

# POLYMERIZATION OF BENZYL ALCOHOL IN GASEOUS PHASE ON A Y ZEOLITE

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## ABSTRACT

Polybenzyl polymers obtaining from benzyl alcohol has been studied in a gas phase reaction at atmospheric pressure, using a Y zeolite, in a fluidized bed reactor. Operating conditions to obtain a good fluidization and an isothermal bed have been determined.

It has been proved that the polymerization occurs on the catalyst active sites via Langmuir-Hinshelwood type mechanism, obtaining the following kinetic equation in the 250-310°C range:

$$r_{po} = P_A^2 \frac{K_M^3 (k'_d + k'_m) P_A + K_M^2 k'_d}{(1 + K_M P_A)^3} \left( \frac{\text{polymer g}}{\text{g cat. min}} \right)$$

## INTRODUCTION

Nowadays there is an increasing interest in obtaining polybenzyl polymers. This interest is due to their high stability at high temperature and to their good electrical properties recently found.

As long ago as 1955, Hass et al [1] determined the tendency of benzyl chloride to polymerize with Friedel-Crafts catalysts. Later [2-6], polymerization studies with different benzyl chloride type monomers have been described, in order to obtain linear structures with high molecular weights.

In spite of a great number of works have been made, the information about the structure, characteristics, properties and applications of these polymers is very short. To determine the structure, mainly the infrared spectra [6] and in some cases ultraviolet or NMR have been used. By TGA and DTA it was found that the polymer is thermally

stable up to 300-450°C and that the glass transition region is between 55 and 80°C. The average molecular weights, determined by vapor-pressure osmometry [7], are in the 1000-2500 range.

Polybenzyl polymers were synthesized by means of gas phase reaction on solid catalysts by Jodra et al [8-10] in the dehydrogenation of benzyl alcohol to benzaldehyde on Cu/asbestos catalysts in a fixed bed reactor in the 250-300°C temperature range. Since then, these polymers were synthesized trying other catalysts for the same reaction such as Cu-Cr<sub>2</sub>O<sub>3</sub>/asbestos [11,12] and Cu/SiO<sub>2</sub> [13].

The polymerization in the latest mentioned works is a secondary process by dehydration reaction which takes place in parallel with the main reaction of dehydrogenation and in which the polymer (coproduct) is the main precursor of the coke that deactivates the catalyst.

In this work a study of polybenzyls direct obtaining by benzyl alcohol polymerization has been carried out in gas phase on acidic catalyst, a Y zeolite, for the first time in bibliography. The use of acidic catalysts such as silica-alumina or zeolites in dehydrations is widely admitted [14,15].

Apart from setting up the reaction system and determining the more suitable experimental conditions for the polymerization kinetic study, in this work it has been tried to make up for the absence of methodology for the kinetic study in gas phase on solid catalysts. That was carried out basing on the methodology already developed for contact catalysis.

## EXPERIMENTAL

### Catalyst

The selection of the MZ-7P catalyst for this reaction has been based on its good behavior (as commercial cracking catalyst) in fluidized systems. This operation regime was determined to be necessary in previous experiments.

The MZ-7P catalyst was supplied by Akzo-Chemie and it has the following characteristics: zeolite containing 10%; zeolite:Y type rare-earth exchanged; chemical composition %: Al<sub>2</sub>O<sub>3</sub>:33, Na<sub>2</sub>O:0.2, Fe:0. SO<sub>4</sub><sup>2-</sup>:0.3; pore volume:0.28 cm<sup>3</sup>/g; surface area: 140 m<sup>2</sup>/g.

## Equipment and operating conditions

The reaction equipment is basically the same utilised in previous works [10-13] for dehydrogenation of benzyl alcohol. It consists of feeding and measuring system of alcohol and  $N_2$  (as inert), preheater-vaporizer of alcohol, reactor of Pyrex glass of 17 mm inside diameter that is provided with a distributor plate of porous glass and condensers to collect the products.

When trying the fixed bed regime for the catalyst, it was found that the fast deposition of polymer among particles and the exothermicity of the reaction make impossible the isothermicity of the catalytic bed. Due to that, serious problems are originated in the flow which cause the formation of preferential ways to let the reactants go through and the plugging of the reactor.

