Monomer-bound ion pairs in the stereoregular polymerization of propylene oxide by the Pruitt-Baggett catalyst

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The Pruitt-Baggett adduct (PBA) ($MW = 438 \, g \, mol^{-1}$) that formed from the reaction of $FeCl_3$ with propylene oxide (PO) was hydrolysed in diethyl ether (ether) solutions at different $r = H_2O/Fe$ molar ratios. The hydrolysates (PBH/r), which were insoluble in ether, could be converted into catalytically active form (PBC/r) by a thermal treatment. PBC/r ($r < 1$) was soluble in etheric solvents and in pyridine. These solutions, in contrast to PBA and PBH/r, were electrical conductors. Profound differences in the electrical conductivity of PBC/r was observed by varying the hydrolysis ratio r. The observed conductivity decayed and finally vanished with a kinetically second-order process. This is explained by the free ions, formed from PBC/0.67 ($MW = 4400 \, g \, mol^{-1}$), being bound together with an ether (or PO) molecule to yield ether- (or PO-) bound ion pairs (PBCB). PBC/0.67 and the electrical conductivity of its freshly prepared solutions could be retrieved by 'driving off' (by drying under vacuum at 40°C) the 'binding molecule' (ether or PO) from PBCB. In contrast to this system, the electrical conductivity of solutions of PBC/0.20 (which shows inferior catalytic activity) did not change with ageing.

(Keywords: propylene oxide; Pruitt-Baggett catalyst; solution properties; electrical conductivity; stereoregular polymerization; monomer-bound ion pairs)

INTRODUCTION

The empirical formula of the Pruitt-Baggett adduct (PBA) that is readily formed from the reaction of $FeCl_3$ with propylene oxide (PO) has been identified[1,2] as:

$$Cl-Fe \left\langle \begin{array}{l} (OCH_2CHMe)_xCl \\ (OCH_2CHMe)_yCl \end{array} \right. \tag{1}$$
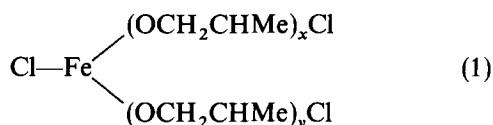
where $x + y \simeq 5$. At elevated temperatures PBA was found to be scarcely active in the stereoregular polymerization of PO, but it could be converted into catalytically active forms (PBC/r, where $r = $ (moles of H_2O)/(moles of Fe)) by addition of water in molar quantities[1,3] and thermal treatment[3]. The catalytic activity of PBC/r can be varied substantially by changing the hydrolysis ratio r. Thus PBC/0.67 was reported as the catalytically most active form[3]. PBC/r was found to be soluble in PO in the range $0 \leqslant r \leqslant 1$.

Possibly owing to accidental admission of water in open or semiclosed systems, and in contrast to the new observations[3], PBA (or PBC/r) has been generally accepted as insoluble in the polymerization medium. Therefore attempts were made to explain the stereospecific action of PBC/r in terms of surface effects[4]. Consequently the solution properties of PBC/r have not been studied.

As a continuation of the previous report[3] we wish to present some experimental data on the solution properties of PBA and PBC/r and relate these data to the nature of the active species in the stereoregular polymerization of PO.

EXPERIMENTAL

Materials

Purification of reagents and solvents and the general procedure adopted in handling them under high vacuum have already been described[3].

PBA was synthesized from sublimed $FeCl_3$ and PO by rigorous exclusion of adventitious water[3]. It was dissolved in ether and this solution was kept in a storage vessel from which known quantities could be measured out via a burette fitted with greaseless taps.

Polymerizations

PO in the presence or absence of additives was polymerized by mixing with PBC/0.75, under high-vacuum conditions at 80°C. The methods used for isolation of polymers and fractionating them into crystalline (K-polymers) and non-crystallizable oily polymers (D-polymers) by thermal precipitation from dilute isooctane solution have been described in detail in the previous communication[3].

