Styrene-divinylbenzene copolymer grafted with phosphonic acid dialkylesters

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Abstract: The functionalization of a crosslinked chloromethylated polystyrene 8% divinylbenzene copolymer with phosphonic ester groups is detailed. The reacton conditions were studied in order to determine the optimal conditions for obtaining only diesters. A statistical method for the calculation of the fraction of repetive units for the inited and final resin is proposed.

*Keywords:* styrene–divinylbenzene, chloromethylated, phosphonic acid dialkylester.

INTRODUCTION

One of the important fields in polymers chemistry is the investigation of the reactivity of syrene-divinylbenzene copolymers for grafting homogenous or enzymatic catalysts onto them or as support for the synthesis of peptides and nucleotides.[1,2] Phosphorus grafted onto polymers are important in catalysis, organic synthesis, trace analysis and environmental separations. Polymers with phosphorus-based ligands displey unique selectivity for metal ions. The ion-exchange reacton is an extremely versatile reaction and one that is well-suited for the complexation of cations and anions through electrostatic bonding.[3,4] Alexandratos and coworkers[5] obtained phosphorylated styrene-divinylbenzene copolymer having a mixture of grafted phosphonic groups (phosphonic acid, phosphonic acid diethylester, or acid-ester).

In this paper some results on the synthesis of styrene-divinylbenzene copolymer grafted with phosphonic dialkylesters using a modified Kinnear-Perren-Klay method are presented (Scheme 1).[6, 7]
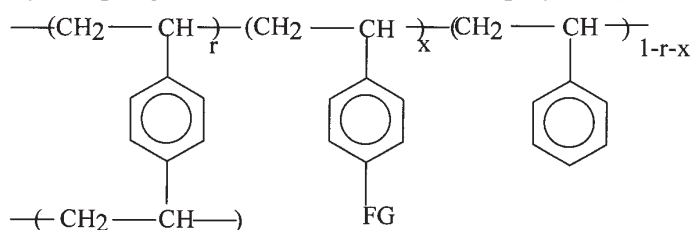
THEORY

Chloromethylated styrene – 8 % divinylbenzene copolymer (16.5 % Cl) was used as the starting material in all synthesis. The fraction of the repetitive units was

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R= CH₃;C₂H₅;C₃H₇;C₄H₉;ClC₂H₄
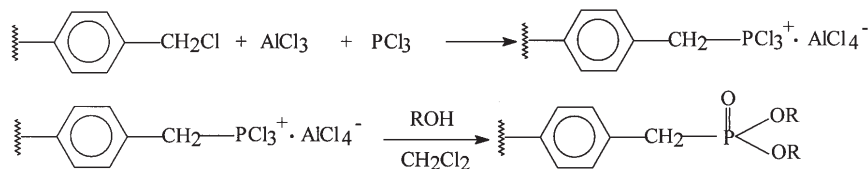
Scheme 1.

determined by accepting the statistical sructure of the polymer (Scheme 2).

where: *r*–fraction of divinylbenzene units; *x*–fraction of units bearing pendant group; 1–*r*–*x*–fraction of styrene units; FG–functional group

Scheme 2.

For this structure, the average molecular weight (M_m) can be calculated (Eq. (1)).

$$M_m = r\, M_{DVB} + x\, M_{SFG} + (1 - r - x)\, M_s \qquad (1)$$

M_{DVB}– molecular weight of divinylbenzene unit; M_{SFG}– molecular weight of functionalized unit; M_S– molecular weight of styrene unit.

For the determination of the functionalization degre (F_D) of a polymer and statistical modeling of the functionalized repeating unit, it is necessary to determine an element E in the functional group. In this work, chlorine was determined in the initial and final polymer and phosphorus in the final product.

Expressing the percent of E as (Eq. 2)

$$\%E = \frac{x A_E}{M_m} \qquad (2)$$

A_E–atomic mass of the element E from function group FG.

The fraction of functionalized styrene units can be calculated using Eq. (3):

$$x = \frac{\%E(1 - r)M_x + \%ErM_{DVB}}{100A_E + \%E(M_{SFG} - M_s)} \qquad (3)$$

and the functionalization degree can be calculated using Eq. (4):

