

THERMAL BEHAVIOR OF THE COPOLYMERS BASED ON STYRYLPHOSPHONIC ACID

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ABSTRACT

The main property of copolymers containing phosphonic acid group at side chain is the proton conductivity, therefore these copolymers have strong metal complexation properties, due to the presence of phosphonic group.

The copolymers of styrylphosphonic acid and acrylic monomer at different molar ratios were synthesized by thermal polymerization and characterized by FTIR, thermal analysis and ion-exchange capacity. The copolymers present good ion-exchange capacity and can be used as potential ion exchangers.

INTRODUCTION

Functionalized crosslinked polymers have gained a great importance in many fields of scientific research as well as for industrial applications, due to their chemical and physical enhanced properties. The presence of functional active phosphonic group in the structure of polymers makes them useful as ion-exchangers, able of retaining various metal ions or radioactive isotopes from waste water [1]. The functional groups in this type of polymers may be introduced as side groups, chain-end, in-chain, block or graft structures and their synthesis means the chemical modification of the already defined polymers or by direct polymerization of the functionalized monomers [2]. Both, vinylphosphonic acid homopolymer and its copolymers are the basis of many products which have found applications as essential components for the polymer electrolyte membranes, used in fuel cell development [3, 4]

In the previous work we synthesized copolymers of vinylphosphonic acid as membranes with potential application as ion exchangers [5].

The aim of this work is to synthesize ion-exchange copolymers with phosphonic acid groups as side groups, starting from styryl phosphonic acid and acrylate monomer, at different composition. The homopolymer of styrylphosphonic acid has no proper physico-mechanical properties to be used as ion-exchanger, hence, the copolymerization with suitable comonomer is needed. The copolymers were characterized by FTIR, thermal analysis and ion-exchange capacity.

MATERIALS and METHODS

Materials

Styrylphosphonic acid (2-phenylethenyl phosphonic acid) (>98%) was obtained from Aldrich. The acrylic co-monomer is a mixture of commercial products from Cognis: Photomer 3015, aliphatic bisphenol A diacrylate oligomer (95%) and Photomer 3016F, trimethylolpropane triacrylate (5%). The role of Photomer 3016F is to assure the fluidization of Photomer 3015 which is very viscous and as crosslinking reagent. Thermal initiator azobisisobutyronitrile was

obtained from Merck. HCl 0.01M solution was used as received. NaCl 2M solutions were prepared.

Copolymer synthesis

The copolymers were obtained by radicalic thermal polymerization. The photopolymerizable formulation contain monomer styrylphosphonic acid (SPA), co-monomer Photomer 3015/Photomer 3016F (PHA) at different ratios, from 1:1 to 5:1, and initiator 2% (w/w versus monomers). The polymerization was performed in sealed teflon tube, in oven at a temperature of 100°C, during 8 hours.

Characterization of the copolymers

Fourier transform infrared spectra (FT-IR) of the polymers were recorded, using Model Jasco FT/IR-4200 apparatus, in KBr pellet, following the band corresponding to the phosphonic groups and the decrease of the band corresponding to the C=C group of monomers, due to the polymerization.

The decomposition process and thermal stability of the copolymers were investigated using Mettler-Toledo thermogravimetric analyzer (TGA-DTA). The TGA measurement were carried out under nitrogen atmosphere at a heating rate of 10°C/min, from room temperature to 750°C. Approximately 20 mg in weight of the samples were used in each analysis and the gas flow rate was kept at 90 mL min⁻¹.

Ion exchange capacity is determined by measuring the amount of specified counter-ions in the membrane by titration after ion exchange with other ions or elution, using a suitable indicator. The ion exchange capacity was determined as follows: the known amount of membrane was immersed in 2N NaCl solution for one hour to obtain sodium form and release protons. The resulting solution was titrated with 0.01N NaOH. The volume of NaOH used to reach the end point (V_{NaOH}), the concentration of the NaOH solution used ($[\text{NaOH}]$) and the dry weight of the membrane (W_{membrane}) were needed to calculate the ion exchange capacity (equation 1) [6].

$$IEC = (V_{\text{NaOH}} \times [\text{NaOH}] / W_{\text{membrane}}) \times 1000 \quad (1)$$

Ion exchange capacity is defined as the millimolar equivalents of reactive (O)P(OH)₂ sites per gram of polymer, of mmeq/g. The measured ion exchange capacity values are compared to the theoretical ion exchange capacity value, based on the moles of phosphonic groups from copolymer [7].

RESULTS

The obtained copolymers are white to light brown colored materials, hard and brittle.

The FTIR spectra confirmed that the polymerization occurred almost completely. In Figure 1 is presented, for example, the FTIR spectrum of PHA:SPA 1:3. In this spectrum can be identified the characteristic bands of P-OH at 952 cm⁻¹, P=O of phosphonic acid group at 1182 cm⁻¹, and phosphonic group at 1126 and 1240 cm⁻¹. Also, an enlarged band of phosphonic acid group can be observed at 3443 cm⁻¹. The FTIR spectrum of the copolymer PHA-SPA 1:3 showed the decrease of the absorption bands attributed to C=C at 1404 cm⁻¹ and 821 cm⁻¹ in comparison with monomers spectra, because the polymerization occurred. The band at 1728 cm⁻¹ corresponds to C=O group from acrylate, and the bands at 2876 and 2956 cm⁻¹ are attributed to aromatic group.

Using thermogravimetric analysis, samples were investigated under an inert environment (nitrogen). Figure 2 shows the overlay of TG curves of copolymers PHA-SPA at different compositions. The degradation temperature of styrylphosphonic acid reported in literature is

around value of 200°C [8], and the degradation temperature of PHA is around value of 310°C [5].

