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Wittig-Horner reactions on styrene-divinylbenzene supports with benzaldehyde side-groups

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Summary

A styrene-divinylbenzene copolymer functionalized with aldehyde was prepared under phase transfer catalyzed (PTC) conditions. A statistical method for the calculation of the degree of functionalization with aldehyde groups is proposed. The degree of functionalization with aldehyde groups is relatively high.

Styrene-divinylbenzene polymers functionalized with benzaldehyde groups were used in Wittig-Horner reaction, in order to introduce double bonds on polymers. The reactions were carried out using PTC method, solid-liquid-solid (s-l-s) (K_2CO_3, tetrahydrofuran, tetraethylammonium iodide) system. Phase transfer catalyzed reactions are often more easily and cheaply carried out than conventional method and they are therefore of particular interest.

Introduction

Since Merrifield reported his method of “solid-phase peptide synthesis” in 1963 [1], there has been increased interest in the application of polymers as participants in catalysis [2-6], organic synthesis [7], environmental separation [8-11] and antibacterial agents [12-14].

When Merrifield was looking for a suitable insoluble support for his solid phase synthesis, his choice ended when he was confronted with a copolymer of styrene and divinylbenzene. Since then, many solid supports had appeared, and some of them, with better properties that the one used by Merrifield, however after 40 years, this is still the most used resin.

Davankov and Tsyumpa [15] have introduced the hypercrosslinked polystyrene, as the first representative of a new class of polymer networks and form the base for the third generation of macroporous hypercrosslinked styrene-divinylbenzene copolymers.

Neutral hypercrosslinked polystyrene having no functional groups was found to display a high affinity for metal ions [16, 17].

Wittig reaction and its variants have been developed as one of the most powerful approaches in constructing carbon-carbon double bonds due to its unambiguous positioning and good stereoselectivity of the double bond [18-21].

It is well-known that phase-transfer catalysis (PTC) is a very convenient and useful method for organic synthesis. This method can also be used for the chemical modification of polymers to synthesize various functional polymers [22, 23].

In literature is presented the chemical modification of commercially available 2%(5%)-cross-linked Merrifield polymer with aldehyde groups [24, 25] using PTC conditions.

In a previous paper we have reported the preparation of 4-benzaldehyde and 2-benzaldehyde grafted on styrene-6.7%divinylbenzene copolymer under PTC conditions and their use in phase transfer catalysed Wittig reactions in solid-liquid-solid (s-l-s) system [21]. Also, we have used the PTC method for the synthesis of the polymers containing the phosphonate groups [26, 27].

This paper presents the obtaining of the macroporous copolymers styrene-divinylbenzene with higher cross-linked degree (6.7%, 7%) grafted with aldehyde groups by PTC method in s-l-s system. The synthesized products were used in obtaining pendant double bond supported by Wittig-Horner procedure in PTC conditions.

The pendant double bonds supported in microbeads could be used as potential sorbents.

Experimental

Reagents

Dimethylphosphonate (Aldrich, 97%), diethylcyanomethylphosphonate (Aldrich, 99%), diethylbenzylphosphonate (Aldrich, 99%), diethylvinylphosphonate (Aldrich, 97%), tetrahydrofuran (Carlo Erba, p.a.), dimethyl-sulfoxide (Fluka, p.a.) sodium hydrogen carbonate (Chimopar, p.a.), methanol (Chimopar, p.a.), 1,2-dichloromethane (Chimopar, p.a.), ethanol (Chimopar, p.a.), diethylether (Chimopar, p.a.), tetraethylammonium iodide (Merck) were used without purification, chlorometylated styrene-divinylbenzene copolymer was used as starting materials (macroporous type) and was supplied by Purolite Victoria Romania (S-6.7%DVB, %Cl= 14.22, G_F = 4.01 mmoles Cl/g. copolymer, S-7%DVB, %Cl= 8.10, G_F= 2.28 mmoles Cl/g. copolymer).

