

# Reaction of crosslinked chloromethylated polystyrene with 4-hydroxybenzaldehyde under phase transfer-catalyzed conditions

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## Abstract

The present work studied factors which may affect phase transfer-catalyzed (PTC) nucleophilic displacement reactions, including chloromethylated polystyrene as polymer-supported alkylating agent and 4-hydroxybenzaldehyde as an O-nucleophilic reagent in presence of representatives for phase transfer catalysts. Some polymer-analogue conversions using the resulting polymer-supported aldehyde have been carried out. © 1998 Elsevier Science Ltd. All rights reserved.

**Keywords:** Chloromethylated polystyrene; 4-hydroxybenzaldehyde; PTC

## 1. Introduction

Some efforts have been done to prepare crosslinked polymers containing an aldehydic group which are useful in many applications [1–4]. The preparation of polymer-supported benzaldehyde under PTC conditions has been reported [5]. Many factors may affect the activity of a catalyst, such as its lipophilicity [6–8], and the bulkiness of groups attached to its key atom [9]. Also, the dependence of the reaction rate on the organic volume fraction percent of the two phase systems has been briefly reported [10]. The present work aims to study factors affecting the reaction of chloromethylated polystyrene with 4-hydroxybenzaldehyde under PTC conditions.

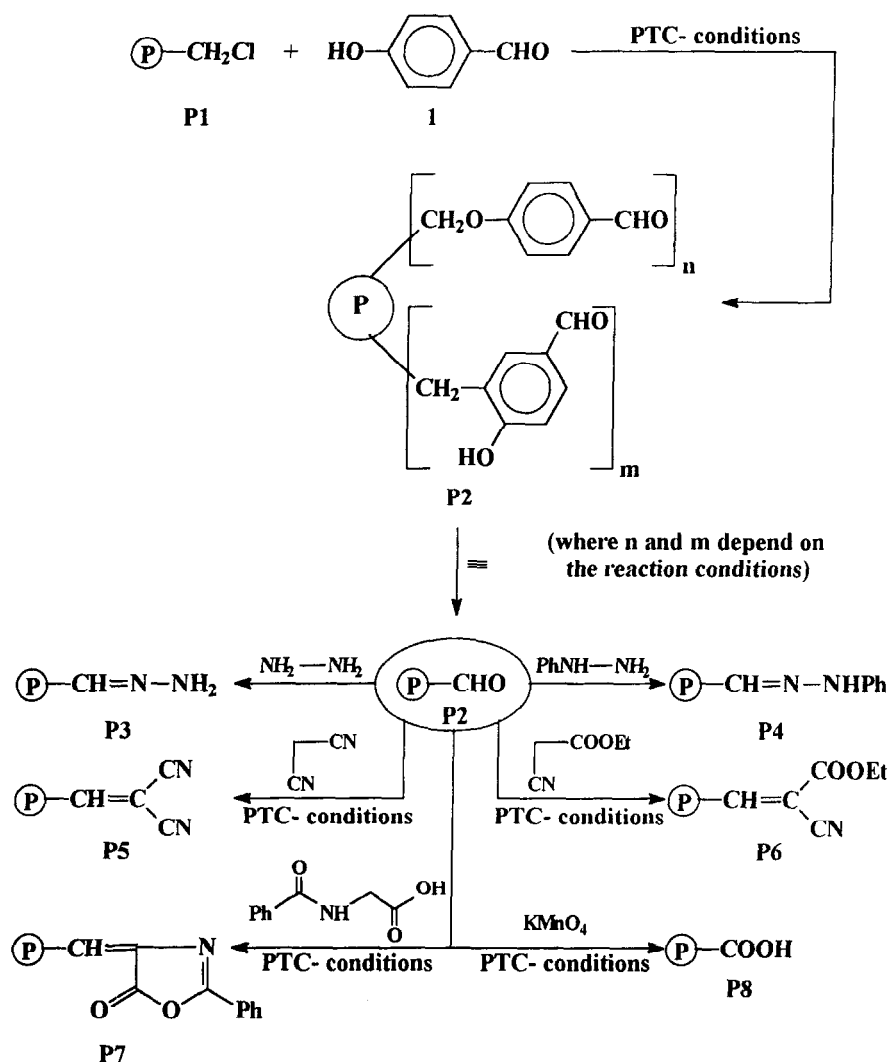
## 2. Results and discussions

The reaction of crosslinked chloromethylated polystyrene (2% divinylbenzene, 4.6 meq. Cl/g) (**P1**) with 4-hydroxybenzaldehyde (**1**) as an O-nucleophile under formation of the corresponding polymer-supported aldehyde was carried out under two systems of phase transfer catalysis (PTC) (Scheme 1). The first is a solid–liquid–solid (SLS) system consisting of the polymer and an inorganic base as two solid phases, and an organic swelling agent as liquid phase. The other is a solid–liquid–liquid (SLL) system consisting of an

organic swelling agent and an aqueous solution of the inorganic base, in addition to the solid polymer as a third phase. Excess amounts of **1** were used in presence of catalytic amounts of desired catalyst. The modified polymeric samples showed i.r. absorption peaks at 1695 and 1150  $\text{cm}^{-1}$  corresponding to C=O and C–O stretching, respectively, which are in accordance with that previously reported [5,11].

