

## THE PRUITT-BAGGETT CATALYST IN THE STEREOREGULAR POLYMERIZATION OF PROPYLENE OXIDE

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### ABSTRACT

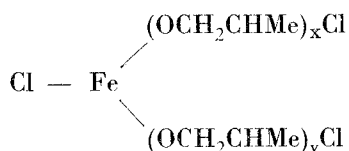
The Pruitt-Baggett adduct (PBA) ( $MW = 438 \text{ g mol}^{-3}$ ) which formed from the reaction of  $\text{FeCl}_3$  with propylene oxide (PO) was hydrolysed in diethylether (ether) solution at different  $r = \text{H}_2\text{O}/\text{Fe}$  mol ratios. The hydrolysates (PBH/r) which were insoluble in ether could be converted into catalytically active form (PBC/r) by a thermal treatment (baking). PBC/r ( $r < 1$ ) was soluble in ether and in PO. PBC/r polymerized PO into a mixture of crystalline polymer and non-crystallizable oily polymer. It was found that the catalytic activity of PBC/r could be varied by changing the hydrolysis conditions and the baking time.

### ÖZET

Propilen oksitin (PO)  $\text{FeCl}_3$ 'le reaksiyonundan meydana gelen Pruitt Baggett ürünü (PBA) ( $MW = 438 \text{ g mol}^{-1}$ ) eter çözeltisinde farklı  $r = \text{H}_2\text{O}/\text{Fe}$  mol oranlarında hidrolizlendi. Eterde çözünmeyen hidroliz ürünleri (PBH/r) termal işlemlerle (fırnlama) katalitikçe aktif hale (PBC/r) dönüştürüldü. PBC/r ( $r < 1$ ) eter ve PO de çözüldü. PBC/r, propilen oksiti kristal polimer ve amorf yağmsı polimer karışımı oluşturarak polimerleştirdi. Hidroliz koşullarının ve fırnlama süresinin değiştirilmesiyle PBC/r'nin katalitik etkinliğinin değiştirilebildiği bulundu.

### INTRODUCTION

Propylene oxide can be polymerized by  $\text{FeCl}_3$  to give products of high molecular weight which are partially crystalline. The reaction has two clearly defined stages (Price and Osgan, 1956). The first stage occurs rapidly at room temperature yielding and adduct of PO with  $\text{FeCl}_3$ . The empirical formula of the Pruitt-Baggett adduct (PBA) has been identified (Borkovec 1959, Corclough et al. 1959) as:



where  $x + y \sim 5$ . In the following stage which took place at elevated temperatures (80–100 °C) PBA polymerized PO into 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 (Borkovec 1959, Gee et al. 1962). The catalytic activity of PBA in the absence of water and variation of the crystalline yield with the  $\text{H}_2\text{O}/\text{PBA}$  molar ratio (Colclough et al. 1959, Gee et al. 1962); solubilities of PBA and  $\text{PBC}/r$  in the polymerization medium (Borkovec 1959, Colecogh et al. 1959); the kinetic order of the polymerization reaction (Colclough et al. 1959, Gee et al. 1962); and the chemical identity of  $\text{PBC}/r$  have not been satisfactorily examined. PBA has been converted into catalytically active forms ( $\text{PBC}/r$ ) by the addition of water in molar quantities (Colclough et al. 1959, Çolak and Alyürük 1989) prior to a thermal treatment (Çolak and Alyürük 1989). The catalytic activity of  $\text{PBC}/r$  can be varied substantially by changing  $r$ . Thus  $\text{PBC}/0.67$  was reported as the catalytically most active form (Çolak and Alyürük 1989).  $\text{PCB}/r$  was found to be soluble in PO in the range of  $0 < r < 1$ .

In this communication we would like to report our experimental data and related conclusions on the variation of catalytic activity by changing the conditions of hydrolysis reaction and pre-heating of the catalysts.

## EXPERIMENTAL

### Materials

Purification of reagents and solvents and the general procedure adopted in handling them under high vacuum have been already described (Çolak and Alyürük 1989).

FBA, was synthesized from sublimed  $\text{FeCl}_3$  and PO by rigorous exclusion of adventitious water (Çolak and Alyürük 1989). 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.

## 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 then sealed and placed into a thermostated bath. The hydrolysis of PBA in the ampoule was allowed to take place at 40 °C and 100 °C for different time intervals. 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 the baking time intervals 0.5 h, 3.0 h, 10.0 h, 90.0 h and at the temperatures varying from 80 °C to 120 °C for a prolonged baking time. The baked hydrolysate PBC, readily dissolved in PO, provided that the hydrolysis ratio  $r = \text{H}_2\text{O}/\text{Fe}$  was kept smaller than unity.

## Polymerizations

PO was polymerized by mixing with PBC/ $r$ , under high vacuum conditions at 80 °C. The reactions were terminated by adding a mixture of methanol and benzene and the solution washed with 2M HCl, filtered. Antioxidant (diphenylamine) in the amount of 1 % of the polymer mass was added and the samples were then freeze-dried (Alyürük et al. 1986).

The products could be fractionated into high molecular weight crystalline (K-polymers) and low molecular weight non-crystallizable oily polymers (D-polymeres) by thermal precipitation from dilute isooctane solution (Alyürük et al. 1986). Both K- and D- polymers were dissolved in benzene, filtered, stabilized with antioxidant and freeze-dried.