Reactions under solid-liquid-solid (s-l-s) condition of chloromethylated styrene-divinylbenzene copolymer with benzaldehyde groups

10 g sample of chloromethylated copolymer, sodium hydrogen carbonate (molar ratio – chloromethyl groups (CH_2Cl) : $NaHCO_3$ = 1:2) and 200 ml dimethyl-sulfoxide were added to a 250 ml round bottom flask fitted with a reflux condenser, mechanical stirrer and thermometer. The mixture was maintained under stirring for 24 h at 130 ^oC. After cooling, the polymer beads were separated by filtration, washed with DMSO (3x20 ml), hot distilled water (3x20ml), methanol (3x20ml), acetone (3x20ml) and finally with diethyl ether (3x20ml) and dried at 50 ^oC for 24 hours.

General procedure for Wittig-Horner reactions in phase transfer catalysis conditions

A mixture of benzaldehyde (4.31 mmoles/g) (1, S-6.7%DVB), respectively (2.25 mmoles/g) (2, S-7%DVB) grafted on styrene-divinylbenzene copolymer (1 g), tetraethylammonium iodide (0.05 g), solvent (THF) (20 ml), K_2CO_3 (0.55 g) and a phosphonate (dimethyl methylphosphonate, diethyl benzylphosphonate, diethyl cyanomethylphosphonate, diethyl vinylphosphonate) were stirred 20 hours at 45 ^oC.

The molar ratio benzaldehyde (type 1), respectively benzaldehyde (type 2), grafted on styrene-divinylbenzene copolymer : phosphonate was 1:2.

The final product was separated by filtration, washed with ethanol (3x20 ml), methylenchloride (3x20 ml), diethyl ether (3 x 20 ml), and then dried at 50 ^oC for 24 hours.

Determination of the chlorine content

A sample of the product, precisely weighted, was burnt out in an oxygen atmosphere, the gases were absorbed in an aqueous solution of H_2O_2 0.15% (w) and the chloride ion was quantitatively determined by potentiometric titration with an aqueous solution of $AgNO_3$ 0.05 M.

Determination of the double bond content

To a sample of the final product, precisely weighted (200 mg), 10 ml carbon tetrachloride, 10 ml distilled water, 40 ml 0.05N $KBrO_3$-KBr and 10 ml 10% H_2SO_4 were added. The mixture was kept under continuously stirring. After 2 hours another 4 ml 0.05 N $KBrO_3$-KBr and 1 ml 10% H_2SO_4 were added and this operation was repeated until the yellow-brown color persists 10 minutes. Then 10 ml 20% KI was added. The iodide was titrated with 0.1 N $Na_2S_2O_3$ until the color is changed in yellow then 0.5 ml 1% starch was added and the titration was continued until complete discoloration.

Results and discussions

Theory

The fraction of repetitive units functionalized with aldehyde groups was determined by accepting the statistical structure of the repetitive unit of final copolymer presented in Figure 1:

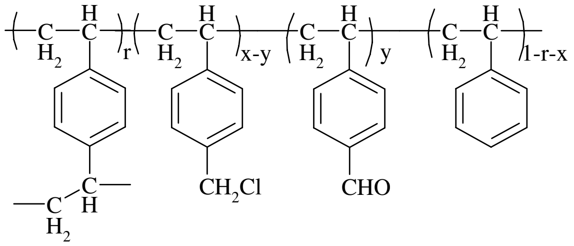


Figure 1. Statistical structure of the repetitive unit of the functionalized copolymer.

Using the notations:
Ff - CHO groups
Fi - CH_2Cl groups
r- Fraction of divinylbenzene (DVB) units
x – fraction of styrene units bearing pendant $-CH_2Cl$ groups (Fi)
y – fraction of styrene units bearing pendant –CHO groups (Ff)
M_{mi} - average molecular weight of the repetitive unit of the initial copolymer
M_{mf} – average molecular weight of the repetitive unit of the final copolymer
$\%Cl_f$ – chlorine percentage in the final copolymer
A_{Cl} – atomic weight of chlorine
M_S – molecular weight of the repetitive unit of the styrene
M_{DVB} – molecular weight of the repetitive unit of the divinylbenzene
M_{SFi} – molecular weight of the repetitive unit of the styrene functionalized unit Fi groups
M_{SFf} – molecular weight of the repetitive unit of the styrene functionalized with Ff groups
G_F – functionalization degree

