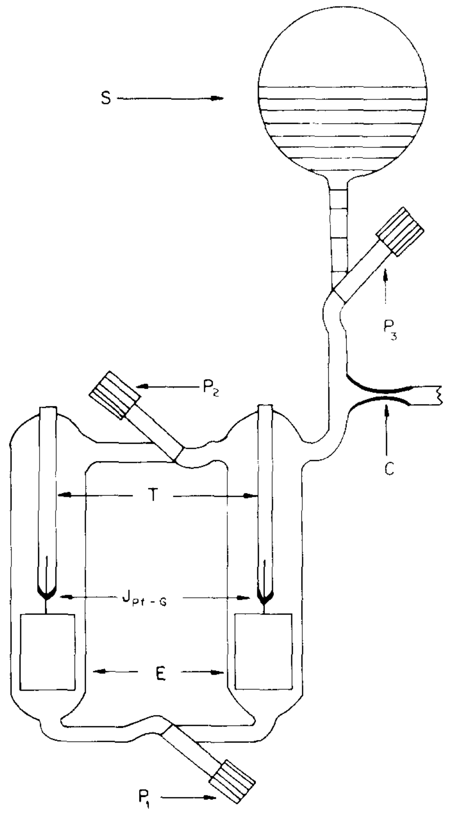


Figure 2 Schematic diagram of the instrument used in the Hittorf electrolysis of PBC and PO-treated PBC. $J_{Pt,G}$, platinum–borosilicate glass joints (cf. ref. 8); E, Pt electrodes; T, electrode-bearing tubes; P_1, P_2 and P_3, Teflon plug taps; C, vacuum connection and constriction; S, sample in acetonitrile

was stopped: the cathode compartment grew darker, while the anode compartment became apparently lighter in colour; and the initially clear solutions became turbid, and a black, muddy precipitate was formed on the cathode (1.7% Fe was precipitated at the cathode).

In PO-treated PBC, electrolysis was carried out under the same conditions but the initial current was only 50 μA, which steadily decreased to 10 μA towards the end of the electrolysis. This electrolysis was continued for ~28 h. At the end of electrolysis the anode and cathode compartments were separated and the total Fe (i.e. the total amount of Fe in solution and in the precipitate) content of each compartment was determined by extracting the mixture with 3 M HNO_3 (aq.).

RESULTS AND DISCUSSION

Structure of PBA

Contrary to the structure shown for PBA earlier, we found that ether–PBA solutions contained free HCl. Moreover, examination of PBA and the organic residue extracted from PBA by i.r. spectroscopy showed the presence of absorption peaks with a doublet character at 1600 cm^{-1}. We attribute this absorption to an unsaturation in the organic residue (i.e. $-O-CH{=}CH-Me$ and $-O-CH_2-CH{=}CH_2$). In fact, by hydrating the organic residue under acidic conditions the peaks around 1600 cm^{-1} almost vanished.

These results raise several questions on the origin of the inorganic chlorine (i-Cl) in PBA (i.e. the Cl atom directly bound to the Fe atom). Two plausible explanations can be proposed to account for the presence of i-Cl: the i-Cl was formed in the reaction between free HCl (f-Cl) with Fe–OR bonds; and the i-Cl is the unreacted Cl atom of $FeCl_3$, since in the formation of PBA, due to steric and/or electronic restrictions, according to the structure shown, only two short PPO chains can grow on each Fe atom. However, the experiments, summarized in *Table 1*, rule out the second explanation.

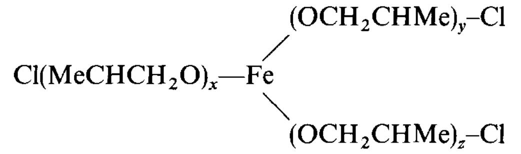
Experiment 1. Ethereal PBA solution was directly extracted with 2 M HNO_3 (aq.) to collect the f-Cl i-Cl and Fe^{3+} ions in the aqueous phase. Thus, the amount of Cl^- in the aqueous phase is the sum of f-Cl and i-Cl.

