# A new model of capsule membrane phase transfer catalysis for oxidation of benzyl chloride to benzaldehyde with hydrogen peroxide

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## Abstract

This work deals with the theoretical and experimental aspects of the capsule membrane supported phase transfer catalysed (CM-PTC) oxidation of benzyl chloride to benzaldehyde using hydrogen peroxide ($H_2O_2$) as the oxidizing agent. A new model is proposed for the CM-PTC oxidation of benzyl chloride using $H_2O_2$ wherein the nucleophile ($H_2O_2$) is transferred from the aqueous phase to the organic phase as a solvate of the catalyst which is supported on the capsule surface. This Langmuir–Hinshelwood type of model with the anchored-quaternary-$H_2O_2$ complex as the active site was found to govern the rate of reaction.

## 1. Introduction

The oxidation of benzyl chloride to benzaldehyde is a reaction of great commercial importance due to the widespread application of the latter in the perfumery, pharmaceutical, dyestuff and agrochemical industries.

Benzaldehyde is mainly produced as a co-product with benzoic acid by the oxidation of toluene and is also manufactured on a smaller scale from benzal chloride [1].

Benzaldehyde can also be prepared by the oxidation of benzyl chloride. Benzyl chloride when reacted with $4\text{-}RC_6H_4N^+Me_3HCrO_4^-$ (R = polymer) in refluxing benzene was found to give 95% yield of benzaldehyde [2]. The reaction of benzyl chloride with $K_2Cr_2O_7$ in HMPT in the presence of $PhCH_2N^+Et_3Cl^-$ is reported to lead to 100% yield of benzaldehyde [3].

The use of hydrogen peroxide ($H_2O_2$) in the oxidation of benzyl chloride merits attention. Suyama and Ishigaki [4] have claimed that when a mixture of benzyl chloride, sodium hydroxide and 60% $H_2O_2$ in $H_2O$–dioxane was stirred at 70°C for 1.3 h, 65.2% yield of benzaldehyde was obtained. While using solvents miscible with aqueous hydrogen peroxide, it is necessary to employ high concentrations of aqueous hydrogen peroxide to avoid undesirable side-reactions. For a potentially economical process a dilute hydrogen peroxide solution would be desirable.

The concept of capsule membrane supported phase transfer catalysis (CM-PTC) was introduced by Okahata et al. [5] in which a phase transfer catalyst (PTC) was grafted onto the surface of a porous nylon capsule membrane. The use

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of CM-PTC has been reported to accelerate reactions between substances in the inner organic phase and water-soluble anions in the outer aqueous phase [5]. Therefore, the capsule membrane-phase transfer catalysed oxidation of benzyl chloride to benzaldehyde using hydrogen peroxide as the oxidizing agent was found to be a virgin area necessitating further research and is covered in this work.

## 2. Experimental procedure

Large, semipermeable ultrathin nylon capsules were prepared from amines and acid chloride by interfacial polymerization by using a drop technique. A small amount of crosslinking agent (trimesoyl chloride) was added to obtain a strong and hard capsule membrane. Two ml ($2 \times 10^{-6}$ $m^3$) of an aqueous solution containing 0.8 M NaOH and a suitable amine (ethylenediamine/diethylenetriamine/triethylenetetramine = 0.38/0.6/0.75 M) was added dropwise from a syringe to a mixture of chloroform ($7.5 \times 10^{-5}$ $m^3$), cyclohexane ($2.5 \times 10^{-5}$ $m^3$), terephthaloyl chloride ($1 \times 10^{-3}$ mol) and trimesoyl chloride ($3 \times 10^{-5}$ mol). Nylon capsules having ultrathin thickness ($7.625 \times 10^{-6}$ m) and small diameter ($1.74 \times 10^{-3}$ m) were obtained [6,7].

Capsules prepared with ethylenediamine were chosen to support the following PTCs: (1) Aliquat-336 (trioctylmethylammonium chloride); (2) tetrabutylammonium bromide (TBAB) and (3) Cetyltrimethylammonium bromide (CTMAB).

The phase transfer catalysts were supported on the capsules by a method similar to that given by Yadav and co-workers [6,7].

The PTC-supported capsules were digested with benzyl chloride. The digestion time should be so chosen as to allow sufficient benzyl chloride to diffuse into the capsules.

