

# Reactivity of some polymer-supported titanium catalysts in transesterification and epoxidation reactions

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## Abstract

Poly(*p*-hydroxystyrene) resins with different crosslink levels have been prepared by suspension polymerization. Their surface area (SA) and pore size distribution (PSD) were determined by the nitrogen adsorption technique. Ti(OiPr)<sub>4</sub> has been grafted on these supports, and the resulting heterogeneous catalysts were used to promote the transesterification of methyl methacrylate (MMA) with 2-ethylhexanol and the epoxidation of various alkenes with tBuOOH. The stability upon recycling of these polymer-supported titanium catalysts has been assessed. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Polymer-supported titanate; Poly(*p*-hydroxystyrene) resins; Transesterification; Epoxidation

## 1. Introduction

Among the numerous advantages provided by solid phase chemistry [1], site isolation via immobilization of active species on a rigid network, can be of a particular value for compounds forming inactive oligomers in solution [2a,b].

Early work by Bonds et al. [3] clearly shows the benefits of grafting titanocene residues on macroporous resin beads. The heterogeneous catalyst thus obtained was 25–100 times more active than the corresponding soluble analogue in the hydrogenation of 1-hexene. The activity of the catalyst proved to increase with decreas-

ing titanocene loading as a result of a better site isolation [4].

Another means of preventing site–site interactions is to reduce the chain mobility of the resin polymer by increasing the extent of crosslinking [5a,b]. This effect was observed by Hodge and Khoshdel in the Wittig reaction with polymer-supported phosphine [6]. However, increasing the degree of crosslinking can also have a detrimental effect on the diffusion of reagents towards the active centres in the polymer matrix [7].

In a previous paper [8], we reported the synthesis and use of a polymer titanate in the transesterification of methyl methacrylate (MMA) with 2-ethyl hexanol and ethyl butyrate with 1-dodecanol. The moderate activity of the

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catalyst and the low Cl/Ti ratio obtained for the grafted titanium chloride onto the same poly(*p*-hydroxystyrene) resins suggested some limitation in site isolation of the titanates residues.

With this in mind, we decided to immobilize an alkoxy titanate,  $\text{Ti}(\text{OiPr})_4$ , on resins with increasing levels of crosslinking and to assess their activity in two probing reactions: (i) the transesterification of MMA with 2-ethylhexanol; and (ii) the epoxidation of cyclohexene with tBuOOH.

## 2. Experimental

### 2.1. Material

All the monomers (styrene (S), divinylbenzene (DVB), *p*-acetoxystyrene (AS)) and other components involved in the polymerisation (azobisisobutyronitrile (AIBN), 2-ethylhexanol, suspension stabilisers) were used as received.

Tetraisopropoxy titanium (Aldrich), cyclohexene (Aldrich) were also used without further purification.

2-Ethylhexanol and MMA were distilled under reduced pressure from  $\text{CaH}_2$ . All solvents were dried according to published procedures.

### 2.2. Synthesis of macroporous poly(4-acetoxystyrene-co-styrene-co-divinylbenzene) beads (ACP)

The suspension polymerization was performed in a parallel-sided glass reactor already described [8]. The organic phase was composed of the comonomers (15 ml), AIBN (1.31 g) as the initiator and 2-ethylhexanol (15 ml) as the porogen. The mixture was suspended in water (240 ml) containing a suspension stabiliser (a mixture of gelatin and poly(diallyldimethylammonium chloride), high molecular weight). The polymerization was performed at 80°C for 8 h after which the resulting spherical particles were

washed with water, ethanol, acetone and dried under vacuum.

### 2.3. Conversion of ACP to poly(4-hydroxystyrene-co-styrene-co-divinylbenzene) beads (HP)

Polymeric particles with a diameter between 200 and 500  $\mu\text{m}$  were hydrolysed. In a typical experiment, the resin beads (10 g) were suspended in dioxane (200 ml), hydrazine hydrate (40 ml) was then added and the reaction medium mechanically stirred for 2 days at 80°C. Then, aqueous HCl was added and the beads were washed successively with water, ethanol, acetone and vacuum dried.

