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Possibilities for poly(aspartic acid) preparation as biodegradable compound

L. E. NIȚĂ, A. P. CHIRIAC*, C. M. POPESCU, I. NEAMȚU, L. ALECU[a]
"Petru Poni" Institute of Macromolecular Chemistry 41 A Grigore Ghica Voda Alley , 700487 Iassy, Romania
[a]ICPE – CCA, Bucharest, Romania

The paper presents the preparation of poly(aspartic acid) (PAAs) from maleic anhydride and ammonia through a two steps reaction: first the polysuccinimide (PSI) obtainment followed by the hydrolysis reaction of PSI in order to open the imide group and to prepare the polyaspartate. Poly(aspartic acid) as friendly environmental and biodegradable product can be used in pharmacy, cosmetics, agriculture, etc.

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Keywords: Poly(aspartic acid), Biodegradable, Friendly environment

1. Introduction

Biodegradable polymers have been developed for being utilized in biomedical and pharmaceutical industries [1–3]. Over the last three decades, polyesters and polyamides have received the most attention as biodegradable polymers from researchers. Polylactide (PLA), typical biodegradable polyester, has been demonstrated to possess good mechanical properties and the necessarily biodegradability and biocompatibility to be used in the areas of tissue engineering and drug delivery [4–7]. However, various control and modification aspects of some of the properties of PLA have proven difficult.

To avoid these problems, various other possibilities to obtain the biodegradable and biocompatible compound have been investigated. Polypeptides consisting of α-amino acids are intriguing polyamides because of their hydrophilic nature and diversity in the various side-chain groups [8]. Polymers having the amino acid moiety in the main chain or in the side chain find a variety of useful applications, such as chelating agents for metal ions, ion-exchange resins, polymer catalysts with enzyme like behavior, and promoieties for preparing polymeric prodrugs [9,10].

Polyaspartate has a linear polyamide backbone structure that enables the polymer to biodegrade rapidly and completely [11-13]. Ecotoxicity studies have shown that polyaspartate is nontoxic and biodegradable and it does not adversely impact the environment [11], whereas other materials that are used presently for the same purposes are either slowly biodegradable, e.g. polyacrylic acid, or harmful to the environment, e.g. polyphosphoric acid.

A great number of publications appeared concerning preparations and uses of polyaspartic acid [7-17]. Polyaspartic acid (PAAs) can be prepared by L-aspartic acid thermally polycondensing procedure, optionally in the presence of acid catalyst, to form polysuccinimide (PSI) sometimes interchangeably called anhydropolyaspartic acid or polyanhydroaspartic acid and then reacting the PSI with aqueous alkali metal hydroxide to form a solution of PAAs metal salt. The cost of PAAs metal salt could be significantly reduced if instead of the procedure using the L-aspartic acid polycondensation it is used the procedure based on maleic anhydride. Thus, polyaspartic acid from maleic anhydride and ammonia reaction is most recently increasingly method and the obtained product being used as a biodegradable alternative to polyacrylates in many applications.

In one of our previous articles [18] it was reported the preparation of poly(aspartic acid) through a classic synthesis from D, L aspartic acid polycondensation reaction in the presence of phosphoric acid. The present paper reports the obtainment of PAAs from maleic anhydride and ammonia through a two steps reaction: the first is the polysuccinimide (PSI) obtainment and the secondly consists in the opening of the imide structure through hydrolysis of PSI followed by acidification in order to obtain poly(aspartic acid).

2. Experimental details

2.1. Syntheses

A) Preparation of Poly(succinimide) (PSI)

A slurry of maleic anhydride (196 g, 2 mol) in deionized water (400 g) was magnetically stirred and heated to 75 °C. The resulted clear solution was cooled to about 20 °C, then 30% ammonium hydroxide was added drop wise. After addition of ammonium hydroxide was complete, the solution was further stirred at 20 °C for 45 min. and at 85 °C for 3.5 hours. The resulted clear solution was transferred to a crystallization dish where was heated at 150 °C in a vacuum oven at <0.1 mm Hg. Water was removed over 1 hour. The resulted white solids were further heated at 150-180 °C under pressure (0,4 mm Hg) for 30 min. and at 180 °C also under pressure (0,4 mm Hg) for 3.5 hours to afford brittle, orange poly(succinimide) solid crystals with a few grams of white solids (probably maleic anhydride) deposited on the window glass of the vacuum oven. The obtained poly(succinimide) was soluble in dimethylformamide (DMF) but insoluble in tetrahydrofuran (THF).