The reactions were studied in a $5 \times 10^{-2}$ m i.d. mechanically agitated contactor of $2.0 \times 10^{-4}$ $m^3$ total capacity equipped with a 6-bladed pitched turbine impeller and reflux condenser. The aque-

ous phase containing the nucleophile (hydrogen peroxide) was added to the reactor, to which the requisite number of capsules containing benzyl chloride were added. In a typical experiment, $5 \times 10^{-5}$ $m^3$ of the outer aqueous phase was used with the appropriate concentration. The reaction was allowed to proceed to the desired time period and then the capsules were removed and broken in chloroform to expose their organic content which was analyzed by gas chromatography.

The reaction mixtures were analyzed by a Chemito 8510 gas–liquid chromatograph with a flame ionization detector (FID). A column packed with Chromosorb WHP impregnated with 10% OV-17 (4 m × 0.0032 m) was used for the analysis of reaction mixtures containing benzyl chloride and benzaldehyde. Small quantities of high boiling substances may also be formed.

## 3. Development of theoretical model

Okahata and Ariga [8] proposed a reaction mechanism for the capsule membrane supported phase transfer catalysed reaction between benzyl bromide and sodium azide. A detailed mechanistic model for CM-PTC and Inverse CM-PTC has been developed by Yadav and co-workers [6,7]. These models are applicable when the nucleophile is transferred from one phase to another in the anionic form.

The interface between the inner and outer phases would lie in the spongy layer of the capsule, wherein the phase transfer catalyst is located. It appears that the reaction occurs at the interface or in the immediate vicinity of the interface in the organic phase. In view of the very small thickness of the membrane, for all practical purposes, the surface of the capsule can be assumed to be the locale of the reaction.

### 3.1. Model for hydrogen peroxide oxidation of benzyl chloride

The role of hydrogen peroxide ($H_2O_2$) in phase transfer catalysed reactions needs to be under-
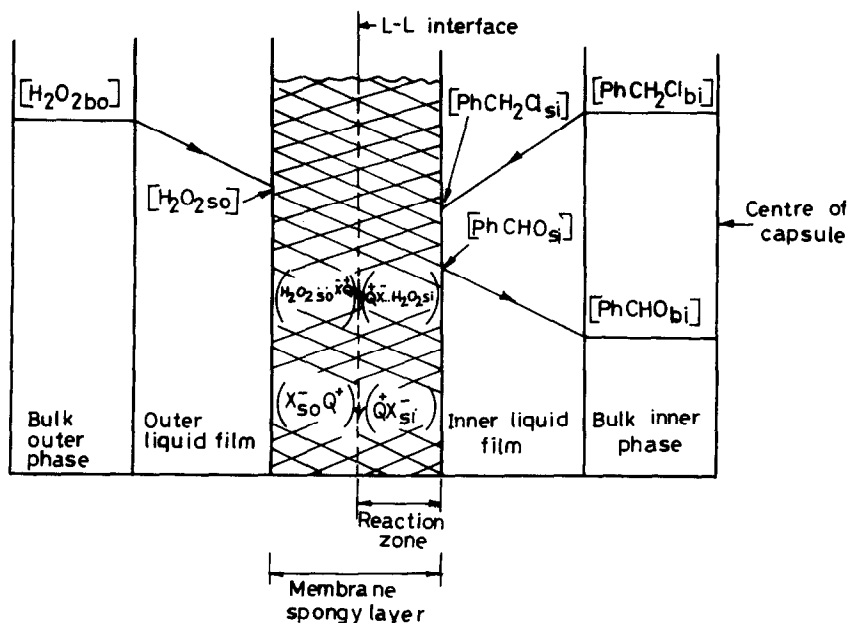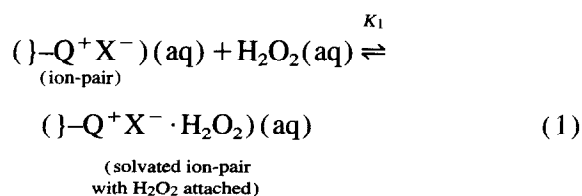
Fig. 1. Capsule membrane–phase transfer catalysed oxidation of benzyl chloride using hydrogen peroxide: concentration profiles.

stood in the context of the current work. It has been proved that $H_2O_2$ is transferred to the organic phase as a solvate of the catalyst and crystalline complexes of the type $[NR_4^+ Br^- \cdot H_2O_2]$ and $[NR_4^+ Cl^- \cdot H_2O_2]$ have been isolated [9].