The degree of conversion percent was estimated on the basis of the normalized net peak area of carbonyl group absorption at 1695  $\text{cm}^{-1}$  against the net reference absorption peak at 1595  $\text{cm}^{-1}$  corresponding to the aromatic nucleus [12]. For this purpose, a FTi.r. calibration curve was made by using mixtures of **P1** and non-functionalized polystyrene doped with known amounts of 4-methoxybenzaldehyde as blank to attain arbitrary composition of the expected reaction products in different yields. The obtained data were corrected on the basis of theoretical calculations to fit the actual system. The corrected normalized carbonyl peak areas were then plotted against the dopant concentration in addition to the corresponding reaction conversion percent calculated for arbitrary suggested modified **P1**. Accordingly, determination of the reaction conversion percent in actually modified **P1** can be directly achieved on the basis of the corresponding FTi.r. C=O absorption peaks at 1695  $\text{cm}^{-1}$  (Fig. 1). In order to differentiate between O- and C-alkylation products, a calibration curve was also made in a similar way on the basis of the C–O stretching absorption band at 1150  $\text{cm}^{-1}$  with the same reference band

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Scheme 1. Chemical modification of P1 into polymer-supported benzaldehyde under PTC conditions and some of its characteristic reactions.

at  $1595\text{ cm}^{-1}$  (Fig. 2). The latter may only account for O-alkylation products, while the former curve may account for the total conversion, i.e. O- and C-alkylation products. Hence, O/C-alkylation ratios can be determined.

### 2.1. Effect of the type of catalyst

The reaction was carried out in  $\text{CHCl}_3/\text{aq. Na}_2\text{CO}_3$  in the case of the SLL-PTC system and in  $\text{DMF}/\text{solid Na}_2\text{CO}_3$  in the case of the SLS-PTC system. In both cases excess amounts of **1** in presence of a catalytic amount of the PT catalyst were used, and the reaction was performed with magnetic stirring at elevated temperature. Benzyltriphenylphosphonium chloride (BTPP); triethylbenzyl ammonium chloride (TEBA); cetyltrimethylammonium bromide (CTMA) and *N*-benzyl-4-dimethylaminopyridinium chloride (BPC) were used as onium catalysts in addition to dibenzo-18-crown-6 (DBC) as a non-ionic one. For practical comparative purposes, in each case changes in other variables are minimized.

Figs 3 and 4 represent the marked improvement of the conversion percent in presence of catalyst as compared with the corresponding non-catalyzed systems. It is clear that the practical effectiveness of the employed catalysts in promoting the formation of the desired product under SLS conditions can be arranged in the order  $\text{BTPP} > \text{CTMA} > \text{BPC} > \text{DBC} > \text{TEBA} \gg \text{none}$ , as shown in Fig. 3, while it can be arranged in the order  $\text{BTPP} > \text{BPC} > \text{TEBA} > \text{CTMA} > \text{DBC} \gg \text{none}$  under SLL conditions, as shown in Fig. 4.

In both SLL and SLS systems, it is evident that BTPP and, to some extent, CTMA are found to be the most effective catalysts. These two catalysts, although belonging to different classes of onium salts, i.e. phosphonium and quaternary ammonium salts, respectively, they possess the most hydrophobic character among the catalysts under investigation. Hence, the main principle of the PTC system is the continuous formation of lipophilic ion-pairs of phenolate anions derived from **1**, with the lipophilic cations ( $\text{Q}^+$ ) supplied by the catalyst. These ion-pairs are able to

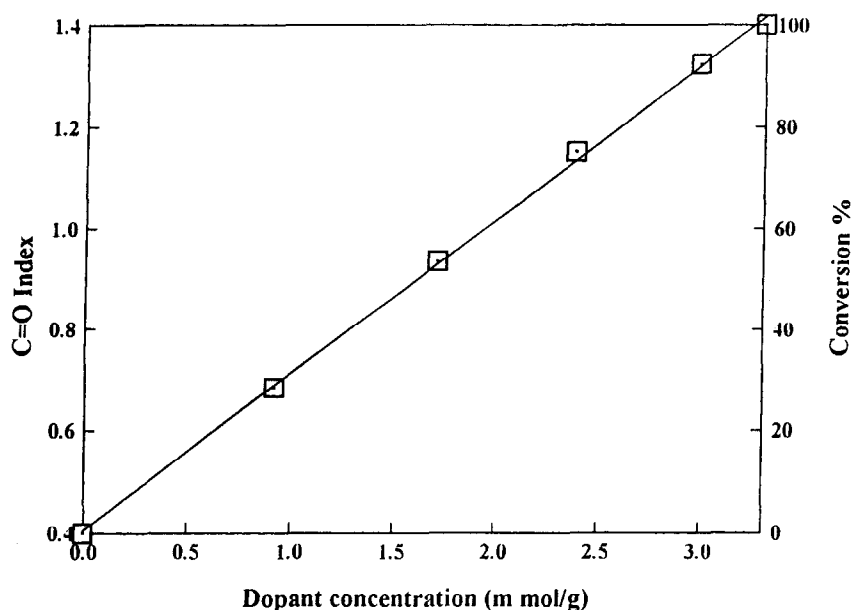


Fig. 1. FTi.r. calibration curve of normalized carbonyl peak area versus  $m$  mol of dopant/g of polymer and the corresponding arbitrary calculated reaction conversion % for O-/C-alkylation.

enter the less polar organic media in which the required displacement reaction takes place [13].

