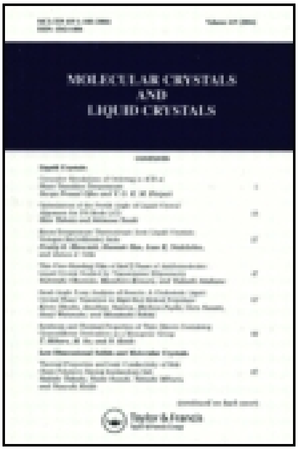

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Chemical Modification of Functionalized Copolymers with Phosphonium Groups by Phase Transfer Catalysed Wittig Reactions

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CHEMICAL MODIFICATION OF FUNCTIONALIZED COPOLYMERS WITH PHOSPHONIUM GROUPS BY PHASE TRANSFER CATALYSED WITTIG REACTIONS

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The interest for using polymers in Wittig reactions increased in the last years, because of their major advantages. Phase transfer catalyzed reactions are often more easily and cheaply carried out than conventional methods and they are therefore of particular interest. The phosphonium salts grafted on styrene-7%(5%) divinylbenzene copolymers used in this paper were obtained by quaternization polymer-analogous reaction. The degree of functionalization with quaternary phosphonium groups are relatively high, ranging from 1.84 to 1.98 mmoles/g of polymer. These grafted copolymers were used in liquid-liquid-solid Phase Transfer Catalysis (PTC) Wittig reaction. The yields were ranging from 1.84 to 1.98 mmoles of double bonds/gram of polymer.

INTRODUCTION

The Wittig reaction has been studied very extensively since its discovery, being the most important reaction in organic chemistry for obtaining alkenes. It was recognized as being the simplest and the most efficient method for synthesis of alkenes with unambiguous position of the double bond. Most of the studies of the Wittig reactions were carried out homogenously in organic solvents [1]. In contrast, less work has been reported for the heterogeneous Wittig reactions carried out in liquid-liquid and liquid – solid systems [2–8]. In spite of its use, there are still three major problems with the Wittig reaction. 1) The stereochemistry often cannot be controlled. 2) Ketones and hindered aldehydes fail to react with phosphorane that are hindered or stabilized by strongly electron withdrawing substitutes. 3) The by-product triphenylphosphine oxide can be difficult to separate from the alkene product. Polymer-supported Wittig reagents

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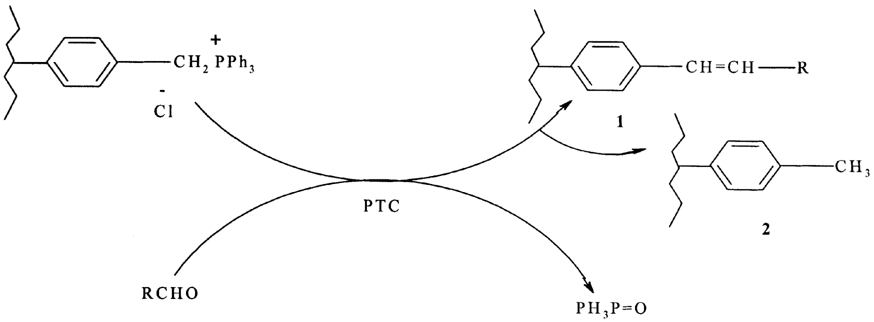


SCHEME 1

overcome the problem of separation of the triphenylphosphine oxide from alkene [9–10].

In this paper we present the use of styrene – divinylbenzene copolymer grafted with triphenylphosphonium salts in phase transfer catalyzed Wittig reaction in (**PTC**) liquid-solid system (Scheme 1).

The advantages of using the phase catalyzed Wittig reactions to modify styrene-divinylbenzene copolymers are as follows:

1. The reaction solvent need not be dry, a cheap base is used, and the reaction proceeds satisfactorily at 20°C.
2. The groups introduced are bound to the polymer by a linkage that is stable to both acid and base.
3. The phosphonium salt that do not react to give compound **1** gives compound **2** and the later will not interfere in subsequent applications.