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Molecular-weight measurements

Molecular weights of PBA and PBC/0.67 were measured isopiestically. For this purpose PBC/0.67 was formed in the isopiestic apparatus (*Figure 1*). The apparatus was attached to the vacuum line (through V_1 and V_2, *Figure 1*). A measured volume of known concentration of azobenzene (the reference substance) in ether was injected into the burette reservoir compartment C_1 through the suba-seal cup, S. The ether was pumped off and constriction K_1 was sealed. Any residual water in the azobenzene was swept off by repeatedly distilling some dry ether in C_1 and then repumping. Finally 5 cm³ of dry ether was distilled in C_1 and the constriction K_2 was sealed. Measured quantities of PBA in ether solution and water were transferred into C_2 and the constriction K_3 was sealed. The apparatus was placed in a bath regulated at 40°C. A dark-brown precipitate formed and increased in amount for 24 h. The apparatus was attached to the vacuum line again (through V_3) and the break-seal B_1 was broken with a magnet. The ether was pumped off and the residue was heated at 80°C for 3 h with continuous pumping (hereafter, this thermal treatment will be referred

to as 'baking'). The baked residue (PBC/0.67) was readily dissolved in 5 cm³ ether to give a clear reddish solution. The constriction K_4 was sealed and the break-seal B_2 was broken. In a constant-temperature bath at 37°C, the apparatus was gently rocked, with the burette arms almost horizontal, by a mechanical device until iso-thermal distillation had stopped. The end of the distilla-tion was checked by observing the reversion of the distillation when a small quantity of ether was intention-ally transferred from one compartment to the other. At equilibrium, readings of the levels in the two burettes were taken and concentrations of azobenzene (C_{AB}) and PBC/0.67 (C_{PBC}) were calculated. In the calculation of C_{PBC} it was assumed that the change in the initial mass of PBA caused by either addition of H_2O or evolution of HCl gas[5] during the hydrolysis and the baking stages was negligible. Since the concentrations of the solutions were sufficiently dilute ($C_{AB} = 1.577 \times 10^{-1}$ g dl^{-1} and $C_{PBC} = 3.812$ g dl^{-1}) the molecular weight of PBC/0.67 was calculated from the following equation:

$$MW_{PBC} = MW_{AB} \times C_{PBC}/C_{AB} \tag{2}$$

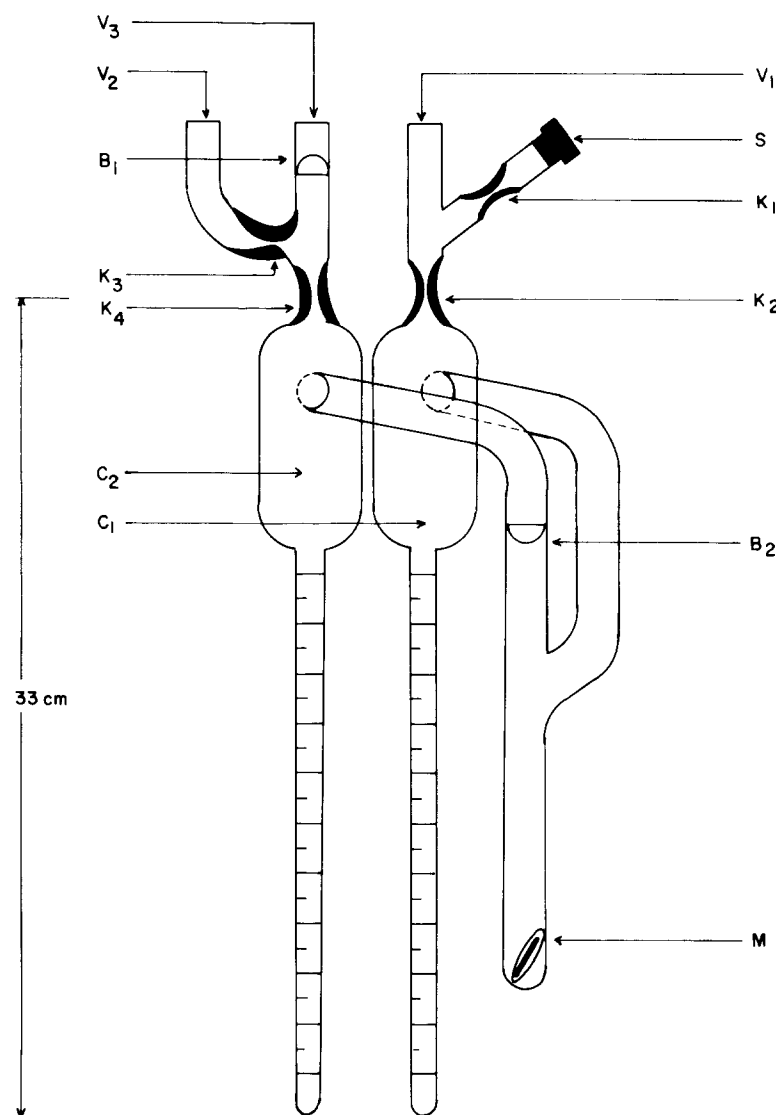where MW_{AB} is the molecular weight of azobenzene.