Working in fluidized bed regime, it has been determined that for particles to be well mixed the following reaction conditions have to be maintained:

Temperature: between 250 and 310°C. The lower limit is fixed to avoid the condensation of alcohol in some point of the reaction system ( $T_b=210^\circ\text{C}$ ). In the other limit, over 330°C the benzyl alcohol cracking is already significative.

Catalyst particle size: +0.15 -0.20 mm

Gas linear velocity: 40 cm/s. Although the minimum fluidizing velocity is 20 cm/s the fact that the catalyst particles size is getting increased outwardly of settled polymer forces to work with higher velocity to keep the fluidization.

Partial pressure of fed alcohol: 0.06-1 atm. At higher pressures the reactor is plugged in very short time making impossible the fluidization.

Catalyst dilution: 10% in silica gel. This way bed isothermicity is favoured and fluidization is maintained longer, in spite of catalyst particles size gets increased progressively.

Space time: 0.4 g cat/h mol.

## Experimental results

In order to calculate the length of time of the initiation step and the rate that corresponds to the end of this period, kinetic experiments of different length of time have been made under the conditions above specified. As temperature values they have been chosen: 250, 270 290 and 310°C and for each temperature the following values of partial pressure of alcohol: 0.06, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0 atm.

As the number of experiments was great the weight of polymer on catalyst was measured by combustion of the catalyst mass increased of polymer. It was not made by mechanical removal because it is too laborious for a so great number of samples.

As an example of the obtained experimental results, Figure 1 shows weight of polymer vs. length of time of experiment, for one of the studied temperatures, 250°C. Each curve corresponds to one partial pressure of benzyl alcohol at inlet.

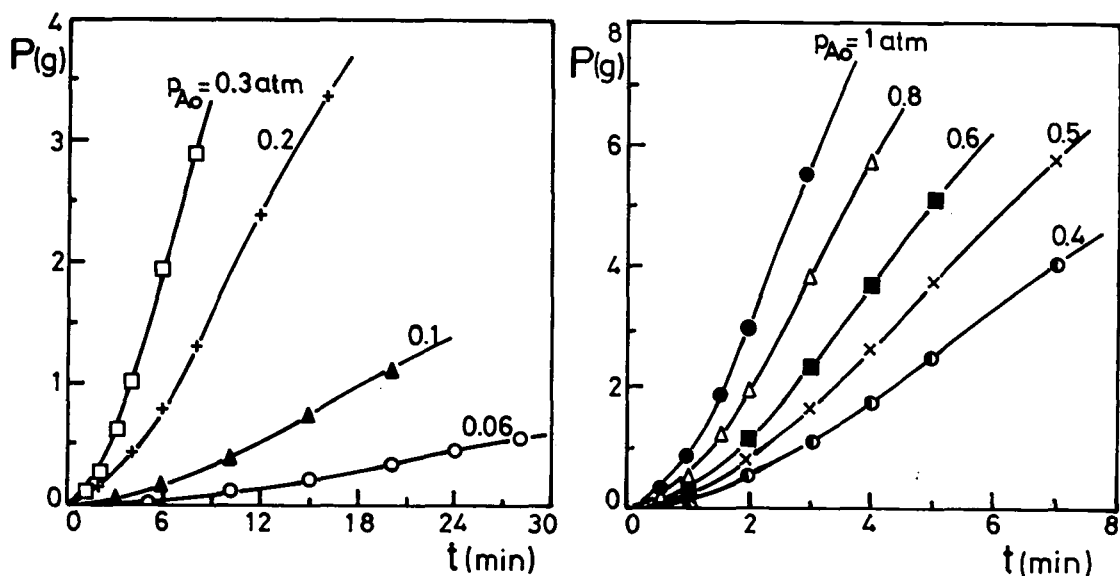
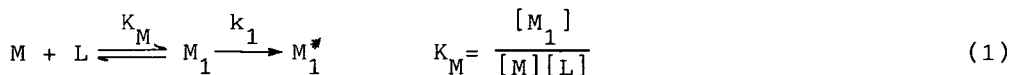


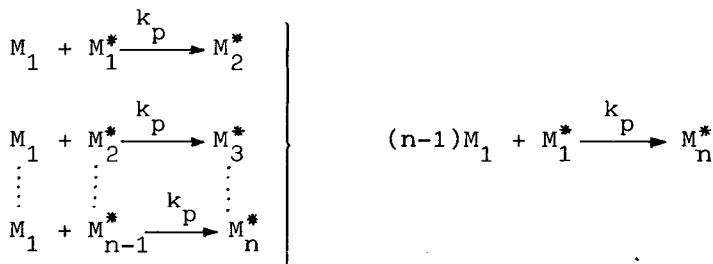
Fig. 1. Weight of deposited polymer vs. time for different partial pressure of benzyl alcohol at reactor inlet. Temperature 250°C.