The fraction of styrene units bearing aldehyde groups, obtained by polymer-analogous reactions was calculated from the chlorine content in the final products:

$$\%Cl_f = \frac{(x-y)\cdot A_{Cl}}{M_{mf}}\cdot 100 \qquad (1)$$

where: $M_{mf} = M_{mi} + y(M_{SFf} - M_{SFi})$ (2)

$M_{mi} = r.M_{DVB} + x.M_{SF}CH_2Cl + (1\text{-}r\text{-}x).M_S$ (3)

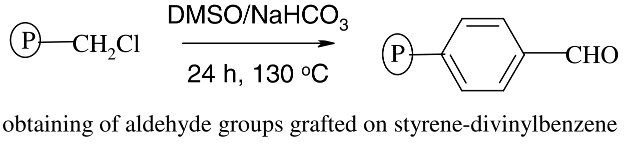
The fraction of the styrene units bearing pendant benzaldehyde groups was calculated with the equation (4): $y = \dfrac{100\cdot x\cdot A_{Cl} - \%Cl_f \cdot M_{mi}}{100\cdot A_{Cl} + \%Cl_f\cdot(M_{SFf} - M_{SFi})}$ (4)

On this basis, the functionalization degree (G_F) with benzaldehyde groups was calculated with equation (5):

$$G_F = \frac{y}{M_{mf}} \qquad (5)$$

Characterization of benzaldehyde (1) and benzaldehyde (2) grafted on styrene-divinylbenzene copolymer

The polymer-analogous reactions are presented in scheme 1:



Scheme 1. The obtaining of aldehyde groups grafted on styrene-divinylbenzene copolymers.

Some general remarks concerning the IR spectra:

- the decrease in the intensity of chloromethyl adsorption band γ CH_2Cl at 1260 cm^{-1} suggests that a reaction of the chloromethyl groups of the initial copolymers took place;
- the formation of the benzaldehyde groups was confirmed by the appearance of the peaks at 1700 and 1050 cm^{-1} corresponding to C=O and C-O stretching and 1600 cm^{-1} corresponding to the aromatic nucleus (see 2, from Fig. 2).

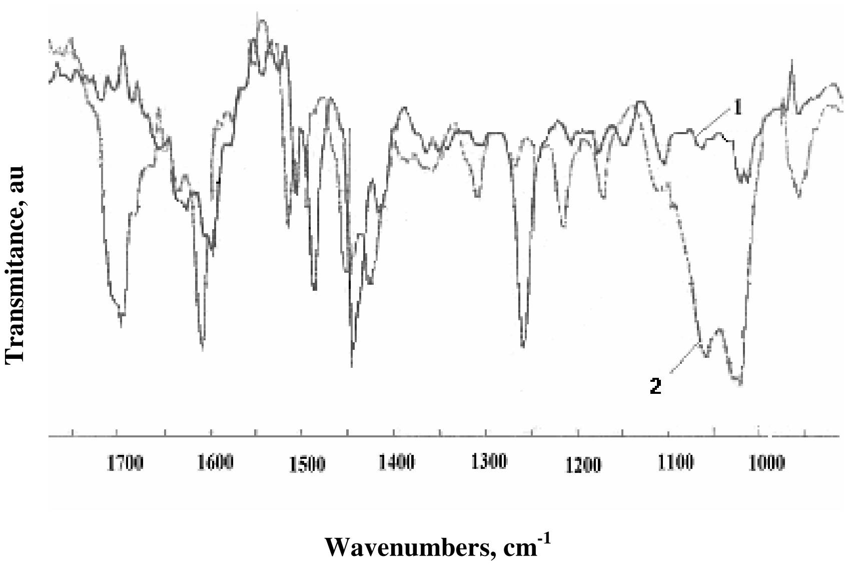


Figure 2. IR spectra: **1**- chloromethylated styrene-6.7%divinylbenzene copolymer (starting support), **2**- chloromethylated styrene-6.7%divinylbenzene copolymer functionalized with aldehyde groups.

The main characteristics of aldehydes grafted on polymeric support by polymer-analogous reactions are given in Table 1.

Table 1. Characteristics of benzaldehyde grafted on styrene-divinylbenzene copolymers.