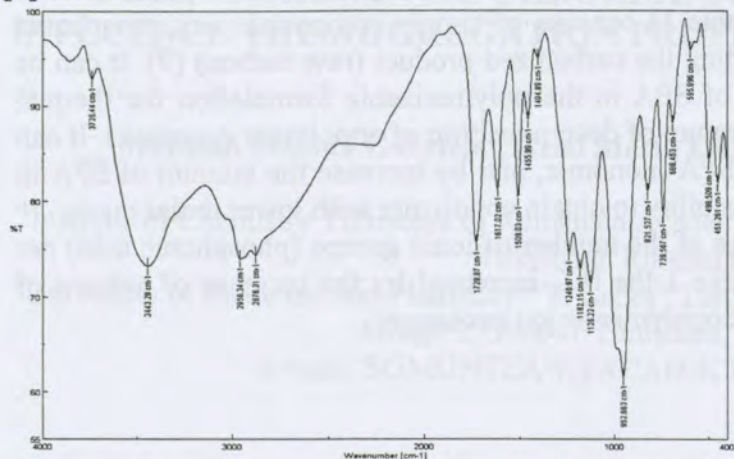


Figure 1. FTIR spectrum of the copolymer PHA:SPA 1:3.

The results reveal that the thermal stability of the copolymers was changed by the modification of the ratio between co-monomers. Table 1 shows their decomposition temperatures of the first and second stages (Td1 and Td2) and the residue amount at 750°C.

Table 1. Phosphorus content and thermal decomposition temperatures of the copolymers.

| Sample | P content (%) ^a | Td1 (°C) | Td2 (°C) | Residue at 750°C (%) | IEC (mmeq/g) |
|-------------|----------------------------|----------|----------|----------------------|--------------|
| PHA-SPA 1:1 | 4.64 | 345,13 | 472,31 | 34,49 | 0.14 |
| PHA-SPA 1:2 | 3.64 | 292,95 | 469,19 | 36,95 | 0.37 |
| PHA-SPA 1:3 | 2.99 | 271,09 | 415,19 | 37,89 | 0.43 |
| PHA-SPA 1:4 | 2.54 | 274,74 | 402,26 | 37,07 | 0.52 |
| PHA-SPA 1:5 | 2.21 | 288,09 | 432,64 | 37,19 | 0.65 |

^a Determined by Schoniger method

The TGA curves for copolymers of styryl phosphonic acid - acrylic monomers at different molar ratios, performed in nitrogen, are shown in Fig. 2. There are two steps of decompositions for all copolymers. The initial mass loss begins at about 200°C and this first step ends at about 370°C in the case of PHA-SPA 1:1 and at about 340°C for the others copolymers. The major mass loss in the first stage was recorded at Td1 (Table 1).

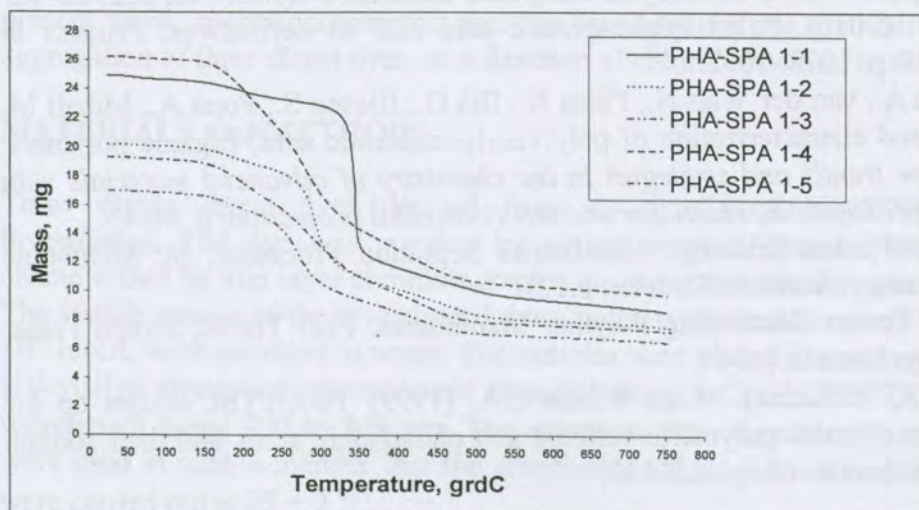


Figure 2. TG curves of copolymers PHA-SPA.

The second stage occurs between 370°C and 550°C for copolymer PHA-SPA 1:1 and between 340°C and 500°C for the others with a less mass loss, at Td2. The destruction process led to the non-volatile residue, at 750°C (Table 1) consists of simple compounds (e.g. phosphorus oxide) and to a carbon frame representing the carbonized product (raw carbon) [9]. It can be observed that by increase of amount of SPA in the polymerizable formulation the thermal stability decreased, because the temperature of decomposition of copolymer decreased. It can be explained by the low reactivity of SPA monomer, and by increase the amount of SPA in polymerizable formulation it is the possibility to obtain copolymer with lower molar mass. The ion exchange capacity is a measure of the number of ionic groups (phosphonic acid) per gram of polymer. As is seen from Table 1 the IEC increased by the increase of amount of SPA, that means a higher reactivity of copolymer as ion exchanger.

CONCLUSIONS

The synthesized copolymers based on styrylphosphonic acid and acrylic monomers at different molar ratios, by thermal initiated radical polymerization, were characterized by FTIR, thermal analysis and ion-exchange capacity.

By the increase of amount of styrylphosphonic acid in the composition of copolymers, the thermal stability decreased. The ion exchange capacity, which is the important property of these polymers, increased with the increase of the amount of styrylphosphonic acid by number of active phosphonic acid groups.

The copolymers based on styrylphosphonic acid can be applied as ion-exchangers.

Acknowledgements

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