Experiment 2. Only f-Cl, which can be distilled out of ethereal PBA solutions, and bulk PBA were collected. In the collected ether phase, no Fe^{3+} but only H^+ cations, equal to the number of moles of Cl^-, were found.

Experiment 3. This experiment was done in two successive steps. In the first step, the f-Cl was collected (as in experiment 2), and then the residue of PBA was decomposed by warm concentrated HNO_3 (aq.). All water-soluble products were produced. Hence, analysis for Cl^- gave the sum of i-Cl and o-Cl (where o-Cl is the organic chlorine attached to the organic residue). The total Cl/Fe (mol/mol) value obtained in experiment 3 (2.79) is somewhat lower than the theoretical value (3.00), however this difference is attributable to the f-Cl that was possibly lost in the preparation of the PBA stock solution. A comparison of the results of experiments 1 and 2 clearly showed that the i-Cl/Fe ratio was not 1.00 as in the structure shown, but was only 0.07 (assuming that in experiment 2 f-Cl was quantitatively collected). Hence we concluded that three PPO short chains can grow on each Fe atom (see below). On the basis of these results the identity of PBA is best described by the following equilibria instead of a single structural formula:

Table 1 Content of free HCl (f-Cl), inorganic chlorine (i-Cl) and organic chlorine (o-Cl) of PBA

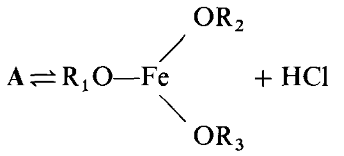
Experiment no.	Type of Cl	Cl/Fe (mol/mol)
1	f-Cl + i-Cl	0.50
2	f-Cl	0.43
3(i)	f-Cl	0.42
3(ii)	i-Cl + o-Cl	2.36
3(i) + 3(ii)	f-Cl + i-Cl + o-Cl	2.79



$$Cl(MeCHCH_2O)_x{-}Fe(OCH_2CHMe)_y{-}Cl(OCH_2CHMe)_z{-}Cl$$

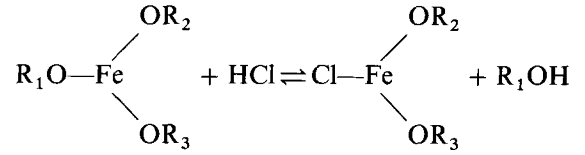
$(x+y+z=6.8)$

A



$$A \rightleftharpoons R_1O{-}Fe(OR_2)(OR_3) + HCl \quad (1)$$

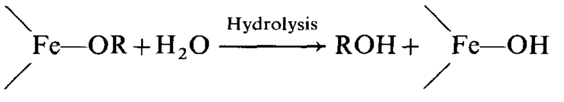
(where R_1O, R_2O and R_3O are PPO chains with either o-Cl or double bond terminal units)



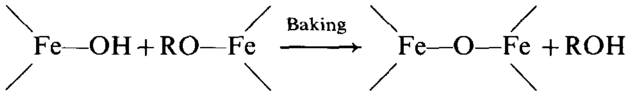
$$R_1O{-}Fe(OR_2)(OR_3) + HCl \rightleftharpoons Cl{-}Fe(OR_2)(OR_3) + R_1OH \quad (2)$$

Conversion of PBA to PBC

With the purpose of shifting the equilibrium in (2) to the left and remove all the f-Cl, PBA was pumped at 80°C for 3 h. (It was found that only a negligible amount of additional f-Cl could be obtained by extending the pumping time to 9 h.) Following the pumping treatment, PBA was dissolved in ether and a calculated amount of H_2O was added. PBH was formed, as a brown precipitate, at 40°C in 48 h. The f-Cl evolved in the hydrolysis was collected and measured. PBH was baked, and the f-Cl formed during the baking process was also collected. It was found that both in the hydrolysis and baking stages only a small amount of f-Cl was formed (f-Cl/Fe < 0.1). Thus, it appears that mainly Fe–OR bonds, and not the previously suggested Fe–Cl bonds[8] were reacted in the hydrolysis [reaction (3)] and baking process [reaction (4)].



$$\rangle Fe{-}OR + H_2O \xrightarrow{\text{Hydrolysis}} ROH + \rangle Fe{-}OH \quad (3)$$



$$\rangle Fe{-}OH + RO{-}Fe\langle \xrightarrow{\text{Baking}} \rangle Fe{-}O{-}Fe\langle + ROH \quad (4)$$

This conclusion was also supported by analytical results (*Table 2*).