### 2.4. Synthesis of catalyst TiHP1

The white opaque resin **HP1** ( $100 < d < 500 \mu\text{m}$ , 2 g, 3.3 mmol of phenoxy groups) was suspended in chloroform (50 ml) in a round-bottomed flask under nitrogen.  $\text{Ti}(\text{OiPr})_4$  (0.94 g, 3.3 mmol) was injected and the reaction mixture was mechanically stirred for 2 days at room temperature after which the resulting orange beads were continuously extracted for 2 days with chloroform using a Soxhlet apparatus. Finally, resin **TiHP1** was dried under vacuum (titanium content: 1.13 mmol/g).

### 2.5. Transesterification of MMA with 2-ethylhexanol

In a typical procedure, resin **TiHP1** (0.5 g, 0.567 mmol of Ti) was suspended in a 50-ml three necked round-bottomed flask containing 2-ethylhexanol (7.32 g, 56.2 mmol), MMA (22.53 g, 225 mmol), diphenyl picryl hydrazyl hydrate (0.05 g, 0.1 mmol) as polymerization inhibitor and tridecane (2 g, 10.8 mmol) as internal standard for GC analysis. The suspension was frozen and degassed three times before being heated at 115°C under argon.

The initial rate constants have been calculated assuming that the rate law of the reaction follows the equation [8]:  $r = k[2\text{-EH}][\text{MMA}][\text{CAT}]$ .

### 2.6. Epoxidation of cyclohexene with *t*-butylhydroperoxide (*t*BHP)

Resin **TiHP1** (0.1066 g, 0.12 mmol), cyclohexene (12.17 g, 148 mmol) and dichlorobenzene (1.31 g, 8.9 mmol) as internal standard were suspended in a 50-ml three-necked round-bottomed flask. The reaction mixture was frozen and deoxygenated three times and then flowed under argon before being heated at 60°C. *t*BHP (4.1 ml of a 2.5 M solution in toluene) was then injected to start the reaction.

In these two reactions, samples were picked up at regular intervals and the products analyzed by GC using routine standardisation and evaluation procedures. After 24 h, the reactions were stopped, the resins were filtered off, washed with dichloromethane (100 ml) and dried under vacuum for further use.

### 2.7. Porosity analysis

The surface area (SA) of the samples was analysed by the nitrogen adsorption BET technique [9]. A Micromeritics Accusorb 1100 E apparatus was employed. Computer calculations were made using the Micromeritics 2100 SA programme. The pore size distribution (PSD) was determined using the BJH model assuming a cylindrical pore geometry [10].

Before each experiment, the samples were degassed at 100°C under 2 μm of Hg for 24 h.

### 2.8. Swellability of beads

The swelling capacities of the beads were obtained as follows: about 5 g of dry spherical beads (range size 200–500 μm) were accurately weighed into a graduated cylinder (i.d. 50 mm). The apparent volume of the dry material was measured ( $V_d$ ). Solvent was added to the tube with gentle shaking to remove all entrapped air. The beads were then allowed to swell without entrapping gas bubbles at room temperature for 48 h and the apparent swollen volume measured ( $V_s$ ). The swelling ratio was calculated according to [11]:

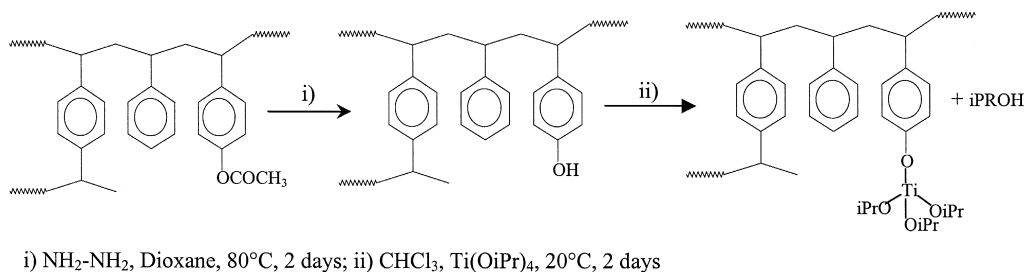
$$S(\%) = \frac{(V_s - V_d)}{V_d} \times 100$$

where  $V_s$  (ml) is the volume of swollen beads and  $V_d$  (ml) is the volume of dry beads.

## 3. Results and discussion

### 3.1. Preparation and porous properties of the polymer supports

Porous poly(4-hydroxystyrene-co-styrene-co-divinylbenzene) **ACP** resins were prepared using a two-step procedure [8] (Scheme 1). The crosslinking ratio of these supports was gradually increased by varying the DVB content in the monomer feed while the amount of acetoxystyrene introduced was kept at 20 mol%.