In addition *N*-benzyl-4-dimethylaminopyridinium chloride (BPC), which was utilized for similar reactions in a previous study [14], was found to be one of the most effective catalysts amongst those investigated. Its catalytic efficiency is comparable with or even higher than that of the considerably more hydrophobic CTMA and the more symmetric TEBA, respectively.

It is noticeable also from Fig. 3 that the PT catalytic efficiency of the crown ether (DBC) under SLS conditions is comparable with, or slightly lower than that of the

employed onium catalysts. In contrast, this catalyst exhibited a significantly lower efficiency than the onium catalysts, if the reactions were carried out under SLL conditions (Fig. 4). This observation can be explained considering that SLS catalytic processes are very similar for both onium salts and crown complexes in the sense that initial dissolution of ion-pairs simply occurs at the surface of the crystal lattice of the employed solid base. However, it is suggested that crown ethers may behave as two-dimensional system with multiple polar sites. They can, therefore, approach a crystal lattice so closely that the required movement of the cation from the lattice to the

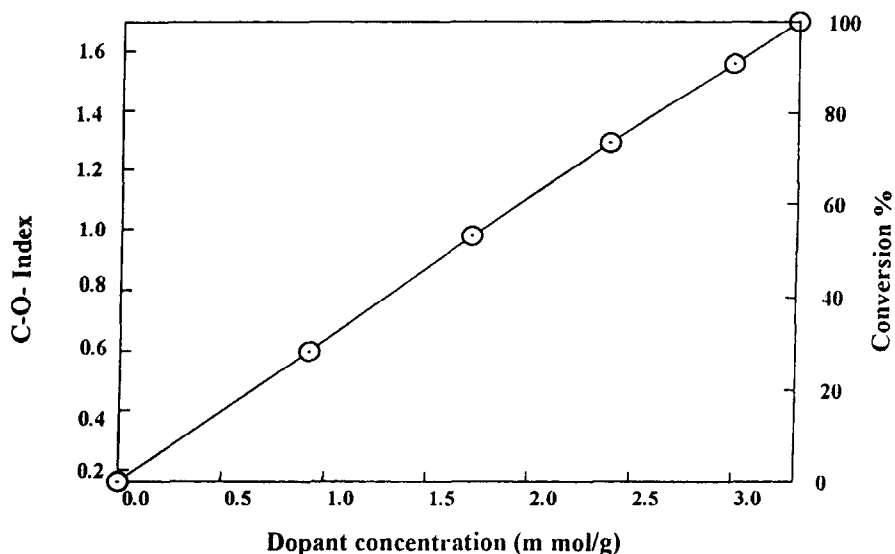


Fig. 2. FTi.r. calibration curve of normalized C-O-C peak area versus  $m$  mol of dopant/g of polymer and the corresponding arbitrary calculated reaction conversion percent for O-alkylation.

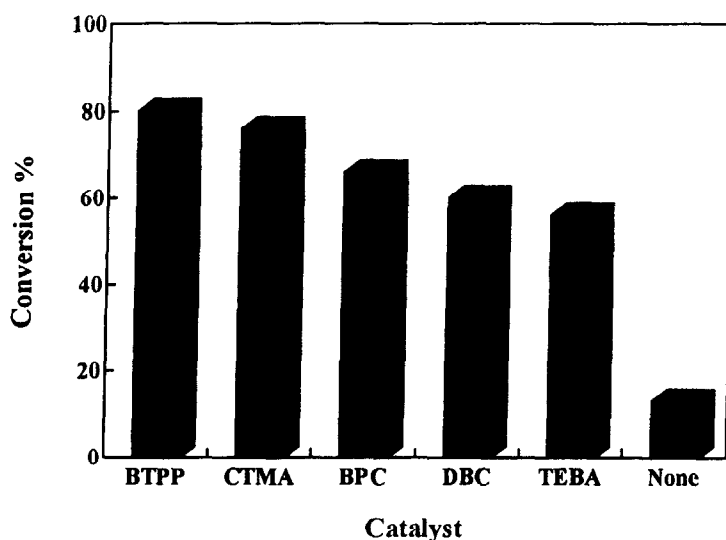


Fig. 3. Dependence of the reaction conversion percent for the reaction of **P1** with **1**, on the type of the PT catalyst under SLS-PT-catalyzed conditions including DMF/solid  $\text{Na}_2\text{CO}_3$  at  $95^\circ\text{C}$  for 6.5 h.

ligand is small. In contrast, onium cations have a sterically shielded positive key atom, so that they cannot approach the lattice closely [15,16]. Under SLL conditions, on the other hand, crowns tend to carry water, more than hydrophobic onium salts, into solvents even as non-polar as chloroform [17]. The anion activation is, therefore, strongly reduced as a result of reducing nucleophilicity because of ion-pair solvation. Thus, the overall rate of the reaction decreases. The two phenomena mentioned above may, at least partially, explain the relatively high difference between the catalytic efficiency in the case

of using crown ethers under SLS and SLL conditions. In fact, catalytic efficiency is a complex function of anion activation, anion exchange and anion transport phenomena, as well as dissolution and complexation of the salt.