Figure 1 Apparatus for isopiestic molecular-weight determination: V_1-V_3, vacuum connections; S, suba-seal cup; K_1-K_4, constrictions; B_1 and B_2, break-seals; C_1 and C_2, burette reservoir compartments for reference substance and sample; M, magnet

For PBA, the equilibrium concentrations of the reference and sample compartments were found to be $C_{AB} = 9.778 \times 10^{-1}\,g\,dl^{-1}$ and $C_{PBA} = 2.348\,g\,dl^{-1}$.

The experimental procedure for the determination of the viscosity-average molecular weight of poly(propylene oxide) has been described elsewhere[3].

Conductimetric measurements

A conductance cell with a Teflon plug tap was constructed (*Figure 2*). The cell constant was measured by using standard KCl solutions. In spite of careful glass-blowing, the Pt–borosilicate glass joints (J_{Pt-G}, *Figure 2*) were not perfectly vacuum-tight. However, the leakage at Pt–glass joints could be satisfactorily prevented (i.e. no increase of pressure was observed for three days when the cell had been initially pumped down to 10^{-5} Torr) by filling the electrode-bearing tubes (T, *Figure 2*) with Hg. Water, solvents, etc., were charged into the cell by means of a rotary reservoir. PBC/r was formed in the cell in a similar procedure to that described in the preceding section. Conductivities of solutions were measured by using a direct-reading Industrial Instruments Inc. model RC B2 conductivity bridge, which could detect conductances down to 4×10^{-7} S. The cell constants of the cells used are given in the relevant tables.
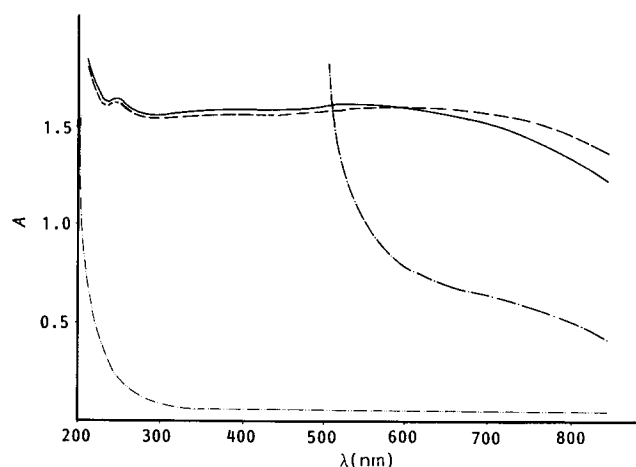
Figure 3 U.v. spectra: (—··—) diethyl ether; (—·—) PBA ($C_{PBA} = 3.93 \times 10^{-3}$ mol Fe/l; (——) freshly regenerated PBC/0.67 solution ($C_{PBC/0.67} = 3.94 \times 10^{-2}$ mol Fe/l; (———) the same PBC/0.67 solution after 1 h at 0°C

Ultra-violet spectroscopy

U.v. spectra were taken by a Bausch & Lomb Spectronic-2000 spectrophotometer. A B-10 ground-joint quartz cell was filled and sealed under vacuum with either PBA ($C_{PBA} = 3.93 \times 10^{-3}$ mol Fe/l) or PBC/0.67 ($C_{PBC/0.67} = 3.94 \times 10^{-2}$ mol Fe/l) solutions in ether. The u.v. cell was not vacuum-tight (PBA solutions became turbid in a few hours). Therefore u.v. spectra of the solution at 0°C were taken 10 min after filling the cell. Possibly owing to the leakage of the cell, the u.v. spectrum of PBC/0.67 showed continuous variation with time (*Figure 3*).

RESULTS AND DISCUSSION

Conversion of PBA into PBC/r

PBA was observed as a dark-brown glassy substance at room temperature, which became a viscous fluid just above room temperature. PBA dissolved in ether (and PO) and exhibited a greenish-yellow colour at extreme dilutions. The u.v. spectrum of PBA showed a broad and strong absorbance, which was suggestive of a charge-transfer complex (*Figure 3*).

Analysis for iron (11.48% Fe) indicated that the molecular weight of PBA was given by the following equation:

$$MW_{PBA} = 430.6n \text{ (g mol}^{-1}) \qquad (3)$$

where n is the number of Fe atoms in a PBA molecule. Isopiestic measurements gave $MW_{PBA} = 437.6\,g\,mol^{-1}$, leading to $n = 1.02$ and showing that PBA was monomeric in dilute solutions.