Scheme 1. Preparation of a macroporous polymer-supported alkoxy titanate.

2-Ethylhexanol was used as a precipitating porogen to form a macroporous structure, hence, providing a good accessibility to the active sites of the resins. The resulting polymer beads were hydrolysed to give macroporous poly(4-hydroxystyrene-co-divinylbenzene) **HP** supports of different porosities.

The specific SA of each sample was determined by the N<sub>2</sub> BET technique and ranges from 50 to 500 m<sup>2</sup>/g. The results are summarised in Table 1. For supports **HP1** and **HP2** (DVB ≤ 50 mol%), the SA decreases after hydrolysis of the acetoxyl moieties. This result indicates a partial collapse of the porous structure of these polymers during this process. As the DVB content increases, the rigidity of the support is enhanced and no decrease in the SA of the sample **HP3** (DVB = 80 mol%) is observed after hydrolysis.

Macroporous resins display three levels of porosity [10] consisting of micropores (5–15 nm), mesopores (20–50 nm) and macropores (> 50 nm). The small-size pores are determined at early steps of the polymerization. These pores are responsible for large SAs. When the amount of DVB is increased, the nuclei are less fused. This effect is confirmed by the pore size distribution of the resins **HP1**, **HP2** and **HP3** described in Fig. 1: The proportion of pores with a radius of 5 nm increases with the crosslinking of the support. This phenomenon accounts for the higher SA of the resin **HP3** compared to the resins **HP1** and **HP2**.

These three resins display a type II isotherm [12] (Fig. 2) although a small, high-pressure hysteresis loop is observed in each case. Therefore, some capillary condensation takes place in

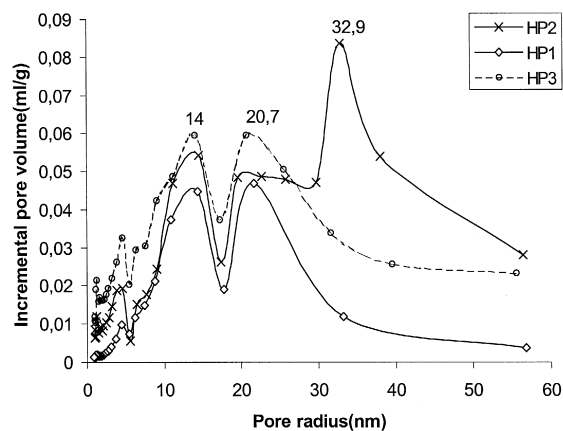


Fig. 1. Pore size distribution by the BJH method.

the supports, which is characteristic of the presence of mesopores. Furthermore, a small, low-pressure hysteresis is found in each isotherm, which has been associated with the swelling of a non-rigid porous structure [13]. This is in agreement with the capacity of these polymer supports to swell in suitable solvents.

The compatibility between the network of the polymer-supported catalyst and the medium used in the performed reaction (i.e. the solvent) is an important parameter for the efficiency of the catalysis even when using macroporous resins. The swelling behaviour of the resins in the different solvents to be used during reactions of the supported catalyst gives a good indication of this compatibility.

The swelling of our resins were studied in (i) ethyl alcohol, (ii) chloroform, the solvent used for the grafting of the titanium alkoxide onto the supports, (iii) cyclohexene, the solvent of the epoxidation experiments and (iv) a mixture of MMA and 2-ethylhexanol (70/30 v/v), corre-

Table 1  
Characteristics of macroporous poly(4-acetoxystyrene) resins

Polymer	Monomer composition (AS/S/DVB)	Resin yield (%)	Particle size distribution (μm)					SA before hydrolysis (m <sup>2</sup> /g)	SA after hydrolysis (m <sup>2</sup> /g)
			> 800	800–500	500–315	315–200	< 200		
<b>ACP1</b>	20/60/20	91%	34	13	16	15	22	106	58
<b>ACP2</b>	20/30/50	87%	30	42	25	2	1	345	300
<b>ACP3</b>	20/0/80	90%	59	34	4	2	1	500	500

