Polymerization of propylene oxide by the Pruitt–Baggett catalyst

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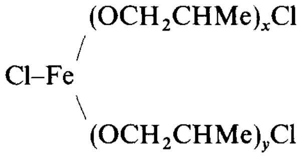
The Pruitt–Baggett adduct (PBA) which formed from the reaction of $FeCl_3$ with propylene oxide (PO) was hydrolysed in diethyl ether (ether) solutions at different $r = H_2O/Fe$ mole ratios. Although the hydrolysates were insoluble in ether they could be converted into PO-soluble form (PBC) by a thermal treatment providing that the r value was kept smaller or equal to unity. PBC polymerized PO concurrently into a mixture of high molecular weight crystalline polymer with low molecular weight non-crystallizable oligomers. The traces catalytic activity shown by PBA substantially enhanced as the hydrolysis ratio r, increased from 0 to 0.5. Although the PBC obtained at $r = 0.50$ gave maximum yield of polymer, the maximum stereoregular yield (crystalline polymer/oligomer mass ratio) was observed at $r = 2/3$ mole ratio.

(Keywords: proplyene oxide; ferric chloride; water activation; stereoregularity; polymerization; fractionation)

INTRODUCTION

M. E. Pruitt and J. M. Baggett[1] have reported that PO can be polymerized by $FeCl_3$ to give products of high molecular weight which are partially crystalline. It was soon observed that the reaction has two clearly defined stages[2]. The first occurs rapidly at room temperature yielding an adduct of PO with $FeCl_3$ (PBA), with the following structure[3,4]:



$$\text{Cl–Fe}\begin{cases}(\text{OCH}_2\text{CHMe})_x\text{Cl}\\(\text{OCH}_2\text{CHMe})_y\text{Cl}\end{cases}$$

where $x + y = 5$. In the following stage which took place at elevated temperatures (viz. 80–100°C) PBA polymerized PO into a stereoregular and high molecular weight polymer. Added water in cocatalytic amounts has been shown to have profound influence on the second stage by accelerating the process and increasing the yield of crystalline polymer[3–6]. It was generally agreed that the added water reacts with PBA to produce a final product, PBC, plausibly with the formation of Fe–O–Fe bonds[3–6]. However some basic questions such as the catalytic activity of PBA in the absence of water and the variation of the crystalline polymer yield with the H_2O/PBA molar ratio[4–6]; solubilities of PBA and PBC in the polymerization medium[2,4–6]; the kinetic order of the polymerization reaction[4–6]; and the chemical identity of PBC[7] have not been satisfactorily answered.

We began some time ago to investigate these aspects systematically. The purpose of this communication is to report our results and related conclusions on the use of a number of water activated Pruitt–Baggett type catalysts in the stereoregular polymerization of PO and on the nature of the products.

EXPERIMENTAL

Materials

All reagents and solvents were purified by standard procedures prior to fractionation through a column with an efficiency of approximately 25-theoretical plates. Calcium hydride was used as a drying agent for solvents and, once purified, all solvents and reagents were handled under high vacuum.

General procedure

All experiments were carried out on a vacuum line, which would allow measurement and transfer of reagents and solvents *in vacuo* and storage of reaction products *in vacuo* with the possibility of handling them (transfer of samples, filtrations, dilutions and mixing with other reagents) without exposure to the atmosphere.

Preparation of PBA stock solution

From a new bottle of Eisen (III) Chlorid Sublimiert; (Reidel De Haen) 5 g of $FeCl_3$ was transferred into a sublimation flask under dry nitrogen atmosphere. The sublimation flask was attached to the vacuum line through a breakseal arm, degassed and filled with rigorously dry chlorine at 40 torr. $FeCl_3$ was transferred into a reactor flask by sublimation. The system was pumped prior to addition of about 40 cm^3 of PO at 0°C into the reactor. At the end of the reaction, excess PO was pumped off and a tacky solid was obtained. About 200 cm^3 of ether was added into the reactor to dissolve the product. A small portion of the product which would

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not dissolve was filtered out. The filtrate was collected in a storage vessel from which known quantities of PBA could be measured out via a burette fitted with greaseless taps. The final solution was a clear dark brown colour and remained so indefinitely. PBA was analysed for Fe and it was found that it contained 11.33% of Fe. This result was in accordance with the proposed structure of PBA.