Neither freshly prepared nor aged ether solutions of PBA were electrical conductors.

Upon addition of water in dilute etheric solutions of PBA, a brown precipitate (PBH/r) formed, which increased in amount in 24 h[3]. In spite of HCl evolution[5] during the hydrolysis no signs of electrical conduction of the supernatant solution could be detected. PBH/r was converted into PBC/r (with further evolution of HCl[5]) by baking it after removal of ether.

PBC/r ($MW_{PBC/0.67} = 4400\,g\,mol^{-1}$) gave reddish solutions in ether, dioxane, pyridine and PO and in ether/cylohexane (80% v/v) and PO/cyclohexane (50% v/v) solvent mixtures. The u.v. spectrum of
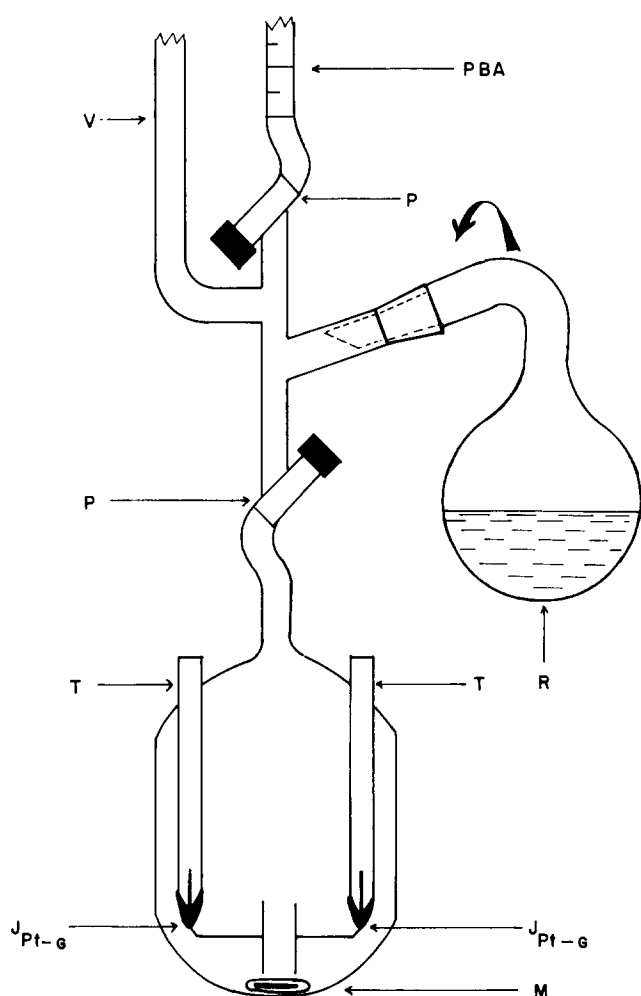
Figure 2 The conductance cell: V, vacuum connection; P, Teflon plug taps; J_{Pt-G}, borosilicate glass–Pt joints; T, electrode-bearing glass tubes; R, rotary reservoir; M, magnet

PBC/0.67 was distinctly different from that of the PBA, both in character and in the strength of the absorbance (*Figure 3*). We conclude that in the baking process, possibly through a condensation process between Fe–OH and Fe–Cl groups, Fe–O–Fe bonds are formed.

The PBC/r solutions were electrical conductors. Thus, electrical conductivity appears to be a common property of the structures with metal–oxygen–metal bonds, which are catalytically active in the stereoregular polymerization of PO (Zn–O–Zn[6], Al–O–Al[7,8]).

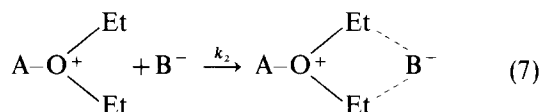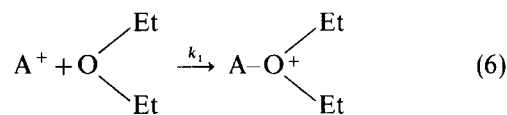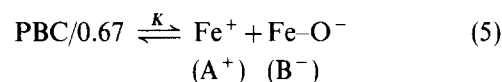### Electrical conductivity of PBC/r solutions