Table 2 Fe content of PBA and PBC/0.50[a]

	Fe (%)
PBA	10.50
PBC/0.50	13.90

[a] Cf. case 1: calculated Fe(%) = 11.0, assuming that in the hydrolysis and baking stages only i-Cl reacted; and case 2: calculated Fe(%) = 14.6, assuming that reactions described in reactions (3) and (4) have taken place

Table 3 Catalytic activities of PBA and PBC from different origins

Experiment no.	Catalyst[a]	Cl/Fe (mol/mol)	P_T[b]	P_K[c]	$100 \times P_K/P_T$
P1	PBA	–	4.0	1.1	27.5
P2	PBA(h)	2.60	4.0	1.1	26.0
P3	PBA(l)	2.36	3.8	1.1	27.7
E-10[d]	PBA	–	7.0	2.5	35.7
P4	PBC	–	34.8	26.3	75.6
E-13[d]	PBC	–	36.0	27.0	75.0
P5	PBC(h)	2.26	34.8	26.3	75.6
P6	PBC(l)	2.11	35.8	26.9	75.2
P7	PBA*	–	7.7	1.5	19.5
P8	PBC*	–	55.7	38.0	68.3
P9	PBC*	–	67.1	44.7	66.6

[a] PBA(h) and PBA(l), PBA with high and low Cl content, respectively; PBC(h) and PBC(l), PBC prepared from PBA(h) and PBA(l), respectively; PBA*, *d*-octane-2-ol-treated PBA; PBC*, PBC prepared from PBA*. For a detailed description of the catalysts, see text

[b] Per cent conversion

[c] Per cent conversion into K-polymer

[d] Experiments reported in reference 7

Catalytic activities of PBA and PBC

Çolak and Alyürük[7] used commercial $FeCl_3$ to synthesize PBA. With the purpose of testing whether any impurity (e.g. H_2O) which might be present in the commercial reagent had affected the catalytic activities of PBA and PBC we have repeated the same polymerization experiments of the above authors, but using laboratory prepared $FeCl_3$ instead (cf. Experimental section). Although the PBA from laboratory prepared $FeCl_3$ was considerably less active, the catalytic activities of the PBCs from the two sources were almost the same (*Table 3*). These results strongly indicate that the observed catalytic activity of PBA is possibly due to the shortcomings of the adopted experimental techniques in completely excluding the H_2O (i.e. adsorbed H_2O on glass or Teflon surfaces, etc.).

Aksoy *et al.*[8] have shown that the catalytic efficiency of PBC (i.e. the K-polymer yield) decreased by a factor of 4 on addition of small amounts of HCl (HCl/Fe = 0.5). This led us to examine whether the Cl content of PBA (and PBC) has any effect on the polymerization [cf. reactions (1) and (2)]. For this purpose, PBA with a low Cl content (PBA(l) in *Table 3*) was prepared by pumping it at 80°C for 9 h. For comparison, a high Cl-content PBA (= PBA(h)) was also prepared by pumping at 0°C for 0.5 h. It was found that Cl content of PBA does not have any appreciable effect on its catalytic activity (*Table 3*). Similarly, the catalytic activities of PBC(l) and PBC(h) [prepared from PBA(l) and PBA(h), respectively] were almost identical.