Hydrolysis of PBA

A measured amount of water vapour trapped in a bulb was condensed into a breakseal ampoule containing the etheric solution of PBA. The ampoule was sealed and placed into a bath regulated at 40°C. A precipitate was formed and increased in amount for 24 h. To ensure complete hydrolysis the ampoule was kept in the bath for 48 h. At the end of the hydrolysis the ampoule was attached back to the vacuum line through the breakseal. Ether and volatile products were pumped off at 80°C for 3 h (hereafter, this thermal treatment will be referred to as 'baking'). The baked hydrolysate PBC, readily dissolved in PO giving reddish solutions, provided that the hydrolysis ratio $r = H_2O/Fe$ (mol/mol) was kept equal or smaller than unity.

Polymerizations

Polymerization reactions were carried out under high vacuum conditions by mixing PO with baked PBA or PBC. The reactions were terminated by adding a mixture of methanol in benzene. The benzene solution of polymers was washed repeatedly with 2 M HCl to remove Fe residues. The final colourless solutions were filtered. Antioxidant (diphenylamine) in the amount of 1% of the polymer mass was added and the samples were then freeze dried.

Fractionation of polymers

The products could be fractionated into two contrastingly different fractions[8,9].

(1) K-polymers: This fraction was the higher molecular weight and crystalline fraction. K-polymers can be further fractionated into fractions differing in structural and/or sterical regularity[9].

(2) D-polymers: This fraction was low molecular weight ($900 < \bar{M}_n < 2000$) non-crystallizable oily polymer. D-polymers contained considerable amounts of cyclic polyethers[8].

Fractionation was carried out by dissolving the polymer in isooctane (1 g/l) and chilling the solution to 0°C for 48 h. At this temperature the supernatant solution was separated from the crystallized K-polymers by filtration through a glass wool pad. D-polymers were obtained as a residue by evaporation of the filtrate. Both K- and D-polymers were dissolved in benzene, filtered, stabilized with antioxidant and freeze-dried.

Characterization of polymers

Viscosity average molecular weights were calculated from the intrinsic viscosities measured in toluene at 25°C using the following relation[10]:

$$[\eta] = 1.29 \times 10^{-4} \bar{M}_v^{0.75}$$

Number average molecular weights of D-polymers were measured cryoscopically in recrystallized benzene. G.p.c. chromatograms were obtained using a Water Associates GPC-200 instrument at 40°C. The flow rate of the solvent (toluene) and 1 cm^3/min, and eluted volumes were measured by a 5 cm^3 siphon counter. The sample column bank consisted of styragel columns with the following pore sizes: 10^7, 10^6, 10^5, 10^4 and 5×10^2 nm. The g.p.c. instrument was calibrated by a 'direct molecular weight' procedure.

RESULTS AND DISCUSSION

Hydrolysis of PBA

Since the added water reacts with PBA to form an entirely new compound, *in situ* preparation of PBC[4,6] (i.e. mixing of PBA with H_2O in the presence of PO) might cause some experimental complications unless the hydrolysis reaction were instantaneous. In order to estimate the time required for the completion of the hydrolysis of PBA in the absence of PO, a set of experiments were carried out. In these experiments the hydrolysis was performed as described in the experimental section but the temperature, as well as the time, allowed for hydrolysis were varied. At the end of given hydrolysis time the solvent and unreacted H_2O was pumped off and the residue was baked. The catalytic activities of these PBCs which were obtained under different hydrolysis conditions were compared with each other and with that of the PBA. In *Table 1* it appears that the per cent polymer yield, P and the per cent of monomer that polymerized into K-polymer, P_K were increased but the per cent of monomer that gave D-polymer, P_D, decreased as the time allowed for hydrolysis increased. The g.p.c. chromatograms of K-polymers obtained from this set of experiments are given in *Figure 1*.