## 2.2. Effect of the type of organic phase

Among the factors affecting the traditional nucleophilic substitution reactions is the type of solvent in which the reaction take place [18]. Parallel to this fact, one could

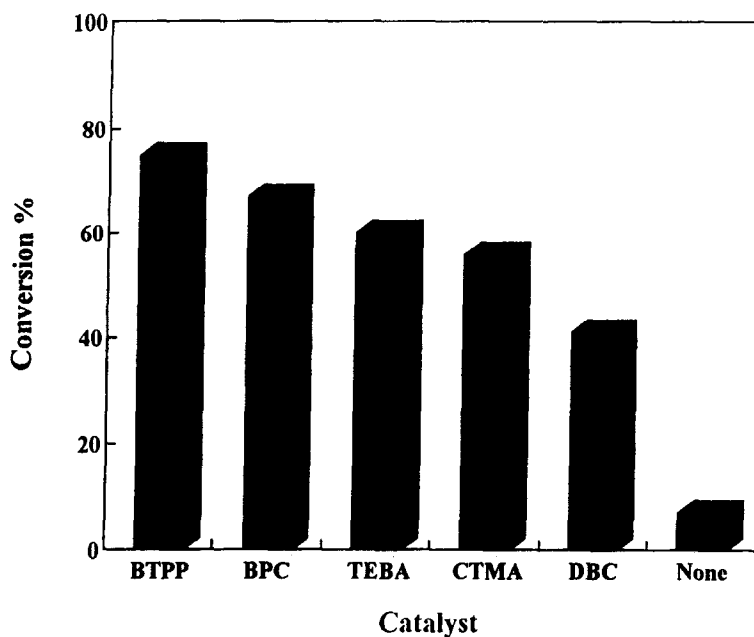


Fig. 4. Dependence of the reaction conversion percent, for the reaction of **P1** with **1**, on the type of the PT catalyst under SLL-PT-catalyzed conditions including  $\text{CHCl}_3$ /aqueous  $\text{Na}_2\text{CO}_3$  at  $55^\circ\text{C}$  for 9 h.

Table 1

Dependence of the conversion percent and the O/C-alkylation ratios, by the reaction of **P1** with **1**, on the type of organic solvents used under both SLS<sup>a</sup>- and SLL<sup>b</sup>-PTC conditions

PTC system	Organic solvent (Temp.)	Conversion percent <sup>c</sup>	O-alkylation <sup>d</sup> (%)	C-alkylation <sup>d</sup> (%)	O/C-alkylation ratio
SLS <sup>a</sup>	DMF (95°)	80	98.9	1.1	89.9
	1,2-Dichloroethane (75°C)	45	78.7	21.3	3.7
	Toluene (75°C)	25	60.0	40.0	1.5
SLL <sup>b</sup>	CHCl <sub>3</sub> (55°C)	75	93.3	6.7	14.0
	1,2-Dichloroethane (70°C)	63	65.5	34.5	1.9
	Benzene (55°C)	35	51.4	48.6	1.1

<sup>a</sup>SLS-PTC conditions: consisting of organic solvent/solid Na<sub>2</sub>CO<sub>3</sub>/catalytic amount of BTTP; 6.5 h reaction time

<sup>b</sup>SLL-PTC conditions: consisting of organic solvent/aqueous Na<sub>2</sub>CO<sub>3</sub>/catalytic amount of BTTP; 10 h reaction time

<sup>c</sup>Percentage of reacted polymer-supported active sites

<sup>d</sup>By taking into account O-/C-alkylation = 100%

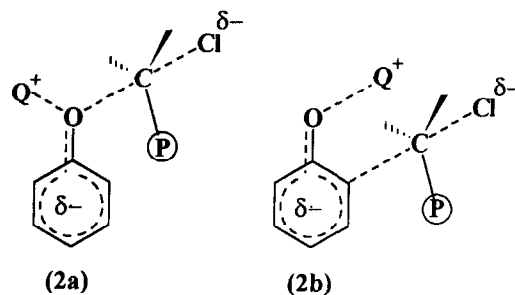
expect a marked effect for the organic phase in which a PT-catalyzed reaction takes place. It was, therefore, of interest to study such effect. Hence, the displacement reaction of **P1** with **1** was carried out under both SLS- and SLL-PTC by using various organic solvents. In both cases, the most effective catalyst (BTTP) was used, and the reaction was done in mixtures of aqueous Na<sub>2</sub>CO<sub>3</sub>/organic solvent for SLL systems and solid Na<sub>2</sub>CO<sub>3</sub>/organic solvent for SLS systems, with stirring at elevated temperature. Chloroform, benzene and dichloroethane were used for SLL systems, while DMF, toluene and dichloroethane were used for SLS systems. These solvents may represent different types of organic solvents with varying polarities.

It is evident from Table 1 that the reaction conversion percent was greatly affected by the type of organic phase. It increased as the polarity of the organic phase increased, apart from the type of the alkylation product (O- or C-alkylation product). This may be attributed to the varying ability of solvents to swell the polymer and to dissolve the ion-pairs consisting of the anions desired for alkylation and cations supplied by the PT catalyst. It is also found that the type of organic phase not only affect the overall reaction conversion percent, but also affect the direction of the alkylation reaction, i.e. O- versus C-alkylation. This is because the phenoxide ion may exist as an ambident anion possessing capability for covalent bond formation at the oxygen atom or at *ortho* ring carbon atoms under formation of the polymer-supported aldehyde **P2** (Scheme 1).