In another attempt to prepare a modified PBA(l) with an exchange reaction [reaction (5)] PBA was dissolved in excess of *d*-octane-2-ol and after 24 h at room temperature, the volatile components were pumped off at 80°C for 3 h.

$$\begin{array}{lcl} Fe(OR)_3 + nC_8^*H_{17}OH & \rightarrow & Fe(OR)_{(3-n)}(C_8^*H_{17}O)_n + nROH \\ \text{(PBA)} & & \text{(PBA*)} \end{array} \qquad (5)$$

The catalytic activity of the modified PBC (PBC*, prepared from PBA*) was remarkably increased (*Table 3*). However, we admit that the present experimental data are not sufficient to explain this result solely on the basis of the 'HCl effect'. It is also worth noting that neither the polymers obtained from PBA* and PBC* nor the unreacted monomers from the polymerization mixtures exhibited any optical activity.

Polymerization study

The catalytic efficiency of PBC, like PBC/0.75[8], did not deteriorate when the monomer was diluted with a low dielectric solvent (experiments P13–P15 in *Table 4*). On the other hand, K-polymer production was greatly depressed in the presence of acetonitrile. We also studied the polymerization of PO by PBC by adding cation (*l*-brucine) or anion (tetracyanoethylene) scavengers in the 0.5 molar ratio of additive to Fe. Both additives almost inhibited the K-polymer production (experiments P16–P18). Thus, the present results provide further support for the previous conclusion[8] that 'neither one of the free ions is solely responsible for the stereoregular polymerization but monomer-bound ion pairs are the catalytically active species'.

Instead of pyridine[8], we used *l*-brucine, which has a chiral tertiary amine group as a cation scavenger. If PBC were a racemic mixture[12], then *l*-brucine would be expected to preferentially block the stereochemically suitable antipode. In such a case, stereoelective polymerization may be expected. However, neither the polymer obtained nor the recovered unreacted monomer from experiment P16 showed any optical activity. The synthesized polymers were brown and dissolved to give quite stable solutions (i.e. even under open conditions no precipitation of the Fe residues was observed). Hence, the polymerization products were dissolved in benzene and extracted repeatedly with 2 M HCl (aq.) to remove any Fe residue from the PPO. The HCl-extracted PPOs were colourless, and the viscosity-average molecular weight (M_v) of the products decreased considerably on extraction (*Table 5*). In order to show that this decrease was not due to a simple degradation that occurred in extraction, a test experiment was carried out. In this experiment, a sample that had already been HCl-extracted was re-extracted under similar conditions. The M_v of the test sample did not decrease further (*Table 5*). We conclude that in the untreated PPO at least two K-polymer chains are connected by an Fe atom.

Identity of PBC ions

Aksoy *et al.*[8] observed that neither PBA solutions, nor the hydrolysis mixtures of PBA (i.e. PBA + H_2O + ether) before baking were electrical conductors, and free PBC ions in ether (and PO) combined to yield ether (or monomer)-bound ion pairs. However, the initially free ions can be regenerated by driving off the binding molecule (ether or PO).

On the basis of the above observations these authors assumed that both the cation and anion of PBC contained

Table 4 Study of the polymerization of PO by PBC in the presence of additives or solvents

Experiment no.	Add.[a]	x_{PO}[b]	ε[c]	r_A[d]	P_T	P_K	P_D[e]	K (%)	M_v[f] ($\times 10^{-5}$)
P10	Nil	1.0	13.1	–	35.8	26.9	8.9	75.0	5.5
P11	AN	0.7	19.8	–	13.8	8.0	5.8	58.0	2.2
P12	AN	0.3	27.7	–	9.6	3.9	5.7	41.0	0.5
P13	Et_2O	0.5	9.0	–	38.1	23.6	14.5	62.0	3.8
P14	CH	0.8	11.3	–	42.6	28.8	13.8	68.0	1.9
P15	CH	0.5	7.4	–	39.2	25.5	13.7	65.0	2.3
P16	l-Bru.	1.0	13.1	0.5	2.1	1.3	0.8	61.0	1.4
P17	TCNE	1.0	13.1	0.5	12.9	6.9	6.0	53.0	0.6
P18	TCNE	1.0	13.1	0.5	13.6	8.4	5.2	62	0.8