A Langmuir-Hinshelwood type mechanism has been proposed which is based on Clark and Bailey's theory [16] and enlarged after by Maiti [17].

1. Adsorption and activation step (Initiation)

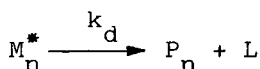


2. Reaction step (Propagation)

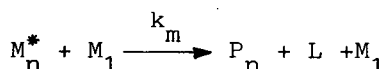


3. Desorption step (Termination)

3.1. Espontaneous desorption



3.2. Desorption by monomer



Defining the rate of polymerization as total number of monomer units in the polymer that is desorbed from unit catalyst mass per second, it will be calculated as the sum of both termination steps:

$$R = \Delta \left( \sum_{n=2}^{\infty} n [P_n] \right) / \Delta t = k_d \sum_{n=2}^{\infty} n [M_n^*] + k_m \sum_{n=2}^{\infty} n [M_n^*] [M_1] \quad (2)$$

Evaluating the summations of eqn(2) it is obtained:

$$R = [M]^2 (2k_d k_p k_1 K_M^2 [L]^2 + 2k_m k_p k_1 K_M^3 [M][L]^3) \quad (3)$$

The total concentration of active sites, [N], is:

$$[N] = \sum_{n=2}^{\infty} [M_n^*] + [M_1] + [L] = K_M [M][L] + [L] \quad (4)$$

If the expression for [L], concentration of free active sites, from eqn(4) is substituted in eqn(3) the following expression is obtained:

$$R = [M]^2 \frac{(k'_d K_M^3 + k'_m K_M^3) [M] + k'_d K_M^2}{(1 + K_M [M])^3} \quad (5)$$

where  $k'_d = 2k_d k_p k_1 [N]^2$  and  $k'_m = 2k_m k_p k_1 [N]^3$  (6)

Eqn(5) can be expressed in a way to permit a more direct evaluation from the experimental data of deposition. Expressing the concentration of monomer as partial pressure of benzyl alcohol in the gas flow:

$$r_{po} = P_A^2 \frac{K_M^3(k'_d + k'_m)P_A + K_M^2 k'_d}{(1 + K_M P_A)^3} \left( \frac{\text{g polymer}}{\text{g cat. min}} \right) \quad (7)$$

In order to verify the validity of eqn(7) for the studied reaction system and so the proposed mechanism, values of  $r_{po}$  have been calculated from experimental data in Figure 1 for 250°C and from the corresponding values at the other temperatures, 270, 290 and 310°C. The computation of  $r_{po}$ , maximum rate of polymerization that corresponds to the end of the initiation period, needs the accurate evaluation of the length of this period,  $t_i$ .

The experimental data P vs. t have been fitted the following empirical equation:

$$P = a \ln \left( \frac{t^2 + t_i^2}{t_i^2} \right) = \left( \frac{dP}{dt} \right)_{t=t_i} \cdot t_i \ln \left( \frac{t^2 + t_i^2}{t_i^2} \right) \quad (8)$$

$$\text{where } \left( \frac{dP}{dt} \right)_{t=t_i} = r_{po} W \quad (9)$$

The fitting has been carried out by non linear regression based on the Marquardt method [18]. The results of this fitting are shown in Table 1, where values of initiation time,  $t_i$ , and their corresponding polymer deposition rates,  $r_{po}$ , are related. The square regression coefficient ( $r^2$ ) is 0.96 in the worst of the cases.

The  $r_{po}$  data related in Table 1 and their corresponding values of average partial pressure between the inlet and the outlet of the reactor have been fitted the eqn(7). The values of the kinetic constants,  $k'_m$ ,  $k'_d$  and  $K_M$  evaluated in this way at the different temperatures of reaction have been related in Table 2. The square regression coefficient is 0.97 in the worst of the fittings.