The phosphonium salt grafted on styrene −7% (5%) divinylbenzene copolymers used in this paper were obtained by quaternization polymer-analogous reaction [11].

EXPERIMENTAL

Reagents

Grafted triphenylphosphonium chloride on styrene −7% (5%) divinylbenzene copolymers (phosphorus content: 6.12% and 5.59% respectively; functionalization degree: 1.98 mmoles P/g. copolymer and 1.84 mmoles P/g. copolymer), formaldehyde (Riedel- del Haën, 36,5%), acetaldehyde (BDH, 99%), salicylaldehyde (UCB, 99%), benzaldehyde (Fluka, 99%), isobutyraldehyde (Reactivul, p.a.), propionaldehyde (Fluka, 99%), methylene chloride (Reactivul, p.a.), sodium hydroxide (Reactivul, p.a.), tetrahexylammonium bromide (Fluka, 99% Bromide), ethanol (Reactivul, p.a.), acetone (Reactivul, p.a.), ethyl ether (Reactivul, p.a.), carbon tetrachloride (Reactivul, p.a.).

1. General Procedure for Wittig Reaction in Phase Transfer Catalysis Condition

A mixture of grafted triphenylphosphonium chloride on styrene −7% (5%) divinylbenzene copolymer (1 g), tetrahexylammonium bromide (0.1 g), methylene chloride (25 ml), 50% aqueous sodium hydroxide (10 ml) and an aldehyde (Table 1) were stirred 60 hours at room temperature, under nitrogen.

The final product was separated by filtration, washed with methylene chloride (3 × 20 ml), carbon tetrachloride (3 × 20 ml), acetone (3 × 20 ml), ethanol (3 × 20 ml), ethyl ether (3 × 20 ml) then dried under reduced pressure at 50°C for 24 hours.

2. Determination of the Double Bond Content

To a sample of final product, precisely weighted, (100–200 mg) 10 ml carbon tetrachloride, 10 ml distilled water, 20 ml 0.1 N $KBrO_3$ – KBr (0,008 g Br_2 in 1 ml solution) and 10 ml 10% H_2SO_4 were added. The mixture was kept under continuously stirring. After 2 hours another 2 ml 0.1 N $KBrO_3$ – KBr and 1 ml 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 iodine 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.

3. Determination of the Phosphorus Content

A sample of the final product precisely weighted was burnt out in oxygen atmosphere and P_2O_5 was absorbed in water. The solution was titrated

TABLE 1 The used Aldehydes

Aldehyde	mmoles aldehyde	Molar ratio aldehyde: $P^+(C_6H_5)_3Cl^-$
Formaldehyde	33.59	17:1
Acetaldehyde	33.59	17:1
Propionaldehyde	11.86	7:1
Isobutyaldehyde	11.86	7:1
Benzaldehyde	11.86	7:1
Salicylaldehyde	11.86	7:1

with an aqueous solution of cerium (III) 0.005 M in the presence of Eryochrome Black as indicator.

RESULTS AND DISCUSSION

The main processes in Wittig reaction are presented in Scheme 2.

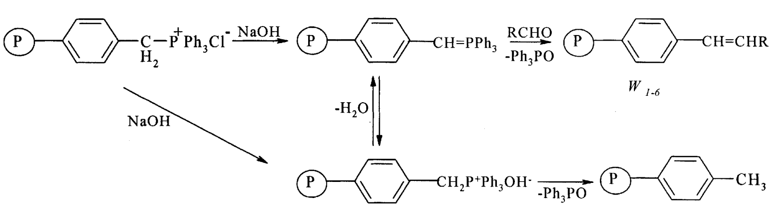
It could be admitted that statistical repetitive unit of modified copolymer through Wittig reaction and the side reaction led to a structure as is presented in Scheme 3.

The calculating method consists in solving a three equation system (1–4) knowing the functionalization degree with double bonds, phosphorus content in the final product, average molecular weight of functionalized copolymer and average molecular weight of starting copolymer, respectively.