It is evident from Table 1 that reactions conducted under SLS conditions in DMF/solid Na<sub>2</sub>CO<sub>3</sub> and under SLL conditions in CHCl<sub>3</sub>/aqueous Na<sub>2</sub>CO<sub>3</sub> in presence of BTTP as PT catalyst led to high amounts of the O-alkyl residues in **P2**. On the other hand, using less polar solvents such as benzene, toluene and dichloroethane under both SLS and SLL conditions led to relatively lower amounts of O-alkyl residues in **P2**. Since the inherent displacement reaction may take place in the organic phase (apart from the employed PTC system), these results may clearly demonstrate the effectiveness of non-polar aprotic solvents in promoting C-alkylation under both SLL and SLS conditions.

Hence, an O/C-alkylation ratio of 1.1–3.7 in the case of using dichloroethane, benzene and toluene may be contrasted with the O/C-alkylation ratio of 14 and 89.9 for the same types of reactions yet carried out in the polar aprotic solvents chloroform and DMF, respectively.

Although the results obtained may reflect the effect of non-polar aprotic solvents in promoting C-alkylation, O-alkylation remains the predominant process by all of the investigated solvents. The relatively high selectivity for O-alkylation is in agreement with reported results including PTC alkylation of various phenols [19–21]. In order to account for the ability of solvents to control the course of ambident anion alkylations, two properties of solvents can be invoked: (a) their dielectric constant, and (b) their capacity for solvating ions. Hence, in case of the aprotic solvents used in the present study, dielectric factors and the capability of solvent molecules for solvating ions combine to influence the free energies of possible transition states.



Hence, in the case of ether formation, a transition state of the type 2a, in which the cation Q<sup>+</sup> (onium ion supplied by the catalyst) is relatively far away from the departing chloride anion, can be suggested. So, the attractive electrostatic forces exerted by Q<sup>+</sup> on the leaving negative charged Cl<sup>-</sup> will be diminished. Because of the tendency of highly polar- aprotic solvents to solvate ions, they can partially compensate the loss of electrostatic attraction between Q<sup>+</sup> and the

negative charged O atom during the formation of the transition state. It can be assumed that this transition state is of significantly lower energy in case of using an aprotic solvent of relatively high dielectric constant such as DMF favoring O-alkylation.

In contrast to the linear O–C–Cl disposition which characterizes the transition state for oxygen alkylation represented by 2a, C-alkylation proceeds through a suggested transition state (2b) with non-linear arrangement in which the departing chloride ion is relatively close to  $Q^+$  leading to an increase of the attractive force exerted by it [22]. So, the coulombic factor, between  $Q^+$  and the departing  $Cl^-$  ion, will become more significant in affecting the energy of this transition state. Thus, in non-polar aprotic solvents, where effective solvation is low, the formation of transition states of the type 2b, become more favorable leading to a more or less increase of the C-alkylated products.

### 2.3. Effect of the organic volume fraction percent ( $V_r$ ) under the SLL–PTC system

It was of interest to study the effect of  $V_r$  [ $V_r = 100 \times V_{org.}/(V_{org.} + V_{aq.})$ ] on the conversion percent by the SLL–PTC reaction of **P1** with **1**. For this purpose **P1** was reacted with **1** by using various volume fractions of an organic phase and aqueous  $Na_2CO_3$  as an aqueous phase in the presence of a catalytic amount of BTTP as PT catalyst. Fig. 5 shows an obvious effect of the organic volume fraction on the reaction conversion percent. Hence, it is clear that a maximum conversion percent of the reaction was obtained when a minute amount of the organic phase was used. This was practically achieved by complete decantation of excess organic phase from the swollen polymer before its addition

to the aqueous phase. By increasing the organic volume fraction, an inverse proportionation of the reaction conversion percent was observed. If, on the other hand, the reaction was carried out under similar conditions but in absence of the organic phase, i.e.  $V_r = 0$ , it is noticeable that the conversion percent was also considerably lower than the case in which a minute amount of the organic phase was used. To explain this behavior one can illustrate the reaction system in three different cases as shown in Scheme 2.

The case, in which there is no organic phase was used ( $V_r = 0$ ), can be designated as a two-phase system consisting of the aqueous phase and the aqueous swollen polymer matrix (Scheme 2a). Since, in this particular case, the inherent displacement reaction takes place in aqueous environment, the anion activation is strongly reduced because of ion-pair solvation leading to the observed reduction of the reaction conversion percent. On the other hand, in case of using large amounts of the organic phase, the reaction system can be designated as three-phase system consisting of an aqueous phase, an organic phase and the organic swollen polymer matrix (Scheme 2c). Increasing the volume of the organic phase may correlate with a reduction of the concentration of ion-pairs in the relatively smaller volume of organic phase inside the polymer matrix to which the alkylating group is supported. As a result, the rate of the inherent reaction and consequently the conversion percent after a certain period of time relatively decrease.