B) 1. In Situ Hydrolysis of PSI

10.0% NaOH solution was added drop wise to a suspension (pH=3.0) of the poly(succinimide) of Preparation A (5.0 g, 0.051 mol) in deionized water at 73 °C at a pH value of 3.0 to 7.2 over 18 min. to afford a red solution. The resultant solution was diluted with deionized water to 100.0 grams. The solution was acidified with 3 N solution of hydrochloric acid to pH 1.5 and was dialyzed against 1% acetic acid and then against distilled water for two days. The dialyzed solution was lyophilized. As indicated by the disappearance of the characteristic infrared absorption band of the imide structure the alkali hydrolyzed almost completely the imide groups of the polymer. [14].

2.2. Analysis method

FTIR spectra were recorded – on a DIGILAB, Scimitar Series, USA, spectrophotometer, the resolution being 4 cm^{-1}, using KBr tablets-3 mg samples as 500 mg KBr).

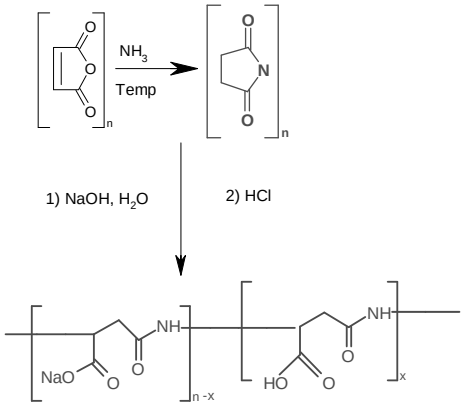
Thermogravimetric measurements were carried out using a TGA apparatus: MOM Budapest derivatograph under the following operational conditions: sample weight 50 mg, heating rate 12 °C /min, in airflow of 30 mL /min and with reference material α-Al_2O_3.

NMR spectra were recorded on a Bruker AMX 500 instrument, data being performed in $CDCl_3$.

X-ray diffractometry. X-ray diffractographs for the powder polymer samples were recorded with a Philips PW 1840 X-ray diffractometer using Ni-filtered CuKα (λ = 1.5418 Å) radiation at 40 kV – 20 mA and scanning speeds of 3° min^{-1} and 1.2° min^{-1}.

3. Results and discussion

The poly(aspartic acid) preparation accordingly to the mentioned procedures follow the next scheme of synthesis:



Scheme 1. The poly(aspartic acid) synthesis based on the reaction between maleic anhydride and ammonia (I) and poly(succinimide) hydrolysis (II).

The FTIR spectra of the products correspondingly to the two steps reaction, respectively poly(succinimide) (I) and for the poly(aspartic acid) (II) are subsequently illustrated (Fig. 1):

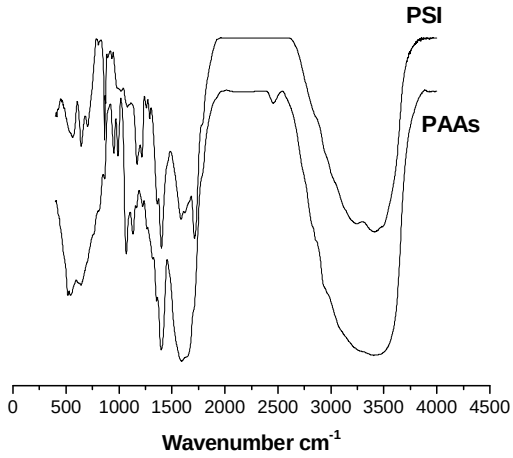


Fig. 1 The FTIR spectra of PSI and PAAs.

The FTIR spectra evidence the peak from 1705 cm^{-1} which is the characteristic absorption of the imide cyclic of poly(succinimide). As it can be observed from Fig. 2 in the case of PAAs the peak characteristic for PSI from region 1700-1800 disappears, which confirms the structure of PAAs after hydrolysis.

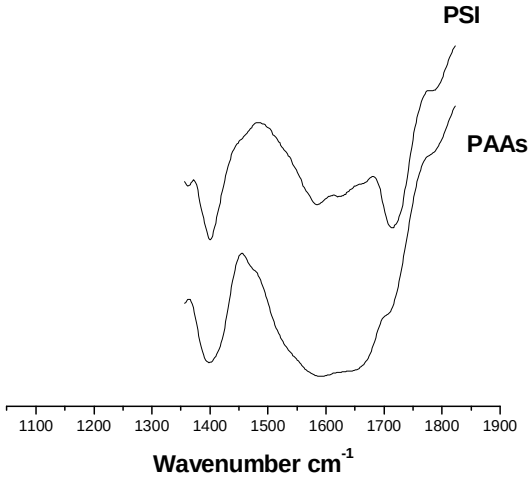


Fig. 2. Region from FTIR spectra of PSI and PAAs.