$$F_D = \frac{x}{M_m} \qquad (4)$$

Using the same method the theoretical content of phosphorus in the final

phosphorilated polymer can be calculated. For the phosphorilated polymer, the fraction of the repetitive units was determined by accepting the statistical structure (Scheme 3).
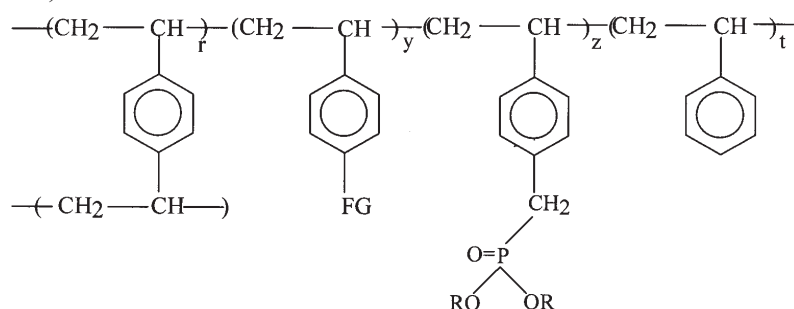
where: r – fraction of divinylbenzene units (0.08); y–fraction of units bearing pendant group FG (chloromethyl group); z – fraction of of units bearing phosphonic group; t – fraction of styrene units; Scheme 3.

For this structure, the average molecular weight (M_{mp}) can be calculated Eq. (5):

$$M_{mp} = r\,M_{DVB} + y\,M_{SFG} + zM_p + t\,M_S \tag{5}$$

M_{DVB}– molecular weight of divinylbenzene unit; M_{SFG}– molecular weight of functionalized unit; M_p– molecular weight of phosphorylated unit; M_S– molecular weight of styrene unit

The chlorine and phosphorus contents in the product were calculated using Eq. (6), respectively:

$$\%Cl = \frac{yA_p}{M_{mP}} \cdot 100 \tag{6}$$

$$\%P = \frac{zA_p}{M_{mP}} \cdot 100 \tag{7}$$

A_{Cl}–atomic mass of chlorine; A_p–atomic mass of phosphorus

Using any of these systems:

(1)   or, (2)

$$M_{mP} = 39.52 + 152.46\ y + z\ M_p \qquad M_{mP} = 39.52 + 152.46\ y + z\ M_P$$

$$\%Cl = \frac{yA_{Cl}}{M_{mP}} \cdot 100 \qquad\qquad \%Cl = \frac{yA_{Cl}}{M_{mp}} \cdot 100$$

$$\%P = \frac{zA_P}{M_{mP}} \cdot 100 \qquad\qquad y + z = 0.64$$

or, (3)

$$M_{mP} = 39.52 + 152.46\,y + z\,M_P$$

$$\%P = \frac{z \cdot A_P}{M_{mP}} \cdot 100$$

$$y + z = 0.64$$

The functionalization degree of the final product can be calculated using Eq. (8)

$$F_{FD} = \frac{z}{M_{mP}} \cdot 1000 \qquad (mmol/g) \qquad\qquad (8)$$

EXPERIMENTAL

Reagents

Chloromethylated styrene-divinylbenzene copolymer ("P.Poni" Research Institute, Iassi), phosphorus trichloride (Aldrich), aluminium chloride (Aldrich), dihloromethane (Chemopar-Romania) and 36 % hydrochloric acid (Chemopar-Romania) were used.

Synthesis of the functionalized polymers

A mixture of 10 g (0.0466 mol) chloromethylated copolymer, 63g (40.6ml, 0.466 mol) phosphorus trichloride was stirred for 2 h at room temperature in order to swell the copolymer beads, then 6.2 g (0.0466 mol) aluminium chloride were added and the mixture was stirred at a certain temperature for different periods of time. The excess of phosphorus trichloride was filtered off, the complex was washed with dichloromethane and then is diluted with 100 ml dichloromethane and the alcohol was added dropwise keeping the temperature below 5 °C. The mixture was stirred for a certain time at 5 °C. The aluminium chloride was hydrolyzed with dilute hydrochloric acid; the product washed with water till no chlorine cound be determined. The product was washed with acetone and dried at 50 °C for 6 h.

Determination of the phosphorus content

Precisely weighed a sample of the final product was burnt out in an oxygen atmosphere and the formed P_2O_5 was absorbed in water. The solution was titrated with an aqueous solution of cerium (III) 0.005 M in the presence of Eryochrome Black as indicator.

Determination of the chlorine content

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

RESULTS AND DISCUSSION

The initial characteristics of the chloromethylated styrene-divinylbenzene copolymer were: $M_{DVB} = 130$; $M_{SFG} = 152.46$; $M_S = 104$; $A_E = A_{Cl} = 35.46$; The fraction of chloromethylated styrene can be calculated using Eq. (3). The chloromethylated styrene-divinylbenzene copolymer used in all the syntheses had 8% divinylbenzene and 16.55 % chlorine. The characteristics of the copolymer are given in Table I.