Scheme 2b represents a special case in which a swollen polymer was separated from the organic phase by decantation before its equilibration with the aqueous phase. In such a case there is almost no organic phase outside the polymer matrix and hence ion-pairs have to overcome only one diffusional limitation in order to reach the reactive centers

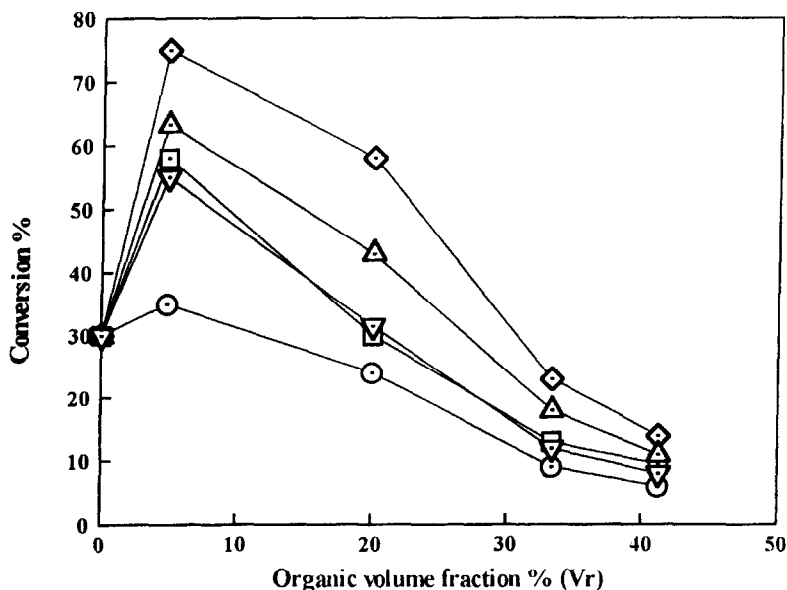
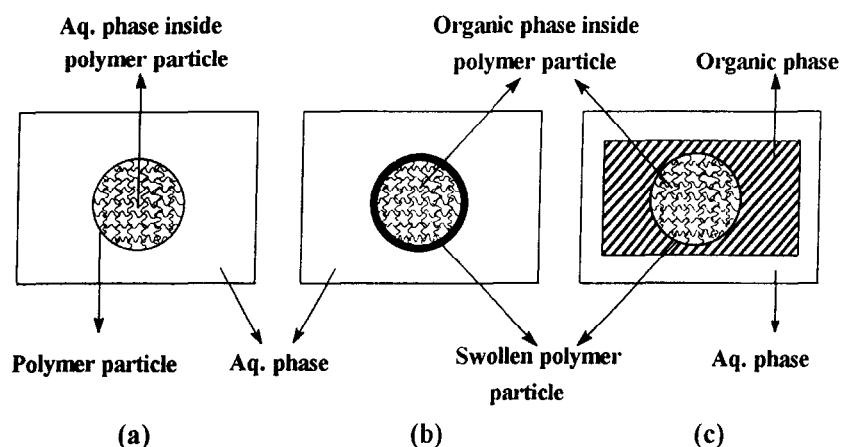


Fig. 5. Effect of the organic solvent/aqueous  $Na_2CO_3$  volume fraction ( $V_r = 100 \times V_{org.}/V_{org.} + V_{aq.}$ ) on the conversion percent by the reaction of **P1** with **1** under SLL–PTC conditions in the presence of BTTP as the PT catalyst for 10 h by using various organic solvents; (◇)  $CHCl_3$  at 55°C, dichloroethane at (□) 53°C and at (△) 70°C, and benzene at (○) 53°C and at (▽) 70°C.



Scheme 2. Schematic representation of different types of PTC systems consisting of  $\text{CHCl}_3/\text{aq. Na}_2\text{CO}_3$ : (a) in absence of  $\text{CHCl}_3$  ( $V_f = 0$ ); (b) in presence of a minute amount of  $\text{CHCl}_3$ ; (c) in presence of increasingly amounts of  $\text{CHCl}_3$ .

in the polymer matrix. This will result in an increase of the overall rate of reaction and consequently to higher conversion percent as shown in Fig. 5. This system can be designated strictly as quasi two-phase system. So, the major synthetic attractiveness of the use of SLL-PTC technique is that only a small quantity of solvents are required. This behavior was not only observed for a particular solvent but also with various solvents such as benzene, chloroform and dichloroethane used in the present study even when the reaction was carried out at different temperatures (Fig. 5). This means that this behavior is not specific for a particular solvent but it would be the case for many organic solvents used in the same manner.

#### 2.4. Effect of the reaction time under the SLS system

The reaction of **P1** with **1** was performed with a 10-fold molar excess of **1** in DMF as swelling agent, BTPP as catalyst and solid  $\text{Na}_2\text{CO}_3$  as base. Fig. 6 shows that the reaction conversion percent increases as the reaction time increases until about 92% conversion was achieved after about 15 h. A similar course of the curve was observed when using DBC instead of BTPP under comparable conditions, yet the conversion percent was generally lower. When the reaction was carried out at 50 instead of 95°C in the presence of DBC, the conversion percent significantly decreased although the course of the curve remains the same. This may be interpreted as the reaction rate being to some extent limited by the diffusion rate of the reactant to the active sites within the polymer matrix, in addition to the rate of the inherent reaction at the active sites [23]. At the beginning, the most accessible reactive sites are involved in the reaction, therefore diffusional limitations are less significant to affect the overall reaction rate. On prolonging the reaction time, the less accessible sites will be involved also, and diffusional limitations significantly affect the overall reaction rate. So, the overall reaction rate decreases as the reaction conversion increase (Fig. 6b).