The characteristic bands of the two compounds from FTIR and H-NMR spectra (not figured in this paper) are presented in Table 1:

Table 1. Characteristics data of the polymers.

Sample	FTIR (cm^{-1})	H-NMR (δ ppm)	Solvents	Nonsolvents	pH
PSI	1672-νCO asim 1705-νCO sim (ring opening)	2.2 - methylene protons 3.75 - methine proton	Dimethyl formamide	Water, alcohols, tetrahydrofuran	7.89
PAAs	1500-1700 νCO ring opening, 3100-3500 OH band	2.8, 2.7, and 2.55- methylene protons 3.7, 3.5 - methine proton	Water, alcohols	Dimethylformamide tetrahydrofuran	3.71

The synthesized macromolecular structures have been characterized from the viewpoint of their thermal stability.

Data acquired from thermogravimetric measurements are presented in Table 2:

Table 2. Thermogravimetric data of the poly(succinimide) and poly(aspartic acid).

Macromolecular compound	T_i (°C)	T_{max} (°C)	T_f (°C)	Ea (kJ/mol)	n
PSI	280	370	480	93.2	0.0
PAAs	167	340	542	38.9	0.8

T_i – temperature correspondingly at the beginning of thermo - oxidative process
T_{max}- temperature of maximum rate of weight loss
T_f – temperatura correspondingly at the ending of thermo - oxidative process
E_a – activation energy
n – reaction order

From Table 2 it can be observed the decrease of the PAAs thermal stability. This can be explained on the basis of the compounds structure. Thus, when PSI is transformed in PAAs the succininmidic rings are opened, which determines a decreasing in the temperatures correspondingly to the beginning of thermo - oxidative process as well for the temperature of maximum rate of weight loss.

The activation energy as well as the reaction order were calculated on the basis of the weight loss during the thermo-oxidative process using the Coats-Redfern calculus method. [19-21] The evolution of the activation energy values during thermal decomposition of poly(succinimide) as well as during thermal decomposition of poly(aspartic acid) is presented in Fig. 3. The dependence in time of these values is in good agreement with the structure of the studied polymers. Thus, higher activation energy values correspond to the poly(succinimide), a polymer containing a cycle in its structure, as compared to poly(aspartic acid), which includes a N – heteroatom.

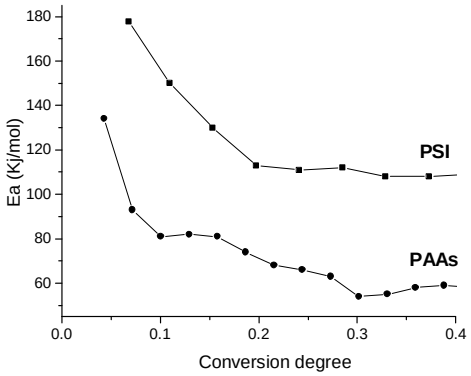


Fig. 3. Activation energy evolution during thermo-oxidative process of poly(succinimide) and poly(aspartic acid).

In the context of the permanent aspiration for tailored material systems, new material combinations and properties, as well for the optimization of the synthesis, X-ray study offers numerous examination methods to characterize a wide variety of different type of substances on a nanometer scale as well as to decode the synthesis process itself. This assay is also the most important non-destructive tool to all kinds of matter, being an indispensable method for materials characterization. The X-ray analysis evidences the differences occuring into the poly(aspartic acid) structure as well of the poly(succinimide) (Fig. 4).

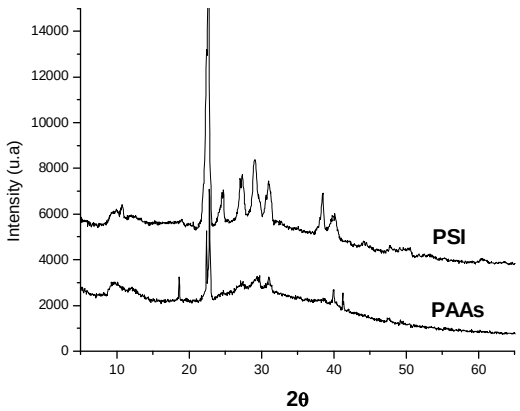


Fig. 4. The X-ray analysis of the PSI and PAAs.

4. Conclusions

The paper confirms the preparation of poly(succinimide) as well of poly(aspartic acid) from a two steps process: first by reaction of maleic anhydride

with ammonia and second by hydrolysis of poly(succinimide) finalized with the preparation of poly(aspartic acid).

The IR, H-NMR spectra, the X-ray analysis as well the thermal characterisation of the synthesised biodegradable polymer confirm the preparation of poly(aspartic acid) by two mentioned ways.

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*Corresponding author: achiriac1@yahoo.com