The reacton conditions for the complexation step are presented in Table II. The complexes used in syntheses of the grafted copolymers were methyl and ethyl esters of phosphonic acid in order the chose the optimal reaction conditions for further esters.

TABLE I. The characteristics of the chloromethylated styrene- 8%divinylbenzene copolymer

Property	Chloromethylated styrene - 8%divinylbenzene copolymer
Monomolecular volume adsorbed: V_m, cm^3/g	8.89
Specific surface: S, m^2/g	29.6
Total volume of pores: V_p, cm^3/g	0.40
% Cl	16.55
Fraction of chloromethylated units: E	0.64
Average molecular weight of repetitive unit: M_m	137.94
Functionalization degree: F_D, mmol/g	4.66

TABLE II. Reaction condition for the synthesis of the complexes

Code	Mole ratio Copolymer/PCl$_3$/AlCl$_3$	Complexation temp./°C	Reaction time h
C1	1/10/1.2	40	2
C2	1/10/1.2	60	2
C3	1/10/1.2	40	4
C4	1/10/1.2	60	4

The reaction conditions and results of the synthesis of methyl and ethyl esters are presented in Table III.

TABLE III. Reaction condition and results of the synthesis of methyl and ethyl esters

Code	Alcohol	Complex	Mole ratio complex/alcohol	Reaction time h
ME1			1/4	10
ME2				15
ME3		Cl	1/6	10
ME4	CH$_3$OH			15
ME5			1/4	10
ME6				15
ME7		C2	1/6	10
ME8				15

TABLE III. Continued

Code	Alcohol	Complex	Mole ratio complex/alcohol	Reaction time h
ME9			1/4	10
ME10		C3		15
ME11			1/6	10
ME12	CH_3OH			15
ME13			1/4	10
ME14		C4		15
ME15			1/6	10
ME16				15
EE1			1/4	10
EE2		C1		15
EE3			1/6	10
EE4				15
EE5			1/4	10
EE6		C2		15
EE7			1/6	10
EE8	CH_3CH_2OH			15
EE9			1/4	10
EE10		C3		15
EE11			1/6	10
EE12				15
EE13			1/4	10
EE14		C4		15
EE15			1/6	10
EE16				15

The characteristics of the functionalized copolymers are presented in Table IV.

The phosphorus content of the complexes C2 and C4 are higher than those of C_1 and C_3. The complexation time has no significant influence on the phosphorus content. The esterification time and the mole ratio influence the phosphorus content in the final product.

The best results were obtained for the syntheses ME16 and EE16, when the phosphorus content was the highest under the presented conditions. From the results presented in Table IV it can be seen that good correlation was obtained between the statistical method and the experimental data.

TABLE IV. The characteristics of the functionalized copolymers

Code	Chlorine determined in the final product/%	y	z	P, calculated/%	P, determined/%	F_{FD}, theoretical mmol/g	F_{FD}, determined mmol/g
ME1	7.45	0.33	0.31	6.27	6.20	2.00	2.00
ME2	7.20	0.30	0.34	6.87	6.81	2.21	2.20
ME3	7.00	0.30	0.34	6.87	6.80	2.21	2.20
ME4	6.75	0.29	0.35	7.07	7.00	2.29	2.20
ME5	6.35	0.27	0.38	7.48	7.40	2.25	2.40
ME6	5.60	0.24	0.40	8.08	7.95	2.60	2.60
ME7	5.15	0.22	0.42	8.50	8.65	2.74	2.80
ME8	4.80	0.21	0.43	8.70	8.75	2.80	2.80
ME9	6.20	0.26	0.38	7.60	7.65	2.40	2.50
ME10	5.95	0.26	0.38	7.60	7.70	2.48	2.50
ME11	5.50	0.24	0.40	8.08	7.95	2.61	2.60
ME12	5.15	0.22	0.42	8.50	8.65	2.74	2.80
ME13	4.80	0.21	0.43	8.70	8.85	2.80	2.90
ME14	4.30	0.18	0.46	9.30	9.40	3.00	3.00
ME15	4.00	0.17	0.47	9.50	9.60	3.06	3.10
ME16	3.70	0.16	0.48	9.70	9.75	3.10	3.10
EE1	7.70	0.37	0.27	5.10	5.20	1.58	1.67
EE2	6.87	0.33	0.31	5.63	5.70	1.82	1.84
EE3	6.04	0.29	0.35	6.58	6.65	2.05	2.15
EE4	5.60	0.27	0.37	6.73	6.80	2.17	2.20
EE5	7.78	0.23	0.41	7.45	7.60	2.41	2.45
EE6	4.37	0.21	0.43	7.82	7.90	2.52	2.55
EE7	3.74	0.18	0.46	8.65	8.75	2.70	2.82
EE8	3.33	0.16	0.48	8.73	8.80	2.87	2.84
EE9	5.20	0.25	0.39	7.09	7.20	2.29	2.32
EE10	4.78	0.23	0.41	7.45	7.65	2.41	2.47
EE11	4.16	0.20	0.44	8.00	8.15	2.58	2.63
EE12	3.74	0.18	0.46	8.90	9.00	2.88	2.90
EE13	3.10	0.15	0.46	8.90	9.00	2.88	2.90
EE14	2.70	0.13	0.51	9.27	9.35	2.99	3.02
EE15	2.50	0.12	0.52	9.45	9.60	3.05	3.10
EE16	2.10	0.10	0.54	9.80	9.90	3.17	3.20