Figure 2 shows the temperature dependency of the kinetic constants in Table 2 by the Arrhenius plot. The following relationships are obtained from fitting these kinetic constants:

$$k'_m = 4.06 \cdot 10^6 \exp\left(\frac{-11000 \pm 1000}{T}\right); k'_d = 1.08 \cdot 10^8 \exp\left(\frac{-12000 \pm 1000}{T}\right) \quad (10)$$

$$K_M = 1.39 \cdot 10^{-9} \exp\left(\frac{11900 \pm 900}{T}\right)$$

Table 1

Calculated values of  $t_i$  (min) and their corresponding polymer deposition rates,  $r_{po}$  (g polymer/g cat. min).  $P_{Ao}$  (atm): At reactor inlet.

T	$P_{Ao}$	0.06	0.10	0.20	0.30	0.40	0.50	0.60	0.80	1.00
250°C	$t_i$	23.4	16.2	9.5	7.0	5.6	4.7	4.0	3.3	2.6
	$r_{po}$	0.16	0.28	0.49	0.63	0.71	0.77	0.82	0.89	0.94
270	$t_i$	29.8	18.2	9.2	6.4	4.9	3.9	3.2	2.6	2.1
	$r_{po}$	0.11	0.23	0.54	0.78	0.98	1.13	1.28	1.48	1.61
290	$t_i$	40.4	22.7	10.4	6.7	4.9	3.9	3.1	2.4	1.8
	$r_{po}$	0.06	0.15	0.44	0.74	0.99	1.21	1.42	1.79	2.09
310	$t_i$	61.7	30.0	12.4	7.9	5.6	4.2	3.4	2.5	1.8
	$r_{po}$	0.03	0.09	0.32	0.55	0.80	1.04	1.28	1.73	2.13

Table 2

Computed values of the kinetic constants

	250°C	270	290	310
$k'_m$	$2.91 \cdot 10^{-3}$	$6.33 \cdot 10^{-3}$	$1.30 \cdot 10^{-2}$	$2.54 \cdot 10^{-2}$
$k'_d$	1.16	2.70	5.93	12.3
$K_M$	9.79	4.25	1.95	0.949

Substituting these values in eqn(7) the kinetic equation for the temperature range between 250 and 310°C is now:

$$r_{po} = P_A^2 \left\{ \frac{[1.39 \cdot 10^{-9} \exp(\frac{11900}{T})]^3 [4.06 \cdot 10^6 \exp(\frac{-11000}{T}) + 1.08 \cdot 10^8 \exp(\frac{-12000}{T})]}{[1 + 1.39 \cdot 10^{-9} \exp(\frac{11900}{T}) P_A]^3} + \frac{[1.39 \cdot 10^{-9} \exp(\frac{11900}{T})]^2 [1.08 \cdot 10^8 \exp(\frac{-12000}{T})]}{[1 + 1.39 \cdot 10^{-9} \exp(\frac{11900}{T}) P_A]^3} \right\} \quad (11)$$