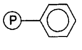
$$\%P_{rez} = \frac{(y - z - u) \cdot A_P}{M_{mf}} \times 100 \qquad (1)$$

where: $\%P_{rez}$ is the phosphorus content in the final product; y-z-u are fractions of units bearing pendant group $-P^+(C_6H_5)_3Cl^-$ (F_P), A_P is the atomic mass of phosphorus and M_{mf} is the average molecular weight of functionalized copolymer;

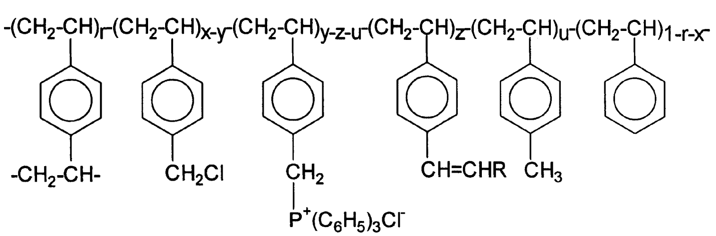
$$G_{Fz} = \frac{z}{M_{mf}} \qquad (2)$$



where:

 - stirene-divinylbenzene copolymer; Ph - phenyl; R - alkyl or phenyl radical; W_{1-6} - products.

SCHEME 2



SCHEME 3

where G_{Fz} is the degree of functionalization with F_z groups and z is fraction of units bearing pendant group $-CH = CHR$ (F_z)

$$M_{mf} = M_{mi} + z \cdot (M_{SFz} - M_{SFp}) + u \cdot (M_{SFu} - M_{SFp}) \tag{3}$$

where M_{mi} is the average molecular weight of starting copolymer, z is the fraction of units bearing pendant group $-CH = CHR$ (F_z), M_{SFz} is the molecular weight of functionalized unit F_z, M_{SFp} is the molecular weight of functionalized unit F_P, u is the fraction of units bearing pendant group $-CH_3$ (F_u) and M_{SFu} – molecular weight of functionalized unit F_u;

$$M_{mi} = r \cdot M_{DVB} + (x - y) \cdot M_{SFi} + y \cdot M_{SFp} + (1 - r - x) \cdot M_S \tag{4}$$

where r is fraction of units bearing divinylbenzene group, M_{DVB} is the molecular weight of divinylbenzene unit, x-y are fractions of units bearing pendant group $-CH_2Cl$ (F_i), M_{SFi} is the molecular weight of functionalized unit F_i, y is the initial fraction of units bearing pendant group $-P^+(C_6H_5)_3Cl^-$, M_{SFp} is the molecular weight of functionalized unit F_P, 1-r-x is the fraction of units bearing styrene group and M_S is molecular weight of styrene unit;

The functionalization degree with methyl group could be calculated using the Eq. (5):

$$G_{Fu} = \frac{u}{M_{mf}} \qquad \text{(mmoles } F_u\text{/g copolymer)} \tag{5}$$

where G_{Fu} is the functionalization degree with F_u groups and u is the fraction of units bearing pendant group $-CH_3$ (F_u);

The yields in functionalization with double bonds and methyl groups can be calculated with Eqs. (6) and (7).

$$\eta_{Fz} = \frac{z}{y} \times 100 \qquad \text{(mol\%)} \tag{6}$$

where: η_{Fz} is the yield of main Wittig reaction and z is the fraction of units bearing pendant group –CH = CHR (F_z) and y is the initial fraction of units bearing pendant group $-P^+(C_6H_5)_3Cl$.

The yield of side reaction.

$$\eta_{Fu} = \frac{u}{y} \times 100 \qquad (\text{mol\%}) \tag{7}$$

where is the fraction of units bearing pendant group –CH_3 (F_u) and y is the initial fraction of units bearing pendant group $-P^+(C_6H_5)_3Cl^-$;

In syntheses were used triphenylphosphonium chloride grafted on styrene-7% divinylbenzene (Q_1P.A) and triphenylphosphonium chloride grafted on styrene-5% divinylbenzene (Q_1P.B), respectively.

In Table 2 is presented the phosphorus content from the functionalized copolymer used in Wittig reaction, determined by modified Schöniger method.

In the limit of experimental errors, in Table 3 are presented the obtained results in characterization of grafted copolymers with double bonds obtained by Wittig reaction.