[a] Additives or solvents: AN, acetonitrile; Et_2O, ether; CH, cyclohexane; l-Br, l-brucine; TCNE, tetracyanoethylene
[b] Mol fraction of PO
[c] Average dielectric constant of the reaction mixture
[d] Moles of additive per mol of Fe
[e] Moles of PO polymerized into D-polymer
[f] M_v of K-polymer (after HCl extractions)

Table 5 M_v ($\times 10^{-5}$) of K-polymer samples before and after HCl extraction

Experiment no.[a]	Before	After
4	2.8	0.8
5	10.1	5.7
6	5.7	5.7[b]

[a] Catalyst: PBC
[b] HCl-extracted sample from experiment 5 was re-extracted with HCl

Table 6 Hittorf electrolysis of PO-treated PBC[a]

	Fe(mol) in the	
	Anode compartment	Cathode compartment
Before electrolysis	3.16×10^{-4}	3.27×10^{-4}
After electrolysis	2.77×10^{-4}	3.66×10^{-4}

$\Delta n_{Fe,A} = -3.9 \times 10^{-5}$ mol, $n_e = 1.9 \times 10^{-5}$ mol, $\Delta n_{Fe,A}/n_e = -2.1$

Table 7 Hittorf electrolysis of PBC[a]

	Fe(mol) in the	
	Anode compartment	Cathode compartment
Before electrolysis	3.31×10^{-4}	3.40×10^{-4}
After electrolysis	2.79×10^{-4}	3.92×10^{-4}

$\Delta n_{Fe,A} = -5.2 \times 10^{-5}$ mol, $n_e = 5.1 \times 10^{-5}$ mol, $\Delta n_{Fe,A}/n_e = -1.0$

(several) Fe atoms. To examine this assumption we have studied the transport properties of PBC in acetonitrile by Hittorf electrolysis. Acetonitrile turned out to be a good solvent for this purpose for the following reasons: it did not bind the free ions together, in the form of 'acetonitrile-bound ion pairs' (i.e. the conductivity of PBC–acetonitrile solutions did not decay by ageing); the conductivity of PBC in acetonitrile was ~200 times larger than that of an ether solution[8]; and PBC solutions in acetonitrile obeyed Ostwald's dilution law, hence we determined the ionization constant of PBC and its conductivity at infinite dilution in acetonitrile ($K_d = 3.48 \times 10^{-3}$ mol l^{-1} and $\Lambda_o = 136$ S cm^2 mol^{-1} at 25°C).

In the following discussion both the anion and cation of PBC were assumed to be univalent ions. In equation (6) the change in the number of moles of Fe atoms, due to electrolysis, in the anode compartment ($\Delta n_{Fe,A}$) is expressed as the number of moles of anions (Δn_a) which have entered minus the number of moles of cations (Δn_c) which have left the compartment:

$$\Delta n_{Fe,A} = f_a \Delta n_a - f_c \Delta n_c \qquad (6)$$

where f_a and f_c are the number of Fe atoms in the cationic and anionic fragments, respectively. Equation (8) was obtained by dividing both sides of equation (6) with the number of moles of electrons (n_e) exchanged in the electrolysis [equation (7)]:

$$n_e = \Delta n_a + \Delta n_c \qquad (7)$$

$$\Delta n_{Fe,A}/n_e = f_a t_- - f_c t_+ \qquad (8)$$

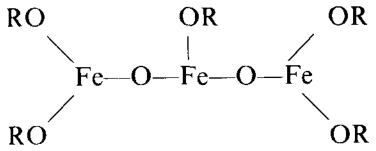
where t_- and t_+ are the transference numbers.

Since K-polymers are strongly attached to Fe atoms, the transference number of the ionic fragment on which K-polymers grow can be taken as zero. In *Table 6* $\Delta n_{Fe,A}$ is calculated as a negative value, so it follows that cations do escape from the anode compartment, and t_- must have zero value in this experiment. Thus taking $t_+ = 1$ and substituting the $\Delta n_{Fe,A}/n_e$ value from *Table 6* into equation (8), f_c was calculated as $2.1 \simeq 2.0$ Fe atoms/cation. Aksoy *et al.*[8] have reported that a PBC molecule contained nine Fe atoms so that f_a turns out to be $6.9 \simeq 7.0$ Fe atoms/anion. Hence we concluded that anionic fragments exclusively bear the K-polymer.