PBC/0.67. Freshly prepared etheric solutions of PBC/0.67 were conductive ($\Lambda^* = (6-10) \times 10^{-2}$ S cm^2/mol Fe). However, the observed conductivity decayed as the solution aged, without formation of any new phase, and finally vanished (i.e. the observed conductance dropped down to the minimum level that the conductivity bridge used in this work could detect). The length of time during which the conductance was observed depended on the initial concentration of PBC/0.67, temperature and solvent. However, when the solvent of an aged PBC/0.67 solution was pumped off followed by heating and pumping the residue at 40°C for 30 min (in the following text this pumping treatment will be termed 'regeneration'), the initial conductivity (Λ^*) of freshly prepared PBC/0.67 solutions could be almost exactly retrieved. The conductivity of the regenerated solutions decayed with almost the same rate as the original solution whether the new solution had been prepared by adding the collected solvent of the original solution or the solvent from another stock. When the reciprocal of the instantaneous molar conductivity (Λ^{-1}) of the solutions was plotted against time, straight lines with high linear regression coefficients (c_{lr}) ($0.978 < c_{lr} < 0.999$) were obtained in accordance with the following rate equation:

$$-d\Lambda/dt = k\Lambda^2 \qquad (4)$$

In *Table 1*, the measured values of slopes (k), reciprocals of the intercepts (Λ^*) and c_{lr} are given. The reproducibility of k and Λ^* values appeared to depend on the length of time taken for the regenerated residue to dissolve (1–1.5 min) and the effectiveness of the stirring during this period (the magnetic stirrer, M (*Figure 2*) stuck on the tacky and swollen residue, hence effective stirring was not possible at the beginning of dissolution).

Based upon these observations we conclude that the decay of the conductivity is because of the formation of solvent-bound ion pairs (PBCB):

$$PBC/0.67 \underset{}{\overset{K}{\rightleftharpoons}} \underset{(A^+)}{Fe^+} + \underset{(B^-)}{Fe-O^-} \qquad (5)$$

$$A^+ + O{\Big\langle}{\overset{Et}{\underset{Et}{}}} \xrightarrow{k_1} A-O{\overset{+}{\Big\langle}}{\overset{Et}{\underset{Et}{}}} \qquad (6)$$

$$A-O{\overset{+}{\Big\langle}}{\overset{Et}{\underset{Et}{}}} + B^- \xrightarrow{k_2} A-O{\overset{+}{\Big\langle}}{\overset{Et}{\underset{Et}{}}}\ B^- \qquad (7)$$

$$PBCB \xrightarrow{\text{regeneration}} PBC/0.67 + Et_2O\uparrow \qquad (8)$$

The second-order rate equation can be tentatively accounted for by assuming that $k_1 > k_2$ and Λ is proportional to the instantaneous concentrations of both AO^+Et_2 and B^- (equations (9) and (10)):

$$\Lambda = k'[AO^+Et_2] = k''[B^-] \qquad (9)$$

(where k' and k'' would be equal to each other if the concentration of A^+ is negligible) and

$$-d\Lambda/dt = d[PBCB]/dt = [k_2/(k'k'')]\Lambda^2 \qquad (10)$$

The Λ^* value of PBC/0.67 solutions increased when solvents of higher dielectric constant (D) were used. The dioxane ($D = 2.2$) solutions were not conductive, whereas $\Lambda^* = 3.4 \times 10^{-2}$, 46×10^{-2} and 70×10^{-2} S cm^2/mol Fe were measured in 80% (v/v) ether/cyclohexane ($D \simeq 4.0$), pyridine ($D = 12.3$) and PO ($D = 13.1$) solutions, respectively. The decay of the conductivity in ether/cyclohexane was so fast that the initially observed conductance disappeared within a few minutes. On the other hand, in pyridine, the conductivity of PBC/0.67 did not decay with ageing, and hence no indication of the formation of PBCB was observed. The effect of pyridine was further tested by adding it in 0.5 molar ratio (pyridine/Fe) to an etheric solution of PBC/0.67. A slight increase in Λ^* was observed (viz. 13×10^{-2} S cm^2/mol Fe) but more strikingly the decay constant k was decreased by a factor of 10^3 ($k = 3 \times 10^{-6}$ Ω cm^{-2} s^{-1} mol Fe; compare the values of k given in *Table 1*). Hence the solution remained conductive for several days. The original decay characteristics of the etheric solutions can also be retrieved when PBC/0.67 was regenerated from the pyridine-added solution.