Prod Code	Cl_f (%,w)	x^c	y	G_F (mmoles -CHO /g of copolymer)	M_{mf}
1^a	0.178	0.527	0.520	4.31	120.662
2^b	0.500	0.272	0.256	2.25	113.752

[a] benzaldehyde grafted on styrene-6.7%divinylbenzene

[b] benzaldehyde grafted on styrene-7%divinylbenzene

[c] $x = \frac{\%E \cdot [(1-r) \cdot M_S + r \cdot M_{DVB}]}{100 \cdot A_E - \%E \cdot (M_{SFi} - M_S)}$ [21]

The chlorine percent decreases as the reaction time increases until about 0.178 and 0.500 (%, w) and they were achieved after about 24 h (Figure 3).

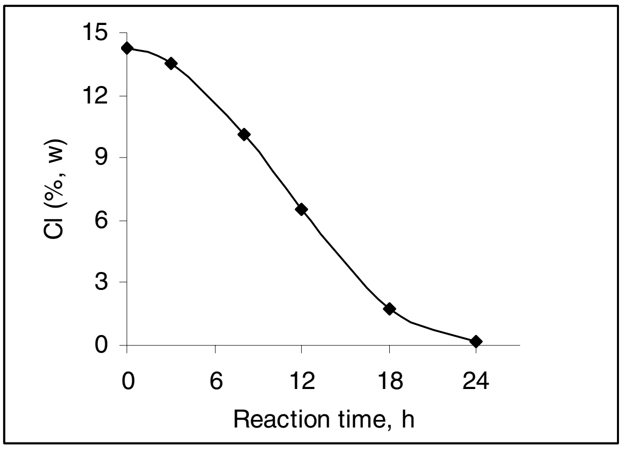


Figure 3. Chlorine percent versus the reaction time using chloromethylated styrene-6.7%divinylbenzene copolymer functionalized with aldehyde groups.

This may be interpreted as at the beginning, the most accessible reactive sites (groups CH_2Cl) are involved in reaction, on prolonging the reaction time, the less accessible sites will be involved also. So, the chlorine content decreases with reaction time.
Figure 4 shows that the reaction conversion increases as the reaction time increases until about 98% and the maximum conversion was achieved after about 24 h.

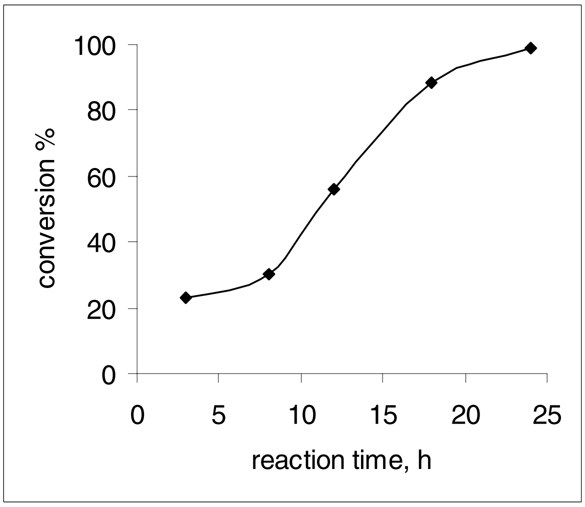


Figure 4. Reaction conversion percent versus the reaction time using styrene-6.7divinylbenzene copolymer functionalized with aldehyde groups.

The degree of functionalization with aldehyde groups is high and it increases as the reaction time increases (Figure 5), ensuring a sufficient concentration of active centers per unit mass of copolymer and being well suited for application as Wittig-Horner reagents.