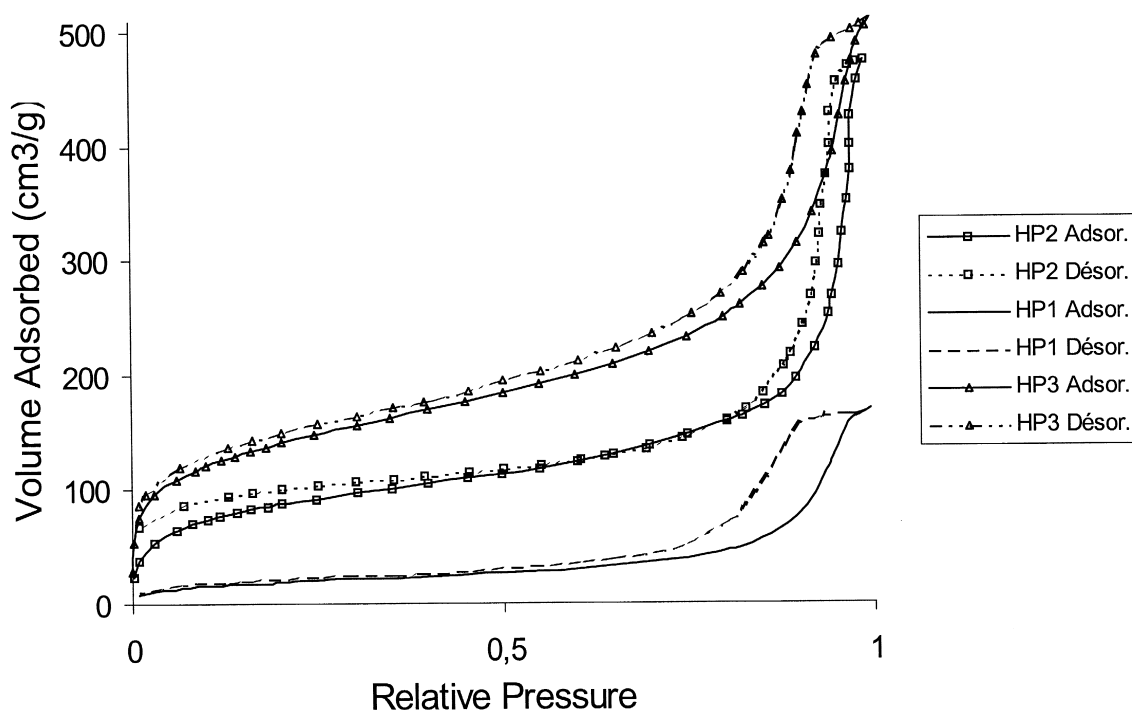


Fig. 2. Nitrogen adsorption and desorption isotherms of resins **HP1**, **HP2** and **HP3**.

sponding to the starting medium of the transesterifications reactions. The results obtained are reported in Table 2.

The swelling behaviour of the supports can be rationalized in terms of solubility parameters (Table 2): the higher the difference between the solubility parameter of the solvent and the polymer, the lower the solvating power of the solvent. A good solvent for a linear polymer will be a good swelling agent for the corresponding

crosslinked resin [14]. Therefore, the swelling of the polymer follows the solvating power of the solvent considered and decreases in the order  $\text{CHCl}_3 > (\text{MMA} + 2\text{EH}) > \text{cyclohexene} > \text{ethyl alcohol}$ .

The solubility parameter of the mixture of MMA (70 vol.%) and 2EH (30 vol.%) was calculated using the following equation [15]:

$$\delta_{\text{Mix}} = \frac{X_{2\text{EH}}V_{2\text{EH}}\delta_{2\text{EH}} + X_{\text{MMA}}V_{\text{MMA}}\delta_{\text{MMA}}}{X_{2\text{EH}}V_{2\text{EH}} + X_{\text{MMA}}V_{\text{MMA}}} \\ = 18.8 \text{ MPa}^{1/2}$$

This value is the closest to the solubility parameter of poly(styrene-co-divinylbenzene) ( $18.6 \text{ MPa}^{1/2}$ ) [16]. Nevertheless, the swelling of our supports in this mixture of solvents is lower than in chloroform. This results from the interactions between 2EH and MMA: It has already been observed that when a mixture of an alcohol and a polar solvent is used as porogen, the hydrogen bonds between the molecules of the solvents exert a strong precipitating effect [17].