Viscosity average molecular weights were calculated from the intrinsic viscosities measured in toluene at 25 °C using the following relation (Allen et al. 1964).

$$[\eta(\text{dl/g})] = 1.29 \times 10^{-4} \bar{M}_v^{0.75}$$

## RESULTS AND DISCUSSION

In order to investigate the effect of the hydrolysis condition on the catalytic activity of PBC/ $r$  the hydrolysis was performed as described in the experimental part but the hydrolysis time and the hydrolysis temperature were varied. In the previous reports, the hydrolysis time and the hydrolysis temperature were studied up to 2 days and 40 °C; respectively and it was found that the catalytic activity of PBC/ $r$  was

maximum for 2 days at 40 °C. In the present study the effect of the prolonged hydrolysis time on the catalytic activity of PBC/r was examined and it was observed that at the prolonged hydrolysis time (i.e. 30 days) the catalytic activity of the catalyst and hence the per cent polymer yield,  $P_T$  slightly decreased (Table-1). In order to check this trend we performed two experiments in which PBA was hydrolysed at 100 °C for one month time. It was observed that under this rigorous hydrolysis conditions catalytic activity of the catalyst nearly vanished and this effect was seen on  $P_T$ ,  $P_K$ ,  $P_D$  (where  $P_K$  and  $P_D$  are the per cent monomer which gave K- and D- polymer; respectively) (Table-2). In this table the results of these experiments were compared with the activity of PBC/r which was prepared by the hydrolysis of PBA under milder conditions (i.e. 2 days at 40 °C). These results may be attributed to the decomposition of the catalyst under rigorous hydrolysis conditions.

Table 1. The effect of hydrolysis time on the polymerization.

Exp. No.	Hydrolysis		Polymerization Time(h)	$P_T$
	T(°C)	Time(day)		
4	40	2	24	36.7
5	40	9	24	35.6
6	40	30	24	24.6
7	40	30	24	26.5

Table 2. The variation of catalytic activity of PBC/r under mild and rigorous hydrolysis conditions.

Exp. No.	Hydrolysis		Polymerization Time(h)	$P_T$	$P_K$	$P_D$	$P_K/P_D$
	Time(day)	T(°C)					
1	2	40	48	62.8	41.9	20.9	2.0
2	30	100	48	6.0	3.8	2.2	1.7
3	30	100	24	Trace	—	—	—

Polymerization temp.=80°C;  $m_{Fe} = 2.4 \times 10^{-3}$  mol Fe/kg PO;  $r = 0.67$ .

It was observed that PBC/r was soluble in etheric solvents, pyridine and these solutions, in contrast to PBA and PBH/r were electric conductors (Aksoy et al. 1990). The electrical conductivity of PBC/r changed as the baking time increased (Aksoy et al. 1990). It was concluded that in the baking process; possibly through a condensation between Fe—OH and Fe—Cl groups; Fe—O—Fe bonds are formed (Aksoy et al. 1990). 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 propylene oxide (Zn—O—Zn (Sakata et al. 1960), Al—O—Al (Ueyama et al. 1973). In order to test any effect of baking (which is applied to hydrolysed PBA before polymerization process) conditions on the catalytic activity of PBC/0.67 a series of PBC/0.67 were prepared under prolonged baking times at high temperatures. The catalytic activities of these catalysts were almost same, in experimental error range (Table-3). We conclude that, PBC/0.67 once formed is quite stable under rigorous baking conditions.

Table 3. The effect of baking time on the polymerization.

Exp.No	Baking time (h)	Baking temperature (°C)	P <sub>T</sub>	P <sub>K</sub>	P <sub>D</sub>	P <sub>K</sub> /P <sub>D</sub>	$\bar{M}_v$ (K-polymer)
8	0.5	80	11.6	—	—	—	—
9	3.0	80	19.0	—	—	—	—
10	10.0	80	15.4	11.5	3.9	3.0	8.3x10 <sup>3</sup>
11	90.0	80	14.7	11.3	3.4	3.3	9.1x10 <sup>3</sup>
12	95.0	80-120	14.8	11.4	3.4	3.4	1.1x10 <sup>3</sup>

Polymerization temp. = 80°C; polymerization time 24 h;  $m_{Fe} = 1.1 \times 10^{-3}$  mol Fe/kg PO;  $r = 0.67$ .

In a sampling experiment, samples were drawn at certain time intervals from a polymerization mixture to find out the variation of the per cent yield with time. The per cent conversion of monomer into total polymer and into K-polymer showed an acceleration period (Alyürük et al. 1989) at the initial stages of polymerization. D-polymer was the major product formed in the acceleration period, but it was the minor product in the later stages of polymerization since K-polymer was produced at faster rates. The molecular weight of K-polymer increased as the polymerization time increased (Table-4). These results are consistent with those of Alyürük et al (Alyürük et al. 1989).

Table 4. The effect of polymerization time on the polymer yield.

Exp. No.	Polymerization time (h)	P <sub>T</sub>	P <sub>K</sub>	P <sub>D</sub>	P <sub>K</sub> /P <sub>D</sub>	$\bar{M}_v$ (K-polymer)
13	0.5	0.8	0.3	0.5	0.6	—
14	1	1.1	—	—	—	—
15	3	1.9	0.5	1.4	0.4	—
16	16	9.7	4.0	5.7	0.7	2.0x10 <sup>3</sup>
17	24	38.6	22.4	16.1	1.4	2.5x10 <sup>3</sup>
18	48	61.3	43.8	17.5	2.5	3.3x10 <sup>3</sup>

Polymerization temp. = 80°C;  $m_{Fe} = 2.4 \times 10^{-3}$  mol Fe/kg PO;  $r = 0.50$

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