Another set of experiments (*Table 2* and *Figure 2*) were carried out to investigate the activites of PBCs which are hydrolysed under identical conditions (at 40°C for 48 h) but at different hydrolysis ratios ($0 < r < 5$). As the hydrolysis ratio remained between zero and unity the

Table 1 The effect of hydrolysis time on the catalytic activity of PBC; polymerizations at 40°

Experiment	$m_{Fe} \times 10^2$ (mol Fe/kg PO)	r	Hydrolysis Time	T °C	Polymerization time (h)	P	P_K	P_D	$\bar{M}_v \times 10^{-5}$ (K-polymer)
E-1	1.73	0.00	–	–	48	1.23	0.37	0.86	0.90
E-2	2.13	0.00	–	–	62	2.02	0.59	1.43	4.80
E-3	2.04	0.50	5 min	18	48	2.77	0.83	1.94	1.50
E-4	2.00	0.50	15 h	0	48	4.21	2.00	2.21	6.60
E-6	2.07	0.50	1 h	40	48	3.02	1.57	1.45	6.50
E-5	2.07	0.50	42 h	40	48	3.88	2.17	1.71	5.10

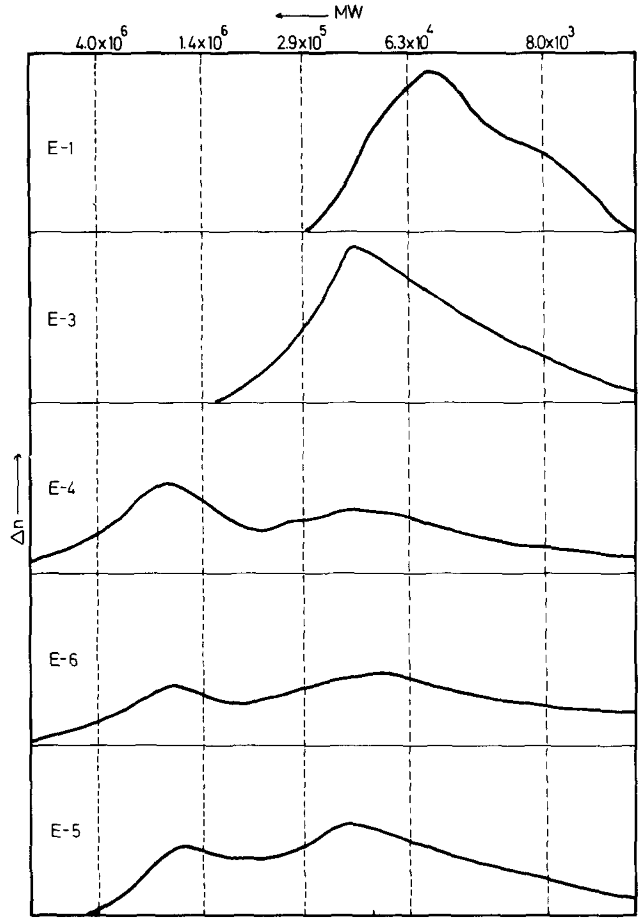

Figure 1 Effect of hydrolysis time on the molecular weight distribution of the poly(propylene oxide) (cf. *Table 1*). Δn, refractive indices difference; CN, count number

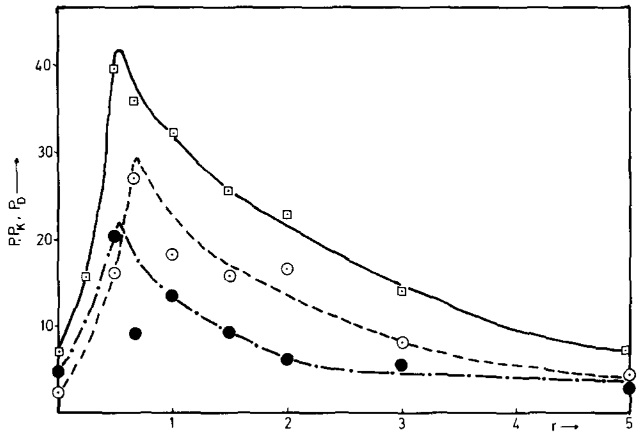

Figure 2 Variation of the yield of polymerization with the hydrolysis ratio:—⊡—⊡—, whole polymer; —⊙—⊙—, K-polymer; —·—●—·—●—·—, D-polymer (cf. *Table 2*)

PBCs formed were readily soluble in PO. On the other hand, as this ratio increased from unity to five, increasingly larger amounts of precipitate were formed which did not dissolve during the polymerization. The results of experiments summarizing the effect of water are given in *Table 2*. To test the reproducibility of our measurements the experiments E-13 and, about two months later, E-40, were carried out under identical conditions (cf. also E-25 in *Table 3*). These results were in accordance with each other, plausibly indicating a leakage-tight (with regard to moisture etc.) vacuum system. However, until the arrival of the results of more rigorous experiments, which are in progress, we would not like to comment on the catalytic activity of PBA in the absence of water (experiment E-10). In *Table 2* and *Figure 2*, it appears that although the highest yield of whole polymerization was obtained at $r = 0.50$, the PBC prepared at $r = 2/3$ value gave the maximum stereoregular yield ($= P_K/P_D$). As this ratio increased the catalytic activity of PBC (both P and P_K) gradually decreased.