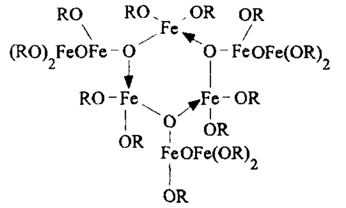
Using the data in *Table 7*, t_+ and t_- values for PBC were obtained from equation (8) as 0.88 and 0.12, respectively. Thus, the limiting molar ionic conductivities at infinite dilution of the PBC cation and anion, turn out to be 120 and 16 S cm^2 mol^{-1} at 25°C, respectively. Such remarkably high ionic conductivities strongly suggest the possibility of the exchange of ions between PBC molecules [cf. equation (15)] leading to a Grotthuss type of conductivity, superimposed on the normal transport process.

PBC and ionization of PBC

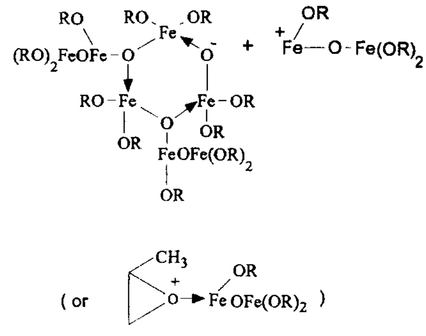
On the basis of stoichiometric reasoning (i.e. 3 mol of PBA reacted with only 2 mol of H_2O), the empirical formula of PBC can be given by:



However, Aksoy *et al.*[8] have measured that PBC molecules (or aggregates in dilute ether solutions) contain nine Fe atoms. In analogy to the cyclic trimer of bisdimethylaluminiumoxide[10], which is also a catalyst for the stereoregular polymerization of PO, the following structure can be postulated for PBC, which is a cyclic (coordination) trimer of the above structure:



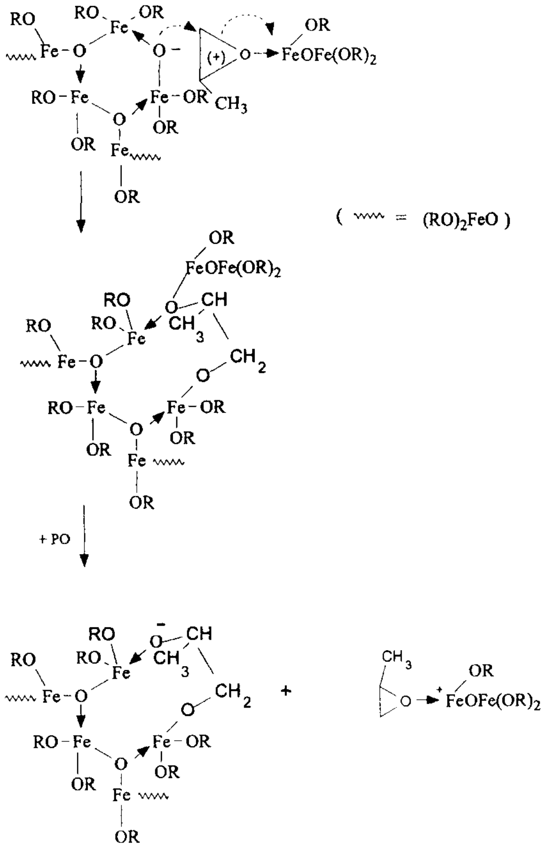
This cyclic trimer explains the ionization of PBC as producing an anion and cation with seven and two Fe atoms, respectively.



