

Synthesis of Aminophosphonates Grafted on Styrene Divinylbenzene Copolymer

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A simple, efficient and general one-pot method has been developed for the synthesis of aminophosphonates grafted on styrene-divinylbenzene copolymers from benzaldehyde grafted on styrene-divinylbenzene copolymer with amines and diethyl phosphite in tetrahydrofuran. The aminophosphonates grafted on insoluble macromolecular supports were characterized by infrared spectroscopy, thermogravimetric analysis and scanning electron microscopy.

Keywords: aminophosphonate groups, styrene-divinylbenzene copolymers

The Kabachnik - Fields reaction is important for the synthesis of α -aminophosphonates, which have applications in the environmental recovery of metal ions. It is also well known that α -aminophosphonates and α -aminophosphonic acids, being structural analogs of α -aminocarboxylic acids, exhibit various biological activities [1-3].

Synthesis of α -aminophosphonates on basis of the Kabachnik - Fields reaction is realized by condensation of a carbonyl compound with a primary amine and a dialkyl phosphite.

The first one-pot synthesis of α -amino phosphonates has been achieved by the reaction of phosphite in the presence of lanthanide triflate [4] as the catalyst with imines generated in situ from aldehydes and amines in organic solvent.

In literature the synthesis of modified polymers with phosphonic acid groups [5, 6], phosphonate groups [7 - 10] and aminoalkylphosphonic groups [11] is mentioned.

In the current research, we have introduced aminophosphonates grafted on styrene-divinylbenzene copolymers through „one-pot” Kabachnik—Fields reaction.

Aminophosphonate resins could be used as potential sorbents in the removal of heavy metal ions from various wastewaters.

Experimental part

Reagents

Isopropylamine (Fluka), propylamine (Fluka), butylamine (Loba), ortho-chloroaniline (Loba), tetrahydrofuran (Fluka), diethylphosphite (Fluka), 1,2-dichloromethane (Chimopar), ethanol (Chimopar), diethyl ether (Chimopar), chloromethylated styrene-divinylbenzene copolymer was used as starting material and was supplied by Purolite Romania (S-6.7%DVB, %Cl= 14.22, $G_F = 4.01$ mmoles Cl/g. copolymer).

Preparation of aminophosphonates grafted on styrene-divinylbenzene

The „one-pot” Kabachnik-Fields reaction was carried out in a 100 mL round bottom flask fitted with reflux condenser, mechanical stirrer and thermometer.

The mixture of 4 g of benzaldehyde grafted on styrene-divinylbenzene copolymer [12] (4.31 mmoles -CHO /g of copolymer (B1)) and 50 mL THF (tetrahydrofuran) was

maintained under stirring for 2 h at room temperature to allow the copolymer beads to swell then the phosphite and amine (isopropylamine, propylamine, butylamine, ortho-chloroaniline) were added. The molar ratio of -CHO groups : diethylphosphite : amine (isopropylamine, propylamine, butylamine, ortho-chloroaniline) was 1:1:1.

The final mixture was maintained under stirring for 20 h at a temperature of 80°C.

After cooling, the final products were separated by filtration, washed with ethanol (3 . 20 mL), 1,2-dichloromethane (3 . 20 mL) and diethyl ether (3 . 20 mL), then dried under a vacuum at 50°C for 24 h.

Determination of the phosphorus content

The phosphorus content of the polymer-supported aminophosphonates was obtained according to the method previously described [9, 10]. The phosphorus content of the polymer-supported phosphonates was obtained by adsorption in water of the P_2O_5 obtained from a sample of the final product precisely weighed and burnt out in an oxygen atmosphere. The solution obtained was titrated with an aqueous solution of $(NH_4)_2Ce(NO_3)_6$ 0.005 M in the presence of Eryochrome Black T as indicator.

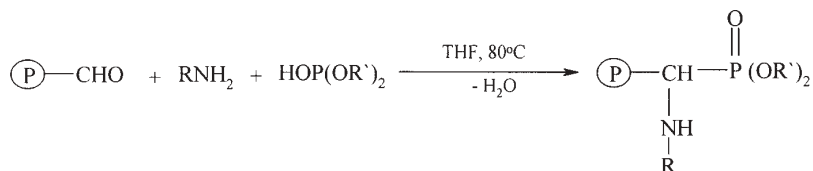
Characterization

The obtained materials were characterized by Fourier transform infrared spectroscopy with a spectrophotometer Shimadzu FTIR, scanning electron microscopy (SEM) with a Philips XL-20 microscope. Thermal properties of the aminophosphonates grafted on insoluble macromolecular supports were characterized through thermogravimetric analysis (TGA) and differential thermal analysis (DTA), which were performed on a TGA/SDTA 851-LF1100 - Mettler apparatus at a heating rate of 10 °C/min under N_2 atmosphere and temperature range from 20 to 600 °C.