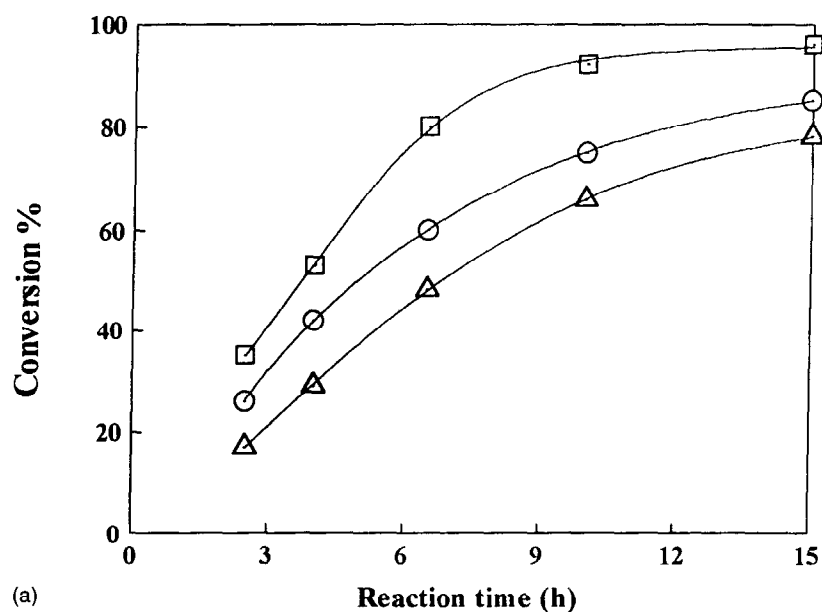
#### 2.5. Some characteristic reactions of **P2**

In order to account for the utility of the aldehyde group in **P2** in chemical transformation, some polymer analogue conversions were carried out. Thus, **P2** was condensed with hydrazine hydrate and phenyl hydrazine in acidic medium under conventional conditions leading to formation of the corresponding hydrazones **P3** and **P4**, respectively. It was also condensed under PTC conditions with some compounds containing active methylene groups such as malononitrile, ethyl cyanoacetate and hippuric acid. The reaction was carried out under PTC conditions by using BTPP as PT catalyst in the presence of aqueous sodium hydroxide and an organic solvent as swelling agent, leading to formation of the polymeric products **P5–P7**. In addition, **P2** was oxidized by using an aq.  $\text{KMnO}_4/\text{CH}_2\text{Cl}_2$  two-phase system in the presence of BTPP as catalyst at 60°C for 4 h. It afforded the polymer-supported carboxylic acid **P8**. Under non-catalyzed conditions there is no reaction occurring, even after longer reaction times. **P5–P8** were characterized by FTi.r. spectroscopic analysis. From the above-mentioned reactions represented in Scheme 1, it can be concluded that the polymer-supported aldehyde group is reactive enough towards many reagents and can therefore be used for many polymer analogue conversions.

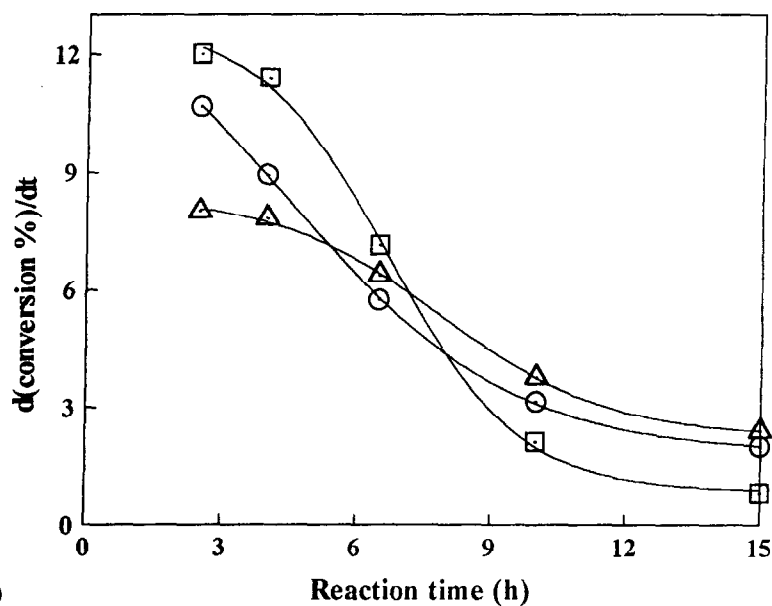
### 3. Experimental part

#### 3.1. Materials and techniques

Commercial chloromethylpolystyrene-co-divinylbenzene (**P1**) (MP-500 A; Bayer Co.; 2% DVB; specific surface area (BET) is 66  $\text{m}^2/\text{g}$  and 4.6 meq. Cl/g resin) was used. 4-Hydroxybenzaldehyde, triethylbenzylammonium chloride (TEBA), dibenzo-18-crown-6 (DBC) and cetyltrimethylammonium bromide (CTMA) (Aldrich) were used as supplied. Benzyltriphenylphosphonium chloride (BTPP)



(a)



(b)

Fig. 6. Effect of time on: (a) the conversion percent and (b) the rate of the reaction of **P1** with **1** under SLS conditions (DMF/solid  $\text{Na}_2\text{CO}_3$ ) using (□) BTTPP at 95°C and DBC at (○) 95°C and at (Δ) 50°C, as catalysts.

and *N*-benzyl-4-(*N,N*-dimethylamino)pyridinium chloride (BPC) were prepared according to Ref. [24]. The reaction conversion percent in all experiments was followed up with the aid of FTi.r. spectroscopic analysis on a Perkin-Elmer 1430 spectrophotometer [12].

