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Synthesis, Analysis and Possibility Application of Cyclic and Linear Forms of Poly(Aspartic Acid) Synthesized Under Microwave Irradiation

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In this paper a new original method of synthesis of poly(aspartic acid) (PAA) from aspartic acid (AA) or maleic anhydride under microwave irradiation is presented. The syntheses carried out mainly without the catalyst, received higher yield in comparison for conventional method. PAA has been characterized by nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR), infrared spectroscopy (FT-IR) and termogravimetric analysis (Tg). Obtained polymer we used for several diversified applications, such as, medicine, agriculture and catalyst for oxidation reactions.

Keywords Microwave irradiation; poly(aspartic acid); polyethylene; polymer catalyst

Introduction

The emergence of microwave-enhanced chemistry as an more efficient alternative and environmentally friendly way of performing chemical synthesis promises to be one of the most significant events of the 1990s with tremendous potential for the 21st century. Polymer synthesis can greatly benefit from the unique featured offered by modern microwave technology, which was demonstrated in many successful applications [1]. Fundamental difference in the heat transfer during material processing in thermal and microwave fields is that microwave energy in contrast to thermal heating, is supplied directly to a large volume, thus avoiding the thermal lags associated with conduction and convection [2].

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. However, various control and modification aspects of some of the properties of PLA have proven difficult [3–5]. The avoid these problems, various other possibilities to obtain the biodegradable and biocompatible compound have been investigated. Polypeptides consisting of α-amino acids are

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intriguing polyamides because of their hydrophilic nature and diversity in the various side-chain groups. 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 [6,7].

To this group of polymers due their advantages e.g., belongs poly(aspartic acid) (here: PAA), which is biologically inert polyamino acid. The name "poly(aspartic acid)" treats to the whole group of polymers differing the structure or molecular weight. In dependence from kind of parent substances, the way of guidance of polyreaction as well as modification chemical or physical it comes into being the well-fitting here into the polymer about diverse proprieties, finding sequence proprieties of uses.

Poly(aspartic acid) – (PAA) shows such specific properties as a toxicity, water solubility, hygroscopicity and its degradation gives amino acids. Owing to unique characteristics PAS and its derivatives it can be exploited for a range of uses both in science and industry e.g., medicine, pharmacology, cosmetics, agriculture, metallurgy, paper processing and others [8]. Well known, are conventional syntheses of PAA from aspartic acid and maleic acid ammonium derivatives [9,10], but these kinds of reaction are carried out at high temperature (150–300°C) for several hours (