Table 1 Decay of the molar conductivity of PBC/0.67 at 15°C with ageing in ether (Exp. Nos 1–7) and in PO (Exp. Nos 8 and 9)

	Exp. no.	RN^a	$C_{PBC/0.67} \times 10^3$ (mol Fe/l)	$\Lambda^* \times 10^{2\,b}$ (S cm^2/mol Fe)	$k \times 10^3$ (Ω cm^{-2} s^{-1} mol Fe)	c_{lr}	T_{obs}^c (min)
Ether	1	1	7.87	7.92	7.7	0.999	145
	2	7	5.24	8.38	14.5	0.981	48
	3	2	3.94	10.14	26.1	0.986	19
	4	3	3.94	7.76	26.3	0.999	17
	5	4	3.94	7.76	26.3	0.999	17
	6	5	3.15	6.02	21.3	0.999	12
	7	6	2.62	5.77	34.4	0.978	5
PO	8	1	7.87	69.6	1.0	0.999	–
	9	2	7.87	69.6	1.0	0.999	–

^{a} The number of times that the sample had been regenerated
^{b} The cell constant $= 0.2466$ cm^{-1}
^{c} The period of time in which the conductivity was observed

In order to avoid the complicating effects of polymerization, the conductivity of PBC/0.67 in PO was studied for short periods (30 min) at 18°C (in 24 h PO was only 2.3% polymerized at 40°C but 36% at 80°C, at comparable PBC/0.67 concentrations[3]). It was found that after 30 min of ageing in PO the conductivity of PBC/0.67 decayed from 70×10^{-2} down to 30×10^{-2} S cm^2/mol Fe. From this aged solution, the initial conductivity of PBC/0.67 could also be retrieved by the regeneration treatment (*Table 1*). On the other hand when the polymerization was allowed to proceed for longer periods the Λ^{-1} *versus* time plots deviated from the straight-line behaviour after the first 90 min (*Figure 4*). The faster rates of decay of the conductivity could be due to the decrease of the mobility of ions, assuming that the polymer chain grows on one of the ions. However, surprisingly, the decay rate of conductivity slowed down and finally the conduc-
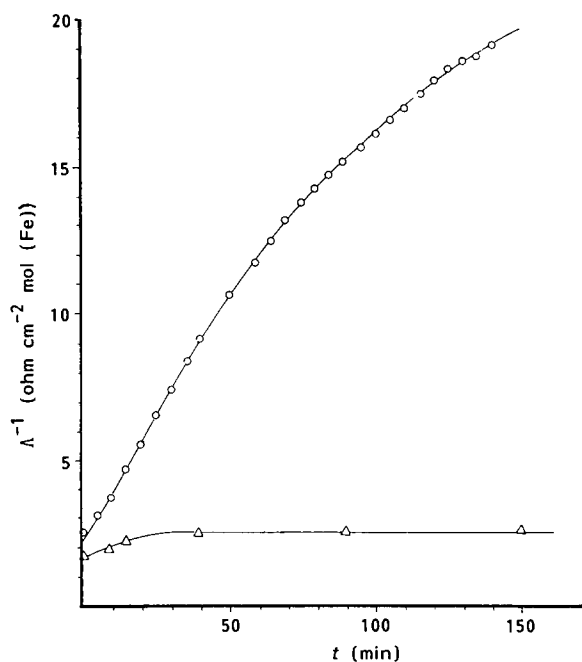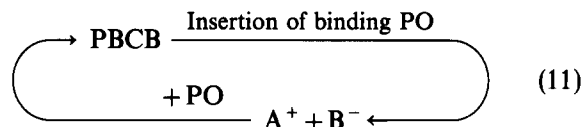
tivity became more or less constant after 14 h of polymerization (the measured conductivity at 48 h was 1.7×10^{-2} S cm^2/mol Fe). This slower rate of decay could be accounted for by the regeneration of the free ions by insertion of the binding PO molecule of the PBCB into the growing chain:

$$\text{PBCB} \xrightarrow{\text{Insertion of binding PO}} \text{A}^+ + \text{B}^- \xleftarrow{\quad} \qquad (11)$$

PBC/0.75. The conductivities of etheric solutions of PBCB/0.75 showed similar characteristics to those of the PBC/0.67 solutions (*Table 2*). However, the decay constant of the former, in contrast to the latter, did not vary with dilution. The considerable increase of the k values with temperature (*Table 2*) indicated a high activation energy (90–120 kj mol^{-1}) for the formation process of PBCB.

PBC/0.50. The decay characteristics of etheric PBC/0.50 solutions differed from those of the PBC/0.67 and PBC/0.75 solutions. Following an initial period of decay, the conductance of PBCB/0.50 solutions reached an equilibrium level (Λ_{eq}). These aged solutions could also be regenerated to retrieve the initial conductivity (*Figure 5*). The observed Λ_{eq} values increased with dilution. Possibly due to the coexistence of different types of ions/ion pairs in the PBC/0.50 solutions, the variation of Λ_{eq} values with dilution did not follow Ostwald's dilution law.