Table 2  
Solubility parameters and swelling ratio of the supports

Solvent	Solubility parameter $\gamma$ ( $\text{MPa}^{1/2}$ )	Swelling ratios $S$ (%)			
		ACPI	HP1	HP2	HP3
$\text{CHCl}_3$	19	108	106	30	17
MMA (70) + 2EH (30) <sup>a</sup>	18.8	–	60	31	15
Cyclohexene <sup>b</sup>	15.2	52	40	22	13
EtOH	26	38	52	18	17

<sup>a</sup>Mixture of MMA (70 vol.%) ( $\gamma = 18 \text{ MPa}^{1/2}$ ) and 2-ethylhexanol (30 vol.%) ( $\gamma = 19.4 \text{ MPa}^{1/2}$ ).

<sup>b</sup>Obtained by Small's method [10].

Table 3

Functionalisation of the poly(4-hydroxystyrene-co-DVB) supports with titanates groups

Starting resin	Theoretical phenol loading <sup>a</sup> (mmol/g)	Grafted support	Theoretical loading Ti (mmol/g) <sup>b</sup>	Measured loading Ti (mmol/g) <sup>c</sup>	Degree of grafting (%)
<b>HP1</b>	1.8	<b>TiHP1</b>	1.3	1.1	85
<b>HP2</b>	1.7	<b>TiHP2</b>	1.2	0.9	75
<b>HP3</b>	1.6	<b>TiHP3</b>	1.2	0.9	75

<sup>a</sup>Estimated from comonomer feed ratios.<sup>b</sup>Estimated from theoretical phenol loading.<sup>c</sup>Estimated from Ti analysis.

Therefore, a mixture of MMA and 2EH can be expected to be a “poorer” solvent compared to chloroform on the account of the hydrogen bonds between the molecules of the solvent mixture.

The swellability of resin **ACP1** in ethanol increases after hydrolysis of the supported acetoxy groups. This effect can be explained by the polarity of the hydroxyl moiety, which results in a better compatibility of the resin **HP1** with ethyl alcohol.

Increasing the DVB content in the monomer feed results in a reduced mobility of the polymer chains in the resin network. Therefore, for high DVB resins content (resin **HP3**), the swelling capacity of the resin looks independent upon the solvating power of the solvent.

### 3.2. Functionalisation of *HP* supports

These resins were functionalized with  $\text{Ti}(\text{OiPr})_4$  by an alkoxy exchange reaction with the phenoxy groups of the supports (Scheme 1).

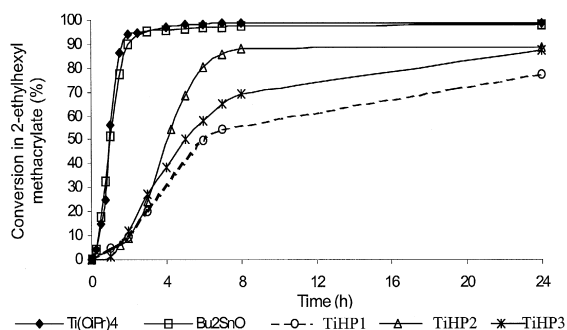


Fig. 3. Transesterification of MMA with 2-ethylhexanol.

Chloroform was used as solvent to allow a good swelling of the polymer matrix and a good accessibility to the phenol moieties of the resins. The results obtained are reported in Table 3. This method enabled good loadings of the catalyst to be obtained. The decrease in the titanium content from **HP1** to **HP2** and **HP3** resins may be attributed to the lower swelling capacity of the supports with high DVB contents.

### 3.3. Reactivity in the transesterification of MMA with 2-ethylhexanol

The synthesis of high boiling point methacrylic esters, a reaction of industrial interest, can be catalyzed by Bronsted or Lewis acids and bases [18]. The most commonly used catalyst is dibutyltin oxide [18]. In a previous paper [8], we reported the use of a polymer-supported chloro-alkoxy titanate to catalyze the transesterification of MMA with 2-ethylhexanol. This method enables a simpler work-up and recycling of the catalyst. In the present work, we have studied the influence of crosslinking level

Table 4

Transesterification of MMA with 2-ethylhexanol: kinetic data

Catalyst	Initial rate constants ( $\times 10^5$ ) ( $\text{mol}^{-2} \text{L}^2 \text{s}^{-1}$ )
$\text{Ti}(\text{OiPr})_4$	180.7
$\text{Bu}_2\text{SnO}$	161.8
<b>TiHP1</b>	27.6
<b>TiHP2</b>	55
<b>TiHP3</b>	35.3