Polymer-analogous Wittig reaction in PTC condition gives good yields in syntheses S_1–S_4 and S_8–S_{10}, when aliphatic aldehydes were used in contrast with syntheses S_1 and S_7 in which formaldehyde was used.

TABLE 2 The Phosphorus Content of the Functionalized Copolymer

Product[a]	R	P_{in}(%)[b]	P_{rez}(%)[c]
W_1.A	–H	6.12	1.78
W_2.A	–CH_3	6.12	3.60
W_3.A	–CH_2CH_3	6.12	4.13
W_4.A	–$CH(CH_3)_2$	6.12	2.52
W_5.A	–C_6H_5	6.12	3.86
W_6.A	–C_6H_4OH	6.12	2.37
W_1.B	–H	5.59	2.53
W_2.B	–CH_3	5.59	3.67
W_3.B	–CH_2CH_3	5.59	3.04
W_4.B	–$CH(CH_3)_2$	5.59	2.72
W_5.B	–C_6H_5	5.59	3.61
W_6.B	–C_6H_4OH	5.59	1.79

Where: [a]A-styrene – 7% divinylbenzene copolymer; B-styrene – 5% divinylbenzene copolymer; [b]phosphorus content in initial polymer; [c]phosphorus content in final product.

TABLE 3 Characteristics of Copolymers Obtained by Wittig Reaction in PTC Conditions

						mmoles/ g. copol.		M_{mf}	η_F(%)	
Synt	Prod[a]	x	y	z	U	CH = CHR[b]	$-CH_3$	(grams)	CH = CHR	$-CH_3$
S_1	W_1.A	0.64	0.56	0.07	0.40	0.48	2.74	145.92	12.50	71.43
S_2	W_2.A	0.64	0.56	0.20	0.14	1.059	0.74	188.81	35.72	25.00
S_3	W_3.A	0.64	0.56	0.20	0.20	1.15	1.15	173.83	35.71	35.71
S_4	W_4.A	0.64	0.56	0.22	0.20	1.28	1.16	171.78	39.29	35.71
S_5	W_5.A	0.64	0.56	0.26	0.02	1.16	0.09	224.28	46.43	3.57
S_6	W_6.A	0.64	0.56	0.22	0.20	1.20	1.09	182.78	39.30	35.71
S_7	W_1.B	0.57	0.47	0.05	0.28	0.29	1.63	171.53	10.64	59.57
S_8	W_2.B	0.57	0.47	0.15	0.10	0.81	0.54	185.84	31.91	21.28
S_9	W_3.B	0.57	0.47	0.16	0.14	0.92	0.81	173.52	34.04	29.79
S_{10}	W_4.B	0.57	0.47	0.18	0.14	1.05	0.82	170.91	38.29	29.79
S_{11}	W_5.B	0.57	0.47	0.21	0.02	1.02	0.097	206.35	44.68	4.26
S_{12}	W_6.B	0.57	0.47	0.18	0.22	1.15	1.41	156.21	38.30	46.8

Where: [a]A-for S-7% DVB; B-for S-5% DVB.

In syntheses S_5, S_{11} and S_6, S_{12}, respectively, when was used benzaldehyde and salicylaldehyde a weak increase of yields were observed than in syntheses with acetaldehyde, propionaldehyde and isobutyl aldehyde.

The functionalization degrees with double bonds are higher and vary between 0.82 for S_8 and 1.28 for S_4 mmoles/gram copolymer, except syntheses (S_1) and (S_7), when functionalization degrees were 0.48 and 0.29 mmoles/gram copolymer, when formaldehyde was used.

CONCLUSION

The introduction of a pendant double bond on macromolecular supports by Wittig reaction in PTC conditions has a lot of advantages as follows:

- High yields and functionalization degree for a polymer-analogous reaction;
- Products with high degree of pendant groups per mass unit of polymer support;
- Reaction takes place at room temperature in three phase system;
- The use of aqueous sodium hydroxide and methylene chloride can be recommended, the yields and functionalization degrees being high for all aldehydes used.

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