PBC/0.20. No variation of the conductivity of etheric PBC/0.20 solutions with ageing was observed. In agreement with Ostwald's dilution law, the measured molar conductivity of PBC/0.20 increased with dilution. In fact, a straight line with a linear regression coefficient of 0.936 was obtained when ΛC (where C is the molar concentration of Fe) is plotted against Λ^{-1}. The dissociation constant (K) of PBCB/0.20 and its conductivity at infinite dilution (Λ_0) were estimated from the measured intercept ($= -K\Lambda_0$) and slope ($= K\Lambda_0^2$) of the above plot as $K = 9.37 \times 10^{-4}$ mol l^{-1} and $\Lambda_0 = 60.6 \times 10^{-2}$ S cm^2/mol Fe.

Figure 4 The decay of the conductivity during polymerization: (○) PBC/0.67; (△) PBC/0.20

Table 2 Decay of the molar conductivity of PBC/0.75 at 15°C (Exp. Nos 10–22) and at 0°C (Exp. Nos 23 and 24) with ageing in ether[a]

	Exp. no.	RN	$C_{PBC/0.75} \times 10^3$ (mol Fe/l)	$\Lambda^* \times 10^2$[b] (S cm^2/mol Fe)	$k \times 10^3$ (Ω cm^{-2} s^{-1} mol Fe)	c_{lr}
15°C	10[c]	4	7.87	4.87	40.1	0.999
	11	5	7.87	5.63	41.1	0.999
	12	6	5.24	3.71	35.5	0.999
	13	7	5.24	7.40	55.2	0.993
	14	8	5.24	7.00	45.4	0.996
	15	9	3.94	6.54	58.8	0.998
	16[c]	1	7.87	6.83	69.7	0.997
	17	2	7.87	11.37	53.3	0.999
	18	3	7.87	5.84	53.2	0.999
	19	4	7.87	6.13	41.0	0.999
	20	5	5.24	6.86	42.3	0.996
	21	6	3.94	6.50	38.0	0.990
	22	7	3.15	8.02	42.7	0.998
0°C	23	8	7.87	6.13	5.7	0.973
	24	9	7.87	5.12	4.5	0.966

[a] For column headings, see *Table 1*
[b] The cell constant $= 0.1370$ cm^{-1}
[c] In experiments 10–15 and experiments 16–24 different batches of PBC/0.75 were used
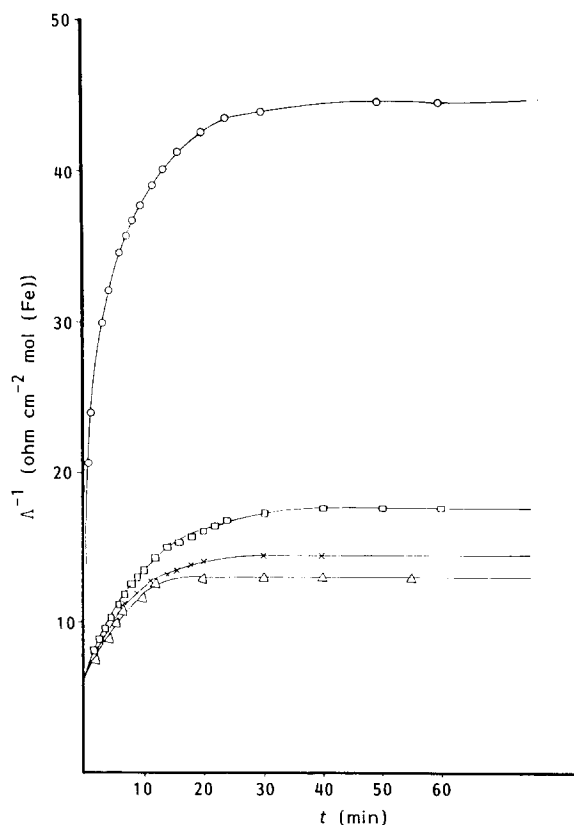
Figure 5 The decay of the conductivity of PBC/0.50 ether solutions: (○) $C_{PBC/0.50}$(after first regeneration) = 7.87×10^{-3} mol Fe/l; (□) $C_{PBC/0.50}$(second regeneration) = 5.24×10^{-3} mol Fe/l; (×) $C_{PBC/0.50}$(third regeneration) = 3.94×10^{-3} mol Fe/l; (△) $C_{PBC/0.50}$ (fourth regeneration) = 3.15×10^{-3} mol Fe/l

In *Table 3* the molar conductivities and estimated degrees of dissociation of PBC/0.20 (Λ/Λ_0) at different concentrations are given.