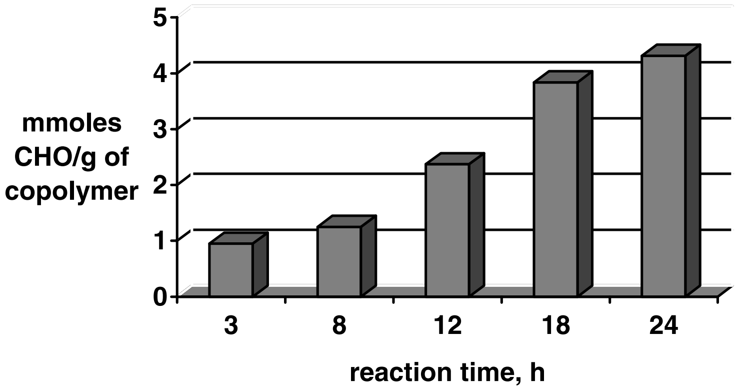
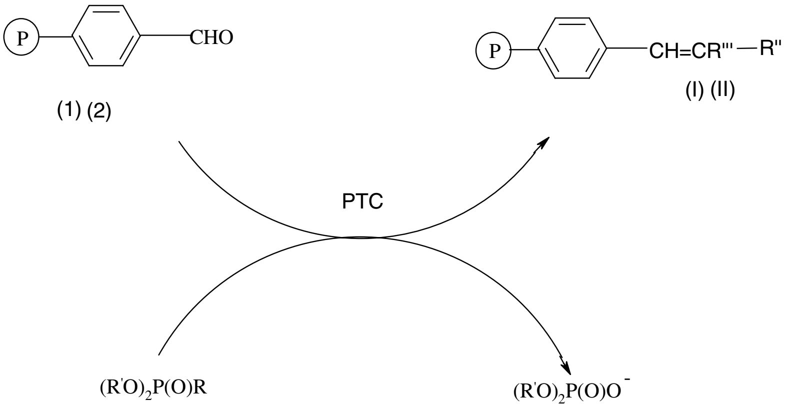


Figure 5. The degree of functionalization with aldehyde groups at the S-6.7%DVB copolymer versus the reaction time.

Characterization of Wittig-Horner reactions on polymer supports

Introduction of a pendant double bonds on polymer supports by Wittig-Horner reactions in PTC conditions is presented in scheme 2:



Scheme 2. Chemical modification of grafted on polymer through Wittig-Horner polymer-analogous reactions in PTC conditions.

These phosphonate carbanions are more nucleophilic than the phosphonium ylide [21], reacting with aldehydes grafted on polymeric support (1, 2) in milder conditions. The soluble phosphate ion in organic phase is separated easily from the resulting alkene polymer (I, II). The main characteristics of the olefin grafted on polymeric supports are given in Table 2.

It can be seen that the practical results are in accordance with the relative reactivity of phosphonate carbanions towards aldehydes.

Table 2. Characteristics of copolymers obtained by Wittig-Horner reaction in PTC conditions.

Olefin grafted on polymer[a]	- R’’	-R’’’	mmoles double bonds/g of copolymer[f]	Yields (%)
I	- H[b]	- H	2.68	62.18
I	- H[c]	- H	1.96	45.48
I	- CHC_6H_5[d]	- H	2.16	50.12
I	$=CH_2$[e]	-	2.32	53.83
II	- H[b]	- H	0.91	40.44
II	- H[c]	- H	0.37	16.44
II	- CHC_6H_5[d]	- H	0.56	24.89
II	$=CH_2$[e]	-	0.75	33.33

[a] I- olefin grafted on styrene-6.7%divinylbenzene, II- olefin grafted on styrene-7%divinylbenzene,[b] R”: - H, from – dimethylmethylphosphonate; [c] R”: -H, from – diethylcianomethylphosphonate; [d] R”: - CHC_6H_5, from diethylbenzylphosphonate; [e] R”: $=CH_2$, from – diethylvinylphosphonat. [f] the values represent the difference between the total double bonds content and residual double bonds from supports (0.15 mmoles/ g. for S-6.7%DVB, 0.20 moles/g. for S-7%DVB)

Wittig-Horner reagents were used in olefination using PTC method in solid-liquid-solid (s-l-s) systems. In the order dimethyl methylphosphonate, diethyl cianomethylphosphonate, diethyl benzylphosphonate, diethyl vinylphosphonate the best functionalization degree were obtained with dimethyl methylphosphonate.

Conclusions

The proposed procedure for the preparation of benzaldehyde groups grafted on “macroporous-type” styrene-divinylbenzene copolymer by polymer-analogous reactions is simple and efficient.

The products obtained have all the needed characteristics which enable their use as Wittig-Horner reagents.

The introduction of a pendant double bond on macromolecular supports by Wittig-Horner reaction in PTC conditions has a lot of advantages as follows: high functionalization degree for obtaining of hypercrosslinkable supports; reaction takes place in multiphase system; the use of anhydrous potassium carbonate and tetrahydrofuran can be recommended.

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