Results and discussions

Benzaldehyde grafted on styrene-divinylbenzene copolymer (B1) with the main characteristics: Cl_f (%) = 0.178, $x = 0.527$, $y = 0.520$, G_F (mmoles -CHO /g of copolymer) = 4.31, $M_{mf} = 120.662$; (where: % Cl_f - chlorine percentage in the final copolymer, x - fraction of styrene units bearing pendant -CH₂Cl groups, y - fraction of styrene units bearing pendant -CHO groups, G_F - functionalization degree, M_{mf} - average molecular weight of the repetitive unit of the final copolymer) was used in polymer-analogous

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Where: (P) - copolymer styrene-6.7%divinylbenzene; R-NH₂= propylamine, isopropylamine, butylamine, ortho-chloroaniline, HOP(OR')₂= diethylphosphite.

Scheme 1. Preparation of aminophosphonates grafted on styrene-divinylbenzene (1B1, 2B1, 3B1, 4B1)

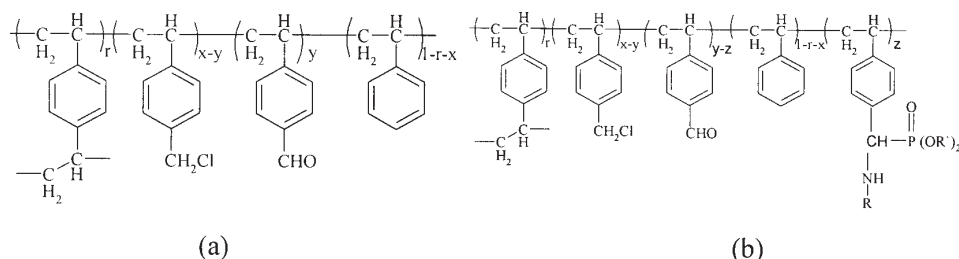


Fig. 1. Statistical structure of the repetitive unit of the functionalized copolymer initial (a, (B1)) and final (b, (1B1, 2B1, 3B1, 4B1))

reactions and its obtaining is described in previous articles [12, 13].

Aminophosphonates grafted on styrene-divinylbenzene copolymers were obtained through „one-pot” Kabachnik–Fields reaction (scheme 1).

The fraction of the repetitive units functionalized with aminophosphonates groups was determined by accepting the statistical structure of the repeat unit of the initial (I) and final copolymer (F), presented in figure 1.

In the statistical calculation [14] of the fraction of the styrene units bearing pendant aminophosphonates groups was used the notation:

- x-y - fraction of styrene units bearing pendant -CH₂Cl groups;
- y-z - fraction of styrene units bearing -CHO groups (F_i);
- z - fraction of styrene units bearing aminophosphonates groups (F_f);
- %P - phosphorus percentage in the final copolymer;
- M_{DVB} - molecular weight of the repetitive unit of the divinylbenzene;
- M_{SFi} - molecular weight of the repetitive unit of the styrene functionalized with F_i groups;
- M_{SFf} - molecular weight of the repetitive unit of the styrene functionalized with F_f groups;
- M_S - molecular weight of the repetitive unit of the styrene;
- 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;
- r - fraction of divinylbenzene (DVB) units;

- A_p - atomic weight of phosphorus; n_p - number of phosphorus atoms in the pendant groups;
- G_F - functionalization degree.

The phosphorus content in the functionalized copolymers was used in order to determine the fraction of styrene units bearing aminophosphonates groups (F_f) and was calculated with the equation (1):

$$z = \frac{\%P \cdot M_{mi}}{100 \cdot n_p \cdot A_p - \%P \cdot (M_{SFf} - M_{SFi})} \quad (1)$$

where:

$$M_{mi} = r \cdot M_{DVB} + (x-y) \cdot M_{SFCH_2Cl} + y \cdot M_{SFCHO} + (1-r-x) \cdot M_S \quad (2)$$

The functionalization degree (G_F) and yields with aminophosphonate groups was calculated with equations (3 and 5):

$$G_F = z / M_{mf} \text{ (mmoles groups Ff/gram copolymer)} \quad (3)$$

where:

$$M_{mf} = M_{mi} + z \cdot (M_{SFf} - M_{SFi}) \quad (4)$$

$$\eta_F = z / y \cdot 100 \text{ (\%)} \quad (5)$$

The main characteristics of the aminophosphonate groups grafted on polymeric support by “one-pot” polymer-analogous reactions are given in table 1.

The phosphorus content in the functionalized copolymers was used in order to determine their functionalization degrees and yields.