(9)

K-polymer production

At first sight, the cationic fragment may appear to be the site at which the stereoregular chains grow[11]. This impression is further upheld by the experimental fact that K- and D-polymer production are concurrent (D-polymers are low molecular weight cyclic ethers and are always formed in the cationic polymerization of PO[11]). Surprisingly, Hittorf electrolysis of PO-treated PBC showed that K-polymers were exclusively attached to the anionic fragments. Thus, we propose an ionic insertion mechanism to explain the results. This process starts with the formation of monomer-bound ion pairs as suggested by Aksoy *et al.*[8] [see (10)] and as a result of the interaction between the transmitted positive charges on the C atoms of the PO ring and the oxyanion, the monomer is inserted into the anionic fragment (i.e. Fe—$^-$OFe bonds) by reforming an ionizable adduct [see (11) and (12)]. According to already published[8] and the present experimental results this insertion reaction cannot be classified as a S_N2 (or S_N1) type reaction. Indeed, the absence of unsaturation at the chain ends has been shown[7,13,14] (expected from a simple anionic polymerization of PO[15]). Conversely, after removal of catalyst residues the products were found to be cyclic or containing OH groups at each chain terminal[7,13,14]. Nevertheless, after Price *et al.*[16,17], the following reactions describe a ring opening by heterolytic cleavage of the primary carbon–oxygen bond. However, this does not exclude ring opening at the secondary carbon–oxygen bond with an inversion of the configuration[18] and forming head-to-head (or tail-to-tail)[16] linkages. Fractionation and spectroscopic studies have also shown that structurally irregular units have larger sequential mole fractions than 20%. However, only ~3% of ring opening at the secondary carbon is expected from a simple S_N2 reaction[19].



(10)

(11)

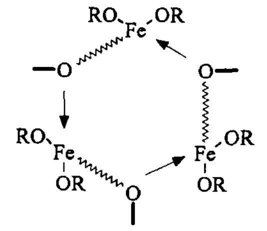
(12)

Ions in reaction (12) reform the monomer-bound ion pairs followed by insertion of monomers to the growing K-polymer (cf. the cycle proposed by Aksoy *et al.*[8] in the Introduction section).

Aksoy *et al.*[8], on the basis of kinetic evidence, concluded that oxonium ion formation of the PBC cation (with either diethylether or PO) occurs in a fast reaction. On the other hand, monomer-bound ion pair formation requires a high activation energy. We have repeated their conductimetric measurements[8] and, in agreement with these authors, found that the activation energy of the diethylether-bound ion pair from the free anion and the oxonium ion is 97 kJ mol^{-1}. [By substituting a diethylether molecule instead of PO, the structure shown in (9) describes the diethylether-bound ion pair.] Such a high activation energy may indicate the presence of severe steric hindrances in the formation of ether (or PO)-bound ion pairs (from the data given in ref. 7, the activation energy of K-polymer formation was roughly estimated to be 60 kJ mol^{-1}). Thus, in the absence of better evidence we suggest that the overall steric control of the process is in the monomer-bound ion pair formation step, (10), but not in the step where the cation, (9), and PO forms the oxonium ion[11].

The structures shown in (9)–(12) have three ionizable

$(RO)Fe^+OFe(OR)_2$ groups. Hence, in agreement with the experimental results, this mechanism is expected to produce K-polymers that are interconnected to each other with Fe atoms:



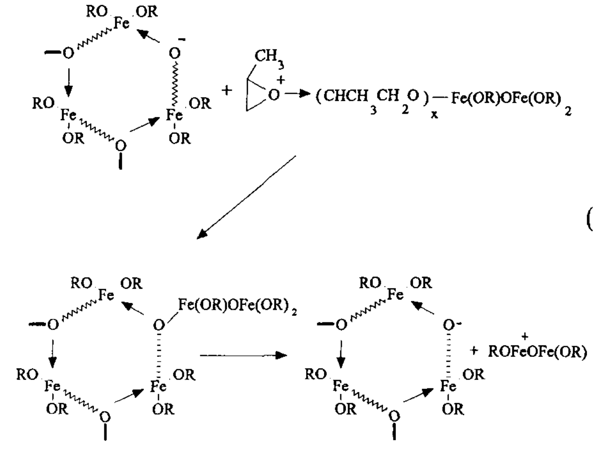
(∿∿∿∿ = $(OCH_2CHCH_3)_n$

(— = $Fe(OR)OFe(OR)_2$)

Apparently, the gradual change of (10) to the above structure in the polymerization process would affect the overall reaction rate. Hence this mechanism also explains the observed acceleration period[7,20] of polymerization. This is also consistent or, rather, does not contradict some of the other observed features of stereoregular polymerization, namely K-polymers contain considerable concentrations of structurally irregular repeating units[14,16] and, the longer the K-polymer chains, the smaller their content of structurally irregular repeating units[14,21].