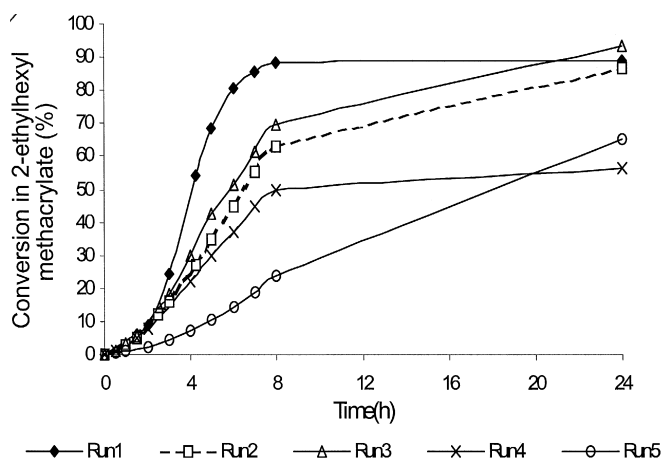


Fig. 4. Transesterification of MMA with 2-ethylhexanol: recycling of catalyst **TiHP2**.

of the polymer-supported alkoxy titanate on the catalytic activity in transesterification.

### 3.3.1. Kinetic study

Kinetic studies were performed at 115°C using a fourfold excess of MMA relative to 2-ethylhexanol and 1 mol% of Ti as catalyst. The kinetic curves for the three supported catalysts are reported in Fig. 3. All these reactions display an induction time of approximately 3 h due to the diffusion of the reagents towards the active centres in the polymer network. This induction time was the same for the three supports tested. This can be explained by considering the pore size distribution obtained from the BJH analysis of the adsorption branch of the isotherms (Fig. 1). For resins with a nominal DVB crosslinking of 20 and 80 mol%, the pore size distribution display a bimodal distribution with pore radius of 14 and 21 nm while for a DVB content of 50 mol%, the distribution dis-

plays another maximum at 33 nm. Therefore, the diffusion effect will be expected to be very similar for each sample resulting in the same induction period regardless of the crosslink ratio of the supports.

The efficiency of the catalysts studied was estimated in terms of initial rate constants and level of conversion reached after 24 h (Table 4). The activity decreases in the order  $\text{Ti}(\text{OiPr})_4 > \text{Bu}_2\text{SnO} > \text{TiHP2} > \text{TiHP3} > \text{TiHP1}$ . The higher efficiency of support **TiHP2** (crosslinked at 50 mol%) compared with **TiHP1** (crosslinked at 20 mol%), can be interpreted as an effect of the better site isolation provided by an increase in the rigidity of the polymer matrix which reduces the dimerisation of the immobilised titanium centres. However, for support **TiHP3**,

Table 5

Transesterification of MMA with 2-ethylhexanol: recycling of catalyst **TiHP2**, kinetic data

Run	Initial rate constants ( $\times 10^5$ ) ( $\text{mol}^{-2} \text{L}^2 \text{s}^{-1}$ )
1	55
2	33.6
3	22.7
4	20.7
5	7.5

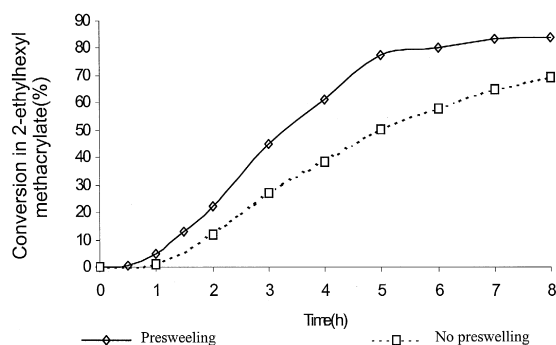


Fig. 5. Transesterification: effect of preswelling on the reactivity of **TiHP3**.

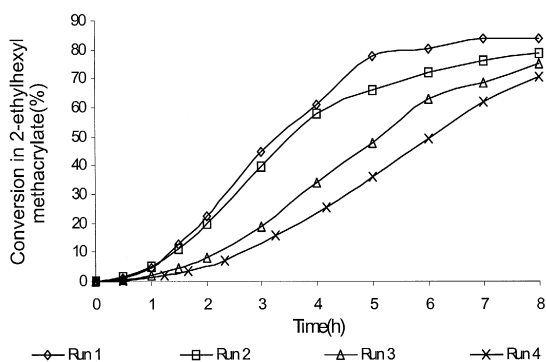


Fig. 6. Transesterification: recycling of **TiHP3**.

which is crosslinked at 80 mol%, the reaction rate is lower, which may be a consequence of the poor swelling of the polymer network in the reaction medium compared to the two other supports.