A esterification temperature along reacton time and an excess of alcohol were used in order to obtain only diesters (the acidity indexes were below 1.5 mg KOH/g). For further phosphorylation, the chosen conditions for complex C_4 were molar ratio complex: alcohol of 1:6 an esterification time of 15 hours and a reaction temperature below 5 °C.

The same conditions were used for the synthesis of the other phosphonic esters grafted on the styrene-divinylbenzene copolymer. The obtained results are presented in Table V.

TABLE V. The characteristic of the final products

Code	Chlorine determined in the final product/%	y	z	P calculated/%	P determined/%	F_{FD} calculated mmol/g	F_{FD} determined mmol/g
PE	4.5	0.24	0.40	6.55	6.80	2.11	2.19
BU	4.7	0.26	0.38	5.90	6.20	1.93	2.00
PN	5.2	0.30	0.34	4.65	4.90	1.50	1.58

For all compounds, the phosphorus content was lower than theoretical but satisfactory taking in consideration the length of the alkyl chains of used alcohols and the characteristics of the initial copolymer.

The chemcial modification of the styrene – divinylbenzene copolymer and the nature of the final products were also confirmed by IR spectroscopy. The presence of a band between 1225 and 1282 cm^{-1} confirms the formation of $P = O$ bands in all the compounds. The P–O–C (aliphatic) group is characterized by a strong absorption bandt at 1010 cm^{-1} for the methyl ester, 1030 cm^{-1} for the ethyl ester, 1000 cm^{-1} for the propyl ester, 1025 cm^{-1} for the butyl ester and 1030 cm^{-1} for the pentyl ester. A second absorption band which further characterizes these compounds lies between 939 cm^{-1} and 970 cm^{-1}. These bands in the spectra of the butyl and pentyl esters were weaker in intesity. Also the band at 1430 cm^{-1} (CH_2O) in the untial copolymer decreased in intensity in the spectra of the final products.

CONCLUSIONS

The synthesis of styrene – 8 % divinylbenzene copolymers grafted with phosphonic acid dialkylesters has been described. The phosphorus content is lower than theoretical but satisfactory and depends on the complexation temperature, esterification time and reaction temperature. The best results were obtained under the following conditions: complex C4; mole ratio complex: alcohol = 1:6; esterification tiem 15 h; reaction temperature below 5 °C. The statistical method gave good correlation with the experimental results and can be successfully used for further studies. The best degrees of functionalization were obtained for ME16 and EE16.

ИЗВОД

СТИРЕН-ДИВИНИЛБЕНЗЕН КОПОЛИМЕР КАЛЕМЉЕН ДИАЛКИЛЕСТРОМ ФОСФОНСКЕ КИСЕЛИНЕ

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Детаљно је приказана деривација умреженог хлорометилованог полистирен-8% дивинилбензен кополимера са фосфонским естарским групама. Одређени су услови реакције који дају оптималне услове за добијање само диестара. Предложена је статистичка метода за израчунавање фракције основних јединица код почетне и крајње смоле.

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REFERENCES

1. C. N. K. Mather, C. K. Harang, *Polymers as Aids in Organic Chemistry,* Academic Press, New York, 1980
2. P. Hodge, D. S. Sherrington, *Polymer-suported. Reaction in Organic Synthesis*, Wiley, London, 1980
3. T. Sekine, Y. Hasagawa, *Solvent Extraction Chemistry*, M. Dekker, New York, 1977
4. M. E. Bates, S. D. Alexandratos, *Macromolecules* **21** (1988) 2905
5. S. A. Alexandratos, D. R. Quillen, M. E. Bates, *Macromolecules* **20** (1987) 191
6. J. P. Clay, *J. Org. Chem.* **16** (1951) 892
7. A. M. Kinnear, E. A. Perren, *J. Am. Chem. Soc.* (1952) 3437.