Table 1
CHARACTERISTICS OF AMINOPHOSPHONATES GRAFTED ON
STYRENE-6.7%DIVINYLBENZENE COPOLYMERS

No. Synt	Code prod	R-NH ₂	R' din HOP(OR') ₂	P (%)	z	G _F (mmoles/g)	η _F (%)
1	1B1	CH ₃ CH ₂ CH ₂ -NH ₂	(C ₂ H ₅ O) ₂ POH	5.56	0.30	1.78	57.69
2	2B1	(CH ₃) ₂ CH-NH ₂	(C ₂ H ₅ O) ₂ POH	5.91	0.33	1.90	63.46
3	3B1	CH ₃ (CH ₂) ₂ CH ₂ -NH ₂	(C ₂ H ₅ O) ₂ POH	4.35	0.23	1.39	44.23
4	4B1	o-Cl-C ₆ H ₄ -NH ₂	(C ₂ H ₅ O) ₂ POH	4.24	0.25	1.36	48.07

As observed from data presented in table 1, the proposed synthesis procedures produced in all cases the desired products, such as aminophosphonate grafted polymer.

The degrees of functionalization with aminophosphonates groups are relatively high, ranging from 1.36 – 1.90 mmoles of functional groups / g. of copolymer.

The aminophosphonate polymeric samples (1B1, 2B1) showed the decrease in the intensity of benzaldehyde groups adsorption bond at 1690 corresponding to $\nu\text{C}=\text{O}$ indicated in figure 2.

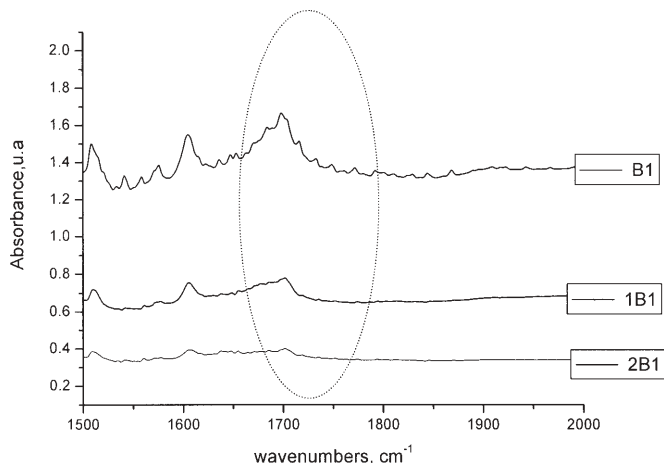


Fig. 2. IR- spectra of polymer-supported aldehyde B1 and polymer-supported aminophosphonates 1B1 and 2B1

The morphology of the polymer support after first step of functionalization was characterized by scanning electron microscopy (fig. 3). Spherical particles and pores between them are typically for a microporous material.

The morphology of styrene-divinylbenzene copolymers with aminophosphonate groups grafted (fig. 4) is a result of particles agglomeration.

The decomposition temperatures of aminophosphonate polymers are presented in table 3.

The thermogravimetric analysis shows a modification of thermal stability of aminophosphonate polymers compared with polymer-supported aldehyde (B1). The thermal stability of the materials, 1-4 from table 3, is a function of functionalization degree with aminophosphonate groups so that the thermal stability increases with increase of functionalisation degree (G_F).

Figure 5 shows the DTA-TG curves for sample 1B1. A weight loss less than 5 wt% before 200°C is due to evaporation of physically absorbed water in the polymers.

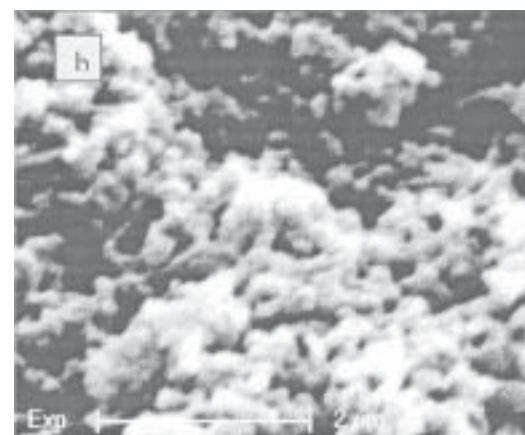


Fig. 3 SEM images of the polymer-supported aldehyde B1

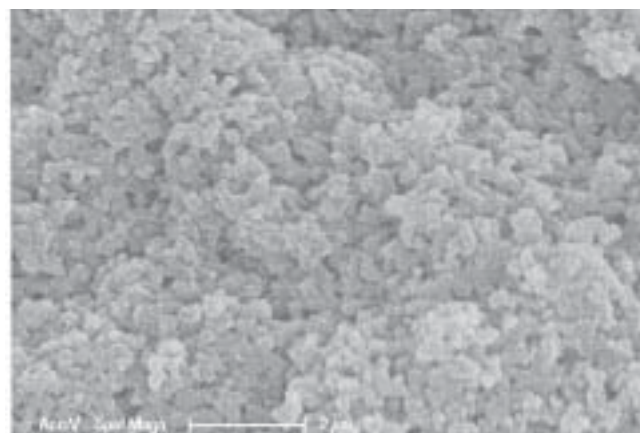


Fig. 4. SEM image of the polymer-supported 3-aminoisopropyl-diethylphosphonates 2B1