### 3.3.2. Recycling

**3.3.2.1. Recycling of TiHP2.** Catalyst **TiHP2** is the most reactive among the supported catalyst obtained, thus, it was important to check its stability in recycling. Hence, we reused the same sample of polymer several times. After each reaction, the beads were filtered, washed with chloroform and dried before reuse. The evolution of the reaction for each run are displayed in Fig. 4. The initial rate constants and the yields of the reactions after 24 h are reported in Table 5. From these results, it appears that the activity of the immobilised catalyst slowly decreases with the successive reuse. An explanation for the decrease in the catalyst efficiency could be a progressive obstruction of the pores of the support. Indeed, under the reaction conditions used (115°C, without solvent), some

polymerisation of the MMA could not be avoided even when using a rather large amount of diphenyl picryl hydrazyl hydrate as an inhibitor and a glassy polymer could be isolated after each run (about 5% of the monomer).

### 3.3.2.2. Impregnation and recycling of TiHP3.

It has previously been assumed that the rather low reactivity of the catalyst **TiHP3** was a result of the poor swelling of this highly crosslinked support in the reaction medium. To check this hypothesis, this polymer-supported catalyst was swollen in the reaction medium overnight at 0°C before uses. The suspension was then heated at 115°C to start the reaction (Fig. 5). As expected, the pre-swelling of the support in the reaction medium results in an increased activity of the catalyst. The catalyst **TiHP3** was then recycled to study its stability. The kinetic curves observed for each run are displayed in Fig. 6. The catalytic activity of **TiHP3** decreases after each reuse as for the recycling of **TiHP2**. The specific SA and the titanium content for these two catalysts were measured after the last run (Table 6). In both cases, the value of the SA of the resins drops dramatically after the recycling confirming the hypothesis of poly(methacrylate) build-up in the supports. This phenomenon can also explain the apparent decrease of the titanium content in the polymer since the mass of the catalyst increases accordingly.

### 3.4. Reactivity in the epoxidation of alkenes with *t*BuOOH

The epoxidation of alkenes is a reaction of industrial and academic interest [19]. Titanium

Table 6  
Titanium content and SA of the catalysts after recycling

Catalyst	Titanium content before recycling (mmol/g)	Titanium content after recycling (mmol/g)	SA before recycling (m <sup>2</sup> /g)	SA after recycling (m <sup>2</sup> /g)
<b>TiHP2</b>	0.9	0.55	300	57
<b>TiHP3</b>	0.9	0.6	500	74



alkoxides are rather poor catalysts for the epoxidation of a variety of alkenes with alkyl hydroperoxides [20]. The activity of these catalysts is increased by immobilisation on solid supports: numerous examples are reported in the literature concerning oxidation catalysts based on mixed oxide networks of titanium and silicon [21,22]. The main drawback of these oxide based catalysts is their small pore size which limits the access by bulky substrates [23] to the active sites of the solid. Only few examples exist in the literature, which deal with the supported titanium species resins and their use as epoxidation catalysts [24]. With this in mind, we decided to assess the catalytic activity of our crosslinked polymer-supported titanium alkoxide in the epoxidation of cyclohexene.

### 3.4.1. Epoxidation of cyclohexene

The kinetic curves for each support are reported in Fig. 7. No induction period was observed and the reactivity of the catalyst decreases with the nominal crosslinking of the support.  $\text{Ti}(\text{OiPr})_4$  is the less active catalyst and is quickly deactivated after 2 h. No by-products are observed, probably due to the lack of oxygen in the reaction medium. Indeed, when the reaction medium is not deoxygenated, up to 15% of 2-cyclohexenol is observed (based on the hydroperoxide introduced).

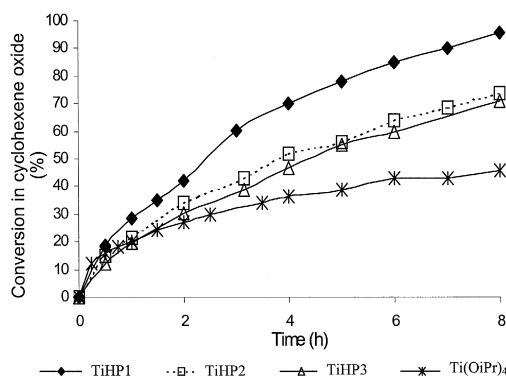


Fig. 7. Catalysed epoxidation of cyclohexene by tBuOOH.