The function of the quaternary compound is two-fold; namely to transfer the $H_2O_2$ to the organic phase, and to prevent its decomposition to water and oxygen.

The various steps that are thought to be involved in the phase transfer catalysed oxidation of benzyl chloride on a capsule membrane include mass transfer and surface reaction as depicted in Fig. 1 and are briefly explained below:
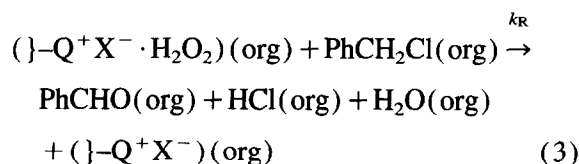
*Step 1: Pairing of the nucleophile ($H_2O_2$) with the phase transfer catalyst (i.e. quaternary ammonium salt) supported on the membrane*
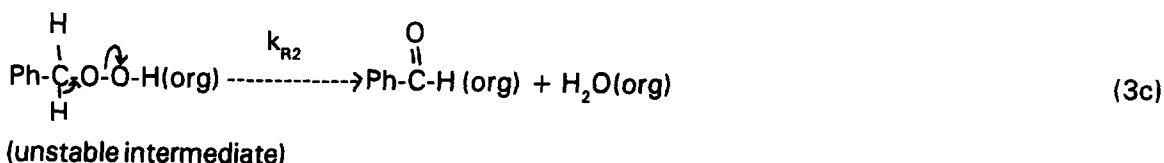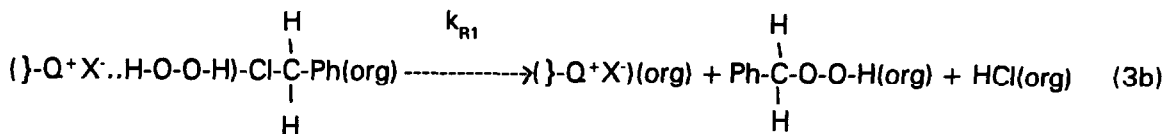
$$( \}-Q^+X^- )(aq) + H_2O_2(aq) \overset{K_1}{\rightleftharpoons}$$
$$\text{(ion-pair)}$$

$$( \}-Q^+X^- \cdot H_2O_2)(aq) \qquad (1)$$
$$\text{(solvated ion-pair}$$
$$\text{with } H_2O_2 \text{ attached)}$$

*Step 2: Transfer of the anchored nucleophile across the interface to the organic phase*

$$( \}-Q^+X^- \cdot H_2O_2)(aq) \overset{K_2}{\rightleftharpoons}$$

$$( \}-Q^+X^- \cdot H_2O_2)(org) \qquad (2)$$
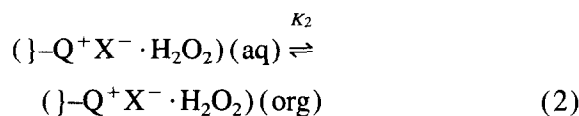
*Step 3: Reaction with the substrate (benzyl chloride) located in the organic phase but in the immediate vicinity of the interface*

$$( \}-Q^+X^- \cdot H_2O_2)(org) + PhCH_2Cl(org) \overset{k_R}{\rightarrow}$$

$$PhCHO(org) + HCl(org) + H_2O(org)$$

$$+ ( \}-Q^+X^- )(org) \qquad (3)$$

Since the CM-PTC reactions are found to be interfacial [6,7] between the anchored nucleophile and the substrate, it can be envisaged that the anchor acts as a catalytic site onto which chemisorption of the substrate (benzyl chloride) takes place similar to the Langmuir–Hinshelwood type of process. The mechanism depicted in Scheme 1 is thus proposed.