Study of polymerization

A sampling experiment was carried out in which samples were drawn at certain intervals from a batch of polymerization mixture. The results of this experiment are given in *Table 3* and *Figure 3*. The following features of the polymerization were inferred from these results:

(1) Per cent conversion of monomer into total polymer and into K-polymer show an 'acceleration period'[6] at the initial stages of polymerization.

(2) D-polymer is the major product formed 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.

(3) The production of D-polymer is not restricted within the acceleration period. On the contrary, it is produced throughout the process.

Table 2 The variation of the catalytic activity of PBC with the hydrolysis ratio, r. Polymerizations at 80°C, for 24 h; $m_{Fe} = 2.06 \times 10^{-2}$ mol Fe/kg PO

Experiment	r	P	P_K	P_D	$\bar{M}_v \times 10^{-5}$ (K-polymer)
E-10	0.00	7.02	2.47	4.56	3.90
E-11	0.20	15.78	–	–	–
E-12	0.50	39.75	16.00	23.75	1.50
E-13	0.68	36.00	27.00	9.00	1.40
E-40	0.66	35.00	–	–	–
E- 8	1.00	32.00	18.30	13.70	1.10
E-14	1.50	25.34	16.01	9.33	3.55
E-15	2.00	22.61	16.64	5.97	5.90
E-16	3.00	14.19	8.29	5.90	1.70
E-17	5.00	7.35	3.93	3.42	4.04

Table 3 The sampling experiments. Polymerization at 80°C; $m_{Fe} = 2.06 \times 10^{-2}$ mol Fe/kg PO; $r = 0.67$

Experiment	Polymerization time (h)	P	P_K	P_D	$\bar{M}_n$ (D-polymer)	Mol D/mol Fe
E-22	0.5	1.25	0.21	1.04	–	–
E-23	2.0	2.72	0.94	1.78	–	–
E-24	8.0	7.95	4.50	3.45	870	1.9
E.25	24.0	31.40	21.20	10.20	1260	3.9
E-26	122.0	91.62	66.67	24.95	1860	6.6
E-27	241.0	100.00	66.30	33.70	–	–

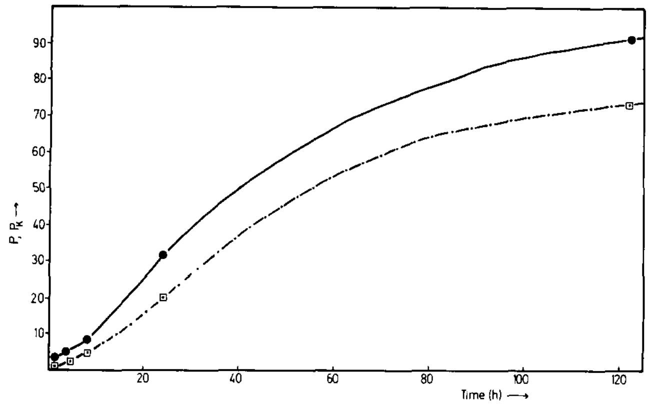

Figure 3 Plot of the polymerization yield against polymerization time: —●-●—, P; – · –⊡– · –⊡– · –, P_K (cf. *Table 3*)