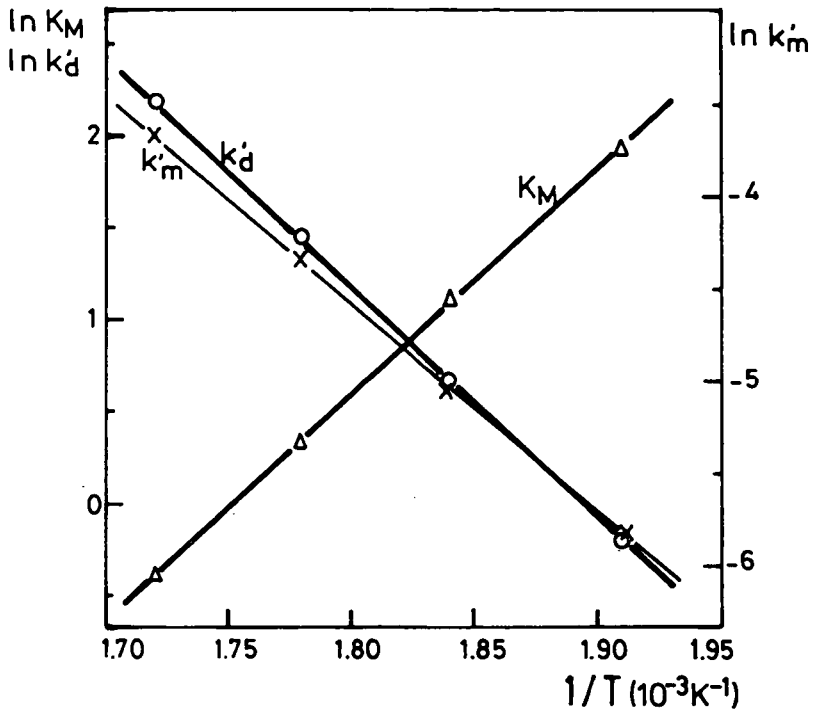


Fig. 2. Temperature dependency of the kinetic constants in eqn(7).

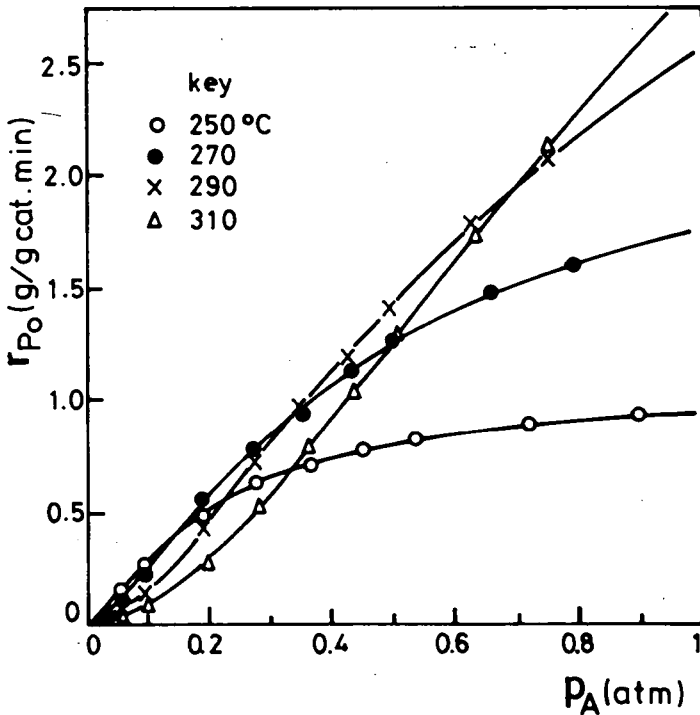


Fig. 3. Kinetic equation checking. Solid lines; computed by eqn(11). Points: experimental.



In Figure 3 is plotted  $r_{po}$  vs.  $P_A$ . In this Figure curves correspond to the values computed with eqn(11) and points are the experimental data related in Table 1. It can be noticed the fitting goodness in all the studied conditions.

It is remarkable the complexity of the  $r_{po}$  vs.  $P_A$  curves shape in Figure 3, where curves corresponding to different temperatures cross each other so that the higher reaction rate correspond to a higher temperature as the partial pressure of benzyl alcohol fed to reactor is increased. On the other hand, reaction rate is sensitive to temperature specially at high temperatures.

## CONCLUSIONS

It has been determined that this zeolite has a high activity to obtain polybenzyls from benzyl alcohol polymerization in gas phase. Polymer production turned out to be so high by this way that it does not admit comparison with any other obtaining process described up to now in bibliography.

The suitable operating conditions for a MZ-7P zeolite catalyst have been determined in a fluidized bed reactor in order to get an isothermal bed and a good fluidization. In this conditions the polymerization kinetics at zero time follows the eqn(11) for the temperature range 250-310°C and partial pressure of benzyl alcohol at inlet reactor lower than 1 atm. This shows that the polymerization in gas phase on the acidic sites of this zeolite occurs via Langmuir-Hinshelwood type mechanism.

After the initiation period, the curves polymer vs. time in Figure 1 and the homonyms at the other temperatures show a fall in their slopes (rate of polymerization), which can be attributed to the catalyst deactivation. This deactivation can be due to the degradation of polymers in the porous structure towards irreversibly adsorbed species on the acidic sites of the MZ-7P catalyst. It has been proved that the deactivated zeolite can be regenerated by combustion of the carbonaceous material with air, recovering its initial activity and also its physical properties and surface acidity.

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