Table 3
THE DECOMPOSITION TEMPERATURE AS FUNCTION OF FUNCTIONALIZED DEGREE OF POLYMER-SUPPORTED AMINOPHOSPHONATE

No.	Code prod	phosphite	R-NH ₂	Td ^a °C	G _F ^b (mmoles/g)
0	B1	-	-	407.6	4.31
1	1B1	(C ₂ H ₅ O) ₂ POH	CH ₃ CH ₂ CH ₂ -NH ₂	420.9	1.78
2	2B1	(C ₂ H ₅ O) ₂ POH	(CH ₃) ₂ CH-NH ₂	422.4	1.90
3	3B1	(C ₂ H ₅ O) ₂ POH	CH ₃ (CH ₂) ₂ CH ₂ -NH ₂	420.2	1.39
4	4B1	(C ₂ H ₅ O) ₂ POH	o-Cl-C ₆ H ₄ -NH ₂	419.7	1.36

^aTd – decomposition temperature, (°C). ^bG_F: (0) -CHO and (1-4) aminophosphonates.

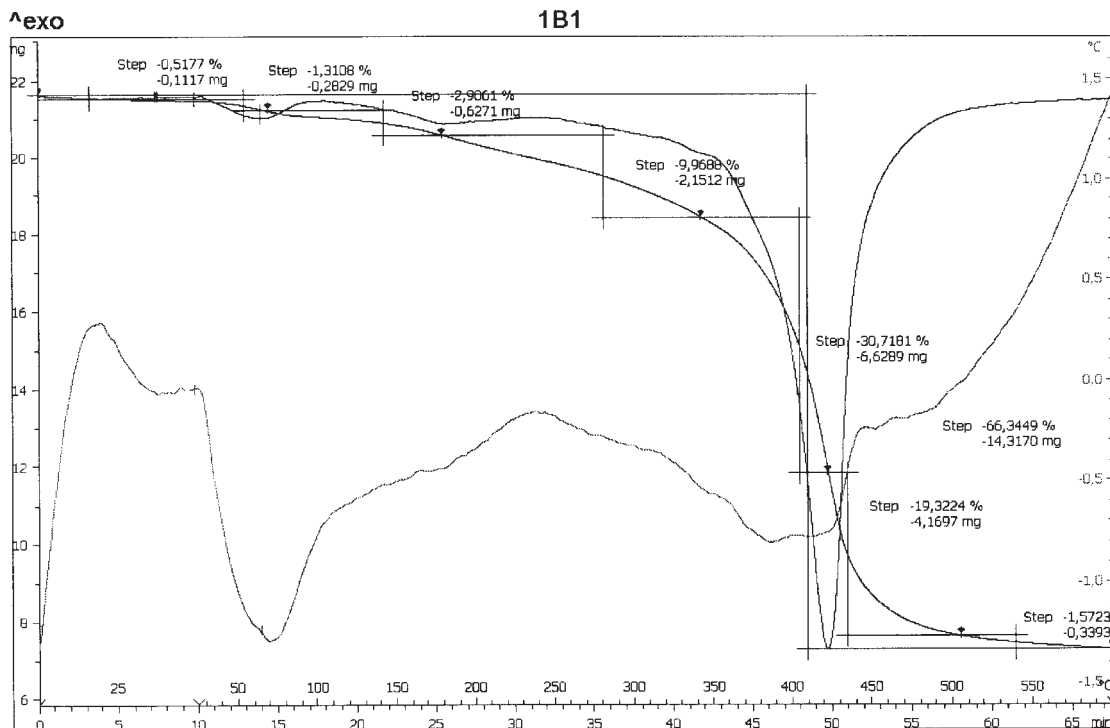


Fig. 5. DTA, TG, DTG curves for sample: 1B1

Two peaks at around 300°C and 420°C with a weight loss are seen, which we propose to be attributed to the decomposition of the side groups and main chain in the polymer phase, respectively.

Conclusions

The proposed procedure for the preparation of new aminophosphonates grafted on styrene-divinylbenzene copolymers by „one-pot” Kabachnik—Fields reaction is simple and efficient for application as supports or adsorbents.

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