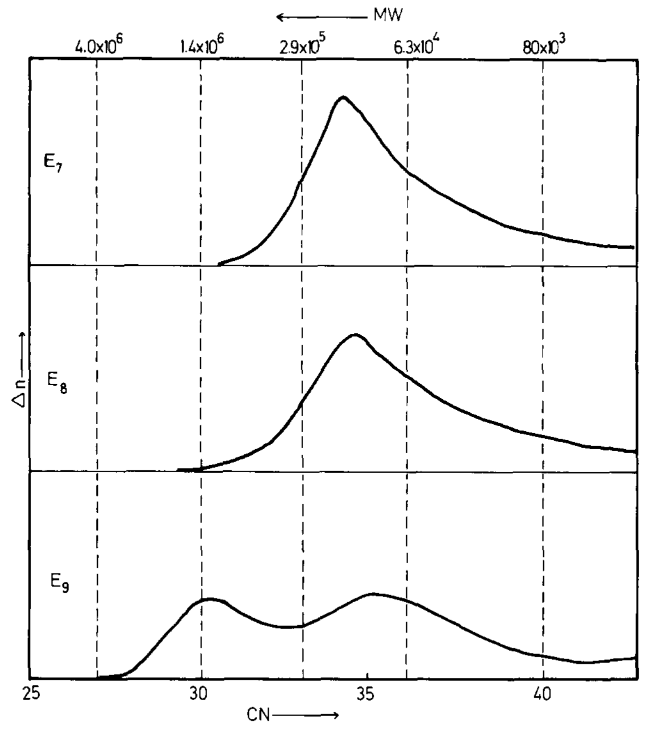

Figure 4 Effect of temperature of the polymerization on the molecular weight distribution of the product (cf. *Table 5*). Δn, refractive indices difference; CN, count number

(4) The measured $\bar{M}_n$ values of D-polymers (experiments E-24, E-25 and E-26) indicate that the number of moles of D-polymer molecules formed per mole of Fe atom used, is considerably larger than unity and it increases as the polymerization proceeds. D-polymer in E-26 was examined by n.m.r. and i.r. spectroscopy: there was no unsaturation but hydroxyl groups were found at the chain ends. Comparing the i.r. spectrum of E-26 with that of the standard polypropylene glycol, the mole per cent of cyclic polyethers in E-26 was estimated[8] to be 25%. Therefore we concluded that the D-polymers were formed during the polymerization by a transfer reaction.

(5) G.p.c. chromatograms indicate that the molecular weight of the K-polymers increases as the polymerization time increases.

The effect of the catalyst concentration on the polymerization was studied by varying PBC concentration by a factor of 25 (*Table 4*). The increased PBC concentration increased the yield of polymerization but decreased the molecular weight of K-polymers and the stereoregular yield very strikingly, for example, the P_K/P_D ratio is 12.3 in E-20 but it is only 1.1 in E-18. We tentatively attribute the adverse effect of the catalyst concentration on the molecular weight and the stereoregular yield to a competitive bimolecular reaction between the active centres, producing D-polymers and plausibly inserting steric and/or structural irregularities on otherwise stereoregular K-polymers[9].

The effect of the temperature on the polymerization was also briefly studied. The polymerization results at different temperatures using PBC ($r=1.00$) are given in *Table 5* and *Figure 4*. However, these data are inadequate for the purpose of activation energy calculations because an induction period reigned for a considerable interval during the polymerization. On the other hand, the increase of the stereoregular yield of the polymerization with increasing temperature indicates that the activation energy of the stereoregular polymerization must be higher than that of the competing reaction which produces D-polymers.

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Table 4 The effect of the PBC concentration on the polymerization. Polymerizations at 80°C, for 24 h

Experiment	r	$m_{Fe}\times10^3$ (mol Fe/kg PO)	P	P_K	P_D	$\bar{M}_v\times10^{-5}$ (K-polymer)
E-20	1.00	2.29	4.18	3.87	0.31	18.4
E-19	1.00	6.85	11.91	9.51	2.40	3.5
E- 8	1.00	20.64	32.00	18.30	13.70	1.1
E-18	1.00	62.52	71.80	37.31	34.49	0.8
E-21	0.67	6.85	12.23	9.51	2.72	7.8
E-13	0.67	20.64	35.95	26.96	8.99	1.4

Table 5 The effect of temperature on the polymerization. Polymerization time: 24 h; hydrolysis ratio of PBA: $r=1.00$

Experiment	$m_{Fe}\times10^2$ (mol Fe/kg PO)	Temperature (°C)	P	P_K	P_D	$\bar{M}_v\times10^{-5}$ (K-polymer)
E-7	2.04	40	2.34	0.85	1.49	1.35
E-8	2.06	80	32.00	18.30	13.70	1.10
E-9	1.87	100	52.22	34.34	17.88	5.50

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