D-polymer production

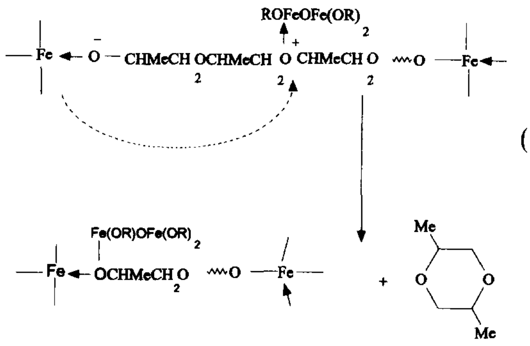
Two mechanisms can be suggested for D-polymer production. In the first, the oxonium ion formed in (9) is the active site for D-polymer production (cf. ref. 5) by a familiar back biting chain transfer process. This mechanism would not contradict the Hittorf electrolysis results, since termination by combination of the countercharges would reform the transportable cationic fragment:



(13)

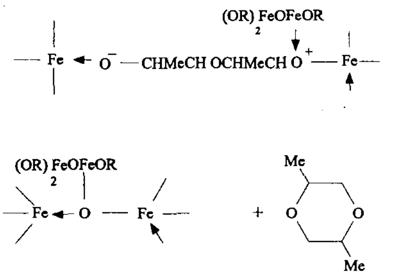
where the stereoblock K and D chain segments are denoted by stacked horizontal bars. Thus, because of this mechanism, K-polymers with stereoblock structures are expected to form[11]. However this mechanism fails to explain the following experimental results: D-polymer production cannot be increased by adding an anion scavenger (i.e. P17 and P18 in *Table 4*), or in high dielectric media (P11 and P12); D-polymer production does not decrease in low dielectric solvents (P13–P15); and D-polymer is the major product in the acceleration period, but it becomes the minor product as the K-polymer is produced at faster rates in the later stages of polymerization[7].

According to the second mechanism, D-polymer formation is due to the oxonium ion formed on the backbone of the growing K-polymer:



(14a)

or



(14b)

Since both the anion and the cation are together, and either one of the ions alone may be responsible for D-polymerization, the mechanism (14a) provides reasonable explanations for the first two of the above objections. Although mechanism (19b) is only a marginal form of (19a), it should be better termed as a transfer to catalyst rather than transfer to polymer. According to this mechanism of counter charge combination, D-polymer production will be faster if the opposite charges are closer to each other. Thus, this mechanism predicts formation of D-polymers at higher rates in the initial stages of polymerization.

Çolak and Alyürük[7] observed almost a second-order increase of D-polymer yield with respect to catalyst concentration, i.e. D-polymer yield increased from 0.30 to 35% as the molality of Fe atoms in polymerization mixture increased from 2.3×10^{-3} to 63×10^{-3} mol kg^{-1} PO. This increase in the catalyst concentration also had a striking effect on the M_v of the product, namely, the M_v of the K-polymers decreased from 1.9×10^6 to 8.0×10^4 g mol^{-1}. The latter mechanism can also offer an explanation for the adverse effect of catalyst concentration on polymerization. As the catalyst concentration increases, the rate of transferring cationic fragments from one PBC molecule to another also increases [reaction (15)]. This intermolecular cation transfer would enhance D-polymer formation according to reaction (14).

$$PBC + PBC \rightarrow PBC^+ + PBC^- \qquad (15)$$

where

$$PBC^+ = PBC + ROFe^+OFe(OR)_2$$

and

$$PBC^- = PBC - ROFe^+PFe(OR)_2.$$

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