In PO the initial molar conductivities of PBC/0.20 and PBC/0.67 were almost equal to each other. In the initial stages of polymerization limited decay of the conductivity of the former was also observed. However within 20 min polymerization the conductivity of the PBC/0.20 catalysed polymerization mixture became constant (*Figure 4*).

Polymerization experiments

Among the questions on the mechanism of stereoregular polymerization of PO that emerge, in the light of the present data the following two are probably the most important.

(i) Are the monomer-bound ion pairs essential entities in the stereoregular polymerization, or is one of the free ions (molecular-weight measurements suggest that they should contain a number of Fe atoms) solely responsible for polymerization?

(ii) If the stereoregular polymerization is due to monomer-bound ion pairs, then which one of the ionic fragments does carry the growing chain?

Further research concerning these and related problems is still in progress[5,8]. However, our preliminary results on the polymerization of PO in the presence of certain additives answer to a certain extent the first of the above questions (*Table 4*).

In contrast to the conductivity results, which showed that pyridine addition inhibited PBCB formation and, hence, increased the free anion (B⁻) concentration, this additive depressed the percentage polymer yield, *P*, considerably. Therefore it should be quite safe to conclude that the anionic fragments cannot be solely responsible for the stereoregular polymerization. On the other hand HCl would possibly protonate B⁻ anions and supply Cl⁻ ions instead. Therefore the observed deterioration in the values of *P* and P_K/P_D (where P_K and P_D are the percentages of monomer that gave K- and D-polymer, respectively) with increasing HCl concentration might be an indication of the importance of the role of the PBCB (which would not form in the deficiency of B⁻ ions) in stereoregular polymerization.

As the conductivity results have shown, in low-dielectric-constant solutions, the ion-pair concentration increases at the expense of free ions. However, it is found that in PO/cyclohexane mixture neither *P* nor P_K/P_D values were greatly depressed. This result also favours the importance of PBCB as an essential entity in the stereoregular polymerization of PO. The interpretation of the effect of added dioxane is rather difficult, since it does not only lower the dielectric constant of the polymerization mixture, but also competes with PO in coordinating A^+ cations.

Conductance measurements in PO have shown that PBC/0.20 does not form (or forms only scarcely) PBCB (*Figure 4*). Therefore the relatively lower catalytic activity of the PBC/0.20 in comparison with that of PBC/0.67[3] might provide further support for the importance of PBCB as an essential entity in the stereoregular polymerization of PO.

Table 3 Variation of the molar conductivity of PBC/0.20 with dilution (in ether at 18°C)

Exp. no.	$C_{PBC/0.20} \times 10^3$ (mol Fe/l)	$\Lambda \times 10^2$ [a] (S cm²/mol Fe)	Λ/Λ_0 [b]
25	7.87	17.4	0.287
26	5.24	21.8	0.359
27	3.94	23.2	0.383
28	3.15	24.2	0.399

[a] The cell constant = 0.1370 cm⁻¹
[b] Degree of dissociation

Table 4 The effect of additives on the stereoregular polymerization of PO by the PBC/0.75 at 80°C

Exp. no.	Additive	r_A [a]	*P*	P_K	P_K/P_D	$M_v \times 10^{-5}$
29	Nil	–	27.6	18.1	1.9	7.0
30	Nil	–	29.7	19.5	1.9	–
31	Ether	LA	26.7	19.8	2.9	2.2
32	Dioxane	LA	11.1	7.6	2.2	8.0
33	Cyclohexane	LA	25.5	19.0	2.9	5.6
34	Pyridine	LA	1.0	–	–	–
35	Pyridine	0.50	6.9	3.9	1.3	1.3
36	Pyridine	0.75	3.8	2.4	1.7	2.7
37	Pyridine	1.50	3.8	2.4	1.7	3.6
38	HCl	0.50	11.2	6.5	1.4	5.7
39	HCl	1.00	10.9	5.8	1.1	5.8
40	HCl	10.00	5.3	1.3	0.3	–

[a] Additives added either in large amounts (LA) (viz. for 1.9×10^{-4} moles of Fe and 10 cm³ PO; 10 cm³ of additive) or in minute amounts; r_A stands for the mole ratio of additive/Fe

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