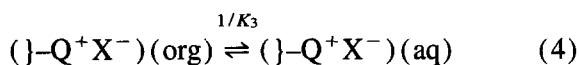$$\{\}\text{-Q}^+\text{X}^-..\text{H}_2\text{O}_2)(\text{org}) + \text{PhCH}_2\text{Cl}(\text{org}) \overset{K_A}{\rightleftharpoons\rightleftharpoons\rightleftharpoons} \{\}\text{-Q}^+\text{X}^-..\text{H-O-O-H})\text{-Cl-}\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{C}}\text{-Ph}(\text{org}) \qquad (3a)$$

$$\{\}\text{-Q}^+\text{X}^-..\text{H-O-O-H})\text{-Cl-}\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{C}}\text{-Ph}(\text{org}) \overset{k_{R1}}{\text{-------------}\!\!\!\rightarrow} \{\}\text{-Q}^+\text{X}^-)(\text{org}) + \text{Ph-}\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{C}}\text{-O-O-H}(\text{org}) + \text{HCl}(\text{org}) \qquad (3b)$$

$$\text{Ph-}\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle H}{|}}{C}}\text{O-O-H}(\text{org}) \overset{k_{R2}}{\text{-------------}\!\!\!\rightarrow} \text{Ph-}\overset{\overset{\textstyle O}{\|}}{C}\text{-H}(\text{org}) + \text{H}_2\text{O}(\text{org}) \qquad (3c)$$

(unstable intermediate)
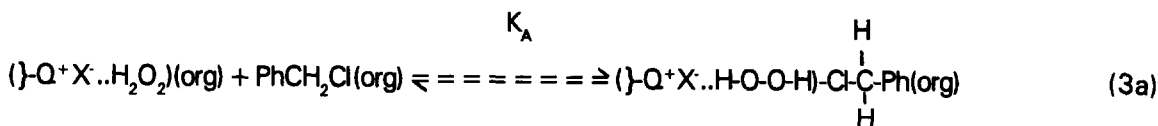
Scheme 1. Mechanism of CM-PTC.

*Step 4: Transfer of the supported phase transfer catalyst across the interface to the aqueous phase for further coupling with H₂O₂*

$$(\}\text{-Q}^+\text{X}^-)(\text{org}) \overset{1/K_3}{\rightleftharpoons} (\}\text{-Q}^+\text{X}^-)(\text{aq}) \qquad (4)$$

*Step 5: Transfer of HCl formed near the interface in the organic phase to the aqueous phase*

The oxidation of HCl to chlorine gas should occur because of the $H_2O_2$ freely available in the bulk aqueous phase. The amount of chlorine formed is negligible, due to the fact that the amount of benzyl chloride taken inside the capsules is very small.

*Step 6: Transfer of H₂O formed near the interface in the organic phase to the aqueous phase*

External as well as internal mass transfer could also affect the rate of reaction.

Step (3a) is like chemisorption and step (3b) is the surface reaction. Step (3c) occurs in the free organic phase. Step (3b) occurs on the anchor (the surface active site in the Langmuir–Hinshelwood model) and hence was initially assumed as rate determining. Further model development was made under this assumption and tested against the experimental data. This is reported in what follows:

For step (3b) as the rate determining step, the specific rate of reaction is

$$R_c = \frac{-\,\text{d}[\text{PhCH}_2\text{Cl}_{si}]}{S\,\text{d}t}$$

$$= k_{R1}\frac{K_A[\text{PhCH}_2\text{Cl}_{si}]}{1 + K_A[\text{PhCH}_2\text{Cl}_{si}]}\frac{\phi K[Q_t][\text{H}_2\text{O}_{2so}]}{1 + \phi K[\text{H}_2\text{O}_{2so}]}$$

$$(5)$$

where $S$ is the total surface area of the capsules ( $= n\pi d^2$ ). When $\phi K[\text{H}_2\text{O}_{2so}] \gg 1$ (i.e. $>50$), Eq. (5) reduces to:

$$\frac{-\,\text{d}[\text{PhCH}_2\text{Cl}_{si}]}{S\,\text{d}t} = k_{R1}\frac{K_A[\text{PhCH}_2\text{Cl}_{si}]}{1 + K_A[\text{PhCH}_2\text{Cl}_{si}]}[Q_t] \qquad (6)$$

Therefore, the rate becomes independent of the concentration of $H_2O_2$ and the phase volume ratio $\phi$. When $K_A[\text{PhCH}_2\text{Cl}_{si}] \ll 1$, Eq. (6) reduces to:

$$\frac{-\,\text{d}[\text{PhCH}_2\text{Cl}_{si}]}{S\,\text{d}t} = k_{R1}K_A[\text{PhCH}_2\text{Cl}_{si}][Q_t] \qquad (7)$$

Since $[Q_t] = $ constant, this equation is a typical first order rate equation which on integration leads to,

$$-\ln(1 - X_A) = S\,k_R[Q_t]t \quad (\text{where } k_R = k_{R1}K_A) \qquad (8)$$

Table 1
Experimental conditions

| | Reaction time s | $N_{A0} \times 10^6$ kmol | $N_{B0} \times 10^3$ kmol |
|---|---|---|---|
| Table 2 | - | 1.20 | 0.0294 |
| Fig. 2 | 1200 | 1.20 | – |
| Fig. 3 | 1200 | – | 0.0294 |

Speed of agitation 5 rps, temperature 333 K; catalyst Aliquat-336; catalyst loading $1.32 \times 10^{-6}$ kmol; $V_o = 50 \times 10^{-6}$ m³; $V_i = 0.14 \times 10^{-6}$ m³; number of capsules 100; polymer membrane EDA; $d$, diameter of the capsules, $1.74 \times 10^{-3}$ m.

Table 2
Yield of benzaldehyde using Aliquat-336 as PTC

| Serial no. | Reaction time s | Yield of benzaldehyde [a] % |
|---|---|---|
| 1 | 600 | 1.4 |
| 2 | 1200 | 2.3 |
| 3 | 1800 | 3.1 |

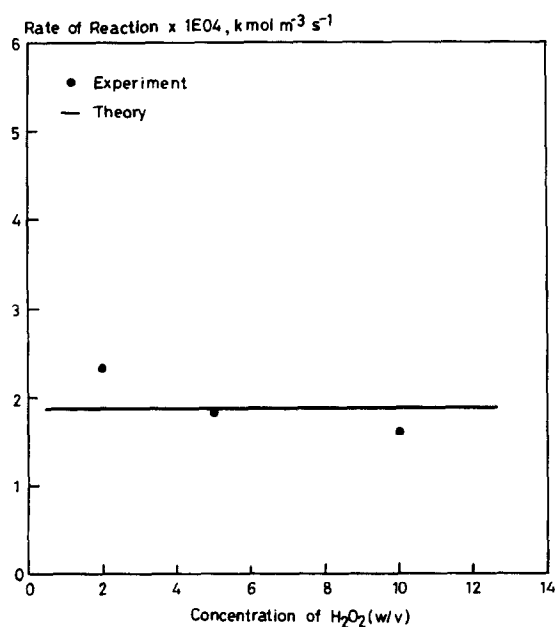[a] Based on moles of benzyl chloride initially taken.



Fig. 2. Effect of concentration of the nucleophile on the rate of reaction.

which shows typical pseudo-first order behaviour. When $K_A[\text{PhCH}_2\text{Cl}_{si}] \gg 1$, Eq. (6) reduces to:

$$\frac{-d[\text{PhCH}_2\text{Cl}_{si}]}{S\,dt} = k_{R_1}[Q_t] = \text{constant} \qquad (9)$$

Therefore, the rate of reaction becomes independent of the concentration of benzyl chloride which shows typical zero order behaviour.

## 4. Results and discussion

The experimental conditions under which the effect of various parameters was studied are listed in Table 1. The results obtained using Aliquat-336 as the phase transfer catalyst for the CM-PTC oxidation of benzyl chloride with hydrogen peroxide are given in Table 2. It was observed that breakage of capsules occurred at speeds greater than 5 rps.

The rate of reaction remains practically constant when the concentration of the nucleophile ($H_2O_2$) is increased fivefold from 2% w/v to 10% w/v (Fig. 2). Therefore, the reaction is zero order with respect to the concentration of the nucleophile. This behaviour is similar to that predicted by using the theoretical model for the case when $\phi K[\text{H}_2\text{O}_{2so}] \gg 1$ (i.e. > 50) as given by Eq. (6).

The effect of concentration of the substrate (benzyl chloride) was studied by preparing different mixtures of benzyl chloride in toluene and placing the required number of capsules in them. It is observed that the rate of reaction is directly proportional to the concentration of benzyl chloride at low values of concentration of benzyl chloride. Therefore, the reaction is first order with respect to the concentration of the substrate. At higher concentrations of the substrate, the rate of reaction is independent of the concentration of the substrate, which indicates typical zero order behaviour (Fig. 3). These experimental observations agree with the proposed theoretical model.

As the concentration of the catalyst (i.e. catalyst loading) increases the rate of reaction increases linearly, which confirms that the reaction is true PTC. This is in accordance with the theory.
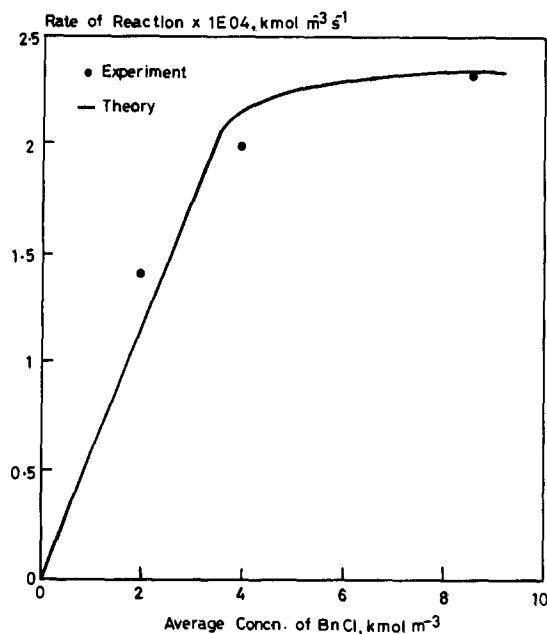
Fig. 3. Effect of concentration of the substrate. Rate of reaction vs. average concentration of benzyl chloride.

## 5. Conclusions

A complete theoretical and experimental analysis of the capsule membrane-phase transfer catalysed oxidation of benzyl chloride to benzaldehyde has been carried out. A Langmuir–Hinshelwood type of model with the anchored-quaternary-$H_2O_2$ complex as the active site was found to govern the rate of reaction.

## 6. Nomenclature

| | |
|---|---|
| $d$ | diameter of the capsule, m |
| $[H_2O_2]$ | moles of hydrogen peroxide, kmol |
| $K$ | equilibrium constant, $kmol^{-1}$ |
| $K_A$ | adsorption equilibrium constant, $kmol^{-1}$ (as in Eq. 3a) |
| $k_R$ | rate constant, $kmol^{-1} s^{-1}$ |
| $k_{R1}, k_{R2}$ | rate constants, $s^{-1}$ (as in Eqs. 3b and 3c) |
| $n$ | number of capsules |
| $N_{A0}$ | initial moles of substrate, kmol |
| $N_{B0}$ | initial moles of nucleophile, kmol |
| $[PhCH_2Cl]$ | moles of benzyl chloride, kmol |
| $[Q_t]$ | total moles of catalyst per unit surface area of the capsule, kmol $m^{-2}$ |
| $R_c$ | specific rate of reaction per capsule, $kmol\ m^{-2}\ s^{-1}$ |
| $S$ | total surface area of the capsules, $m^2$ |
| $t$ | time, s |
| $V_i$ | inner phase volume, $m^3$ |
| $V_o$ | outer phase volume, $m^3$ |
| $X_A$ | fractional conversion of A (substrate) |

### Greek letters

| | |
|---|---|
| $\phi$ | phase volume ratio $= V_i/V_o$ |

### Subscripts

| | |
|---|---|
| i | inner phase |
| o | outer phase |
| b | bulk phase |
| s | capsule surface |

## References

[1] R.E. Kirk and D.F. Othmer, Encyclopedia of Chemical Technology, 3rd Ed., Vol. 3, John Wiley and Sons, New York, 1978.
[2] G. Cardillo, M. Orena and S. Sandri, Tetrahedron Lett., (1976) 3985.
[3] W. Kumpf and D. Martinetz, Z. Chem., 24 (5) (1984) 182, cf. C.A. 102, 5633t (1985).
[4] S. Suyama and H. Ishigaki, Japan Kokai Tokkyo Koho 74,133,345 (1974), cf. C.A. 82 139687r (1975).
[5] Y. Okahata, K. Ariga and T. Seki, J. Chem. Soc., Chem. Commun., (1985) 920.
[6] G.D. Yadav and P.H. Mehta, Catal. Lett., 21 (1993) 391.
[7] G.D. Yadav, P.H. Mehta and B.V. Haldavanekar, Stud. Surf. Sci. Catal., 78 (1993) 503.
[8] Y. Okahata and K. Ariga, J. Org. Chem., 51 (26) (1986) 5064.
[9] E.V. Dehmlow and S.S. Dehmlow, Phase Transfer Catalysis, 3rd Ed., Verlag Chemie, Weinheim, 1993.