### 3.2. Reaction of **P1** with **1** under PTC conditions

When not otherwise stated the reactions were performed as follows:

#### 3.2.1. Under solid–liquid–solid (SLS) conditions

In a 50 ml round bottom flask, 100 mg (0.46 meq.) chloromethylated polystyrene (**P1**) was soaked overnight in 5 ml of an organic solvent as swelling medium. To the swollen polymer, 620 mg (5 mmol) 4-hydroxybenzaldehyde (**1**), 0.2 mmol of the investigated catalyst and 90 mg sodium carbonate as a base were added. The reaction mixture was heated on a water bath and stirred magnetically for desired period of time at the desired temperature. After cooling, the modified polymeric product was filtered off,



washed thoroughly with methanol, distilled water, acetone and finally with diethyl ether. The polymeric product was then dried at 40°C overnight.

### 3.2.2. Under solid–liquid–liquid (SLL) conditions

One hundred mg (0.46 meq.) of **P1** was soaked overnight in an organic solvent as swelling medium. After decantation of the solvent, the swollen polymer was treated with 620 mg (5 mmol) of **1**; 0.2 mmol of the investigated catalyst and 3 ml aq. Na<sub>2</sub>CO<sub>3</sub> (30%). The reaction mixture was magnetically stirred for 10 h at the desired temperature on a water bath. After cooling, the modified polymeric products were treated as mentioned above. All the polymeric products exhibited i.r.-absorption bands at 1695 cm<sup>-1</sup> (C=O stretching) and 1150 cm<sup>-1</sup> (C–O stretching) in agreement with previous reports [5,11].

### 3.3. Condensation reactions of **P2**

#### 3.3.1. With hydrazines

In a 50 ml round-bottom flask was placed 100 mg (0.46 meq.) of **P2** with 0.82 mmol of the desired hydrazine in 10 ml absolute alcohol and a catalytic amount of glacial acetic acid. The reaction mixture was heated at 80°C for 4 h. The polymer was then filtered off and washed successively with ethanol, THF, methanol, acetone, and finally with ether. I.r. (KBr): 1670 cm<sup>-1</sup> (–C=N stretching) for hydrazone **P3** and 3430 and 1670 cm<sup>-1</sup> (–NH– and –C=N stretching) for phenyl hydrazone **P4**.

#### 3.3.2. With malononitrile

One hundred mg of **P2** was swollen in 10 ml DMF and mixed with 20 mg (0.08 mmol) BTTP, 400 mg (3.8 mmol) solid Na<sub>2</sub>CO<sub>3</sub> and 125 mg (3 mmol) malononitrile. The reaction mixture was stirred magnetically at 80°C on a water bath for 3 h. The resulting polymer **P5** was filtered off and washed thoroughly with methanol, water, THF, acetone and finally with ether. I.r. (KBr): 2200 cm<sup>-1</sup> (–C≡N stretching), 1360 cm<sup>-1</sup> (O–H bending).

#### 3.3.3. With ethyl cyanoacetate

The reaction was carried out on 50 mg of **P2** swollen in 6 ml dichloroethane, then 200 mg (1.77 mmol) ethyl cyanoacetate, 20 mg (0.08 mmol) BTTP and 150 mg (3.7 mmol) solid NaOH were added. This mixture was stirred at 90°C for 6 h. The resulting polymer **P6** was filtered off and washed successively with methanol, water, THF, acetone and finally with ether. I.r. (KBr): 2200 cm<sup>-1</sup> (–C≡N stretching), 1750 cm<sup>-1</sup> (–C=O stretching).

#### 3.3.4. With hippuric acid

Two hundred mg of **P2** was placed in 20 ml acetic anhydride containing 200 mg freshly fused sodium acetate in a round-bottom flask. Two hundred and thirty mg (0.9 mmol)

hippuric acid and 80 mg (0.2 mmol) of BTTP were then added. The reaction mixture was heated in a boiling water bath and stirred magnetically for 4 h. After cooling, 20 ml ethanol was cautiously added to the mixture. The reaction mixture was then heated under reflux for 30 min to decompose the acetic anhydride, and left to cool. After filtration, the polymeric product **P7** was washed successively with methanol, water, acetone, ethanol and finally with ether. I.r. (KBr): 1780 cm<sup>-1</sup> (C=O stretching of  $\gamma$ -lactone) and 1650 cm<sup>-1</sup> ( $\alpha,\beta$ -unsaturated C=N).

### 3.4. Oxidation of **P2**

Fifty mg of **P2** swollen in 5 ml dichloroethane was placed into a 50 ml round-bottom flask. Fifteen mg (0.058 mmol) of DBC and 100 mg (0.63 mmol) of KMnO<sub>4</sub> in 2 ml of water were added, and the reaction mixture was heated in a water bath at 60°C and stirred magnetically for 2 h. After filtration, the resulting polymer **P8** was washed successively with methanol, water, dilute HCl, ethanol and finally with ether, then dried at 40°C. I.r. (KBr): 1700 cm<sup>-1</sup> (C=O stretching), 2730 cm<sup>-1</sup> (H-bonded, O–H stretching).

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