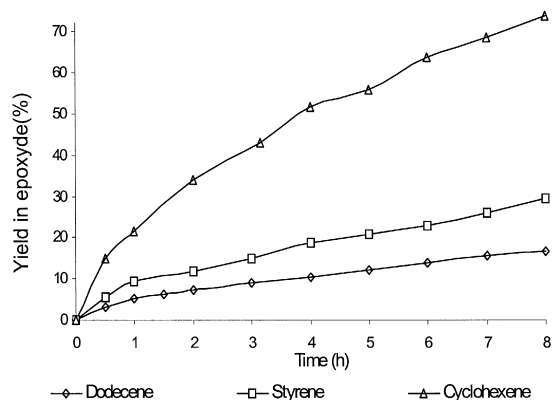


Fig. 8. Epoxidation of styrene and dodecene by tBuOOH catalysed by **TiHP2**.

### 3.4.2. Epoxidation of other alkenes

The kinetic curves of the epoxidation of styrene and dodecene are displayed in Fig. 8. The introduction of an aromatic ring decreases the electron density of the double bond which makes the epoxidation of styrene slower than the epoxidation of cyclohexene [25–28]. Dodecene is less reactive toward epoxidation due to the lower reactivity of long chain alkenes and lower compatibility between this substrate and the polymer support [29].

### 3.4.3. Recycling of **TiHP1**

The stability of the catalyst **TiHP1** was studied on the epoxidation of cyclohexene (Fig. 9). After the first run, the yield in cyclohexene oxide falls from 95% to 50% and remains constant afterwards. A similar phenomenon has been

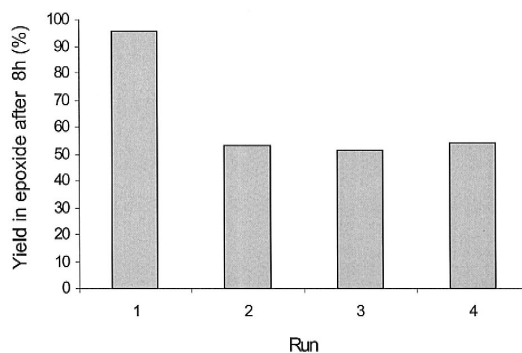
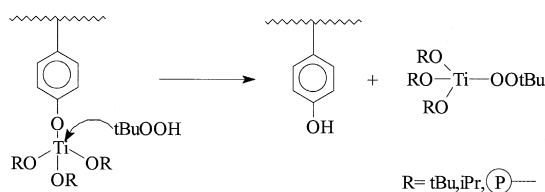


Fig. 9. Epoxidation: recycling of **TiHP1**.



Scheme 2. Proposed mechanism of titanium leaching during the epoxidation of cyclohexene.

observed by Miller and Sherrington [30] with polymer-supported molybdenum catalysts: The content of Mo-supported catalysts decreases after the first run and stays constant with a pre-activated catalyst. Nevertheless, they observed an increasing induction period after each recycling which is not the case with our catalyst. The titanium content in the polymer decreases from 1.1 to 0.8 mmol/g after the last run. Therefore, some titanium seems to be released in the reaction medium probably by an exchange reaction between tBuOOH and the support (Scheme 2).

#### 4. Conclusion

Suspension copolymerisation of *p*-acetoxy-styrene lead to porous poly(*p*-hydroxystyrene) resins after hydrolysis with different cross-linking levels. The porosity of the three supports obtained has been analysed by the N<sub>2</sub> BET technique. The SA increases with the DVB level as a result of the presence of small pores with a radius of around 5 nm. In the case of the MMA transesterification with 2-ethylhexanol, the activity of the polymer-supported titanium catalysts, obtained by grafting Ti(OiPr)<sub>4</sub>, increases with the crosslink level of the support. However, the reaction rate of the transesterification slowly decreases upon recycling due to some poly(methacrylate) build up in the pores of the resins.

These heterogeneous catalysts exhibit a higher activity than Ti(OiPr)<sub>4</sub> in the epoxidation of cyclohexene with tBuOOH. In this case, the activity of these catalysts decreases when the crosslink density of the support is increased.

Furthermore, although the yield in cyclohexene oxide is strongly decreased in the second run, the catalyst has been recycled three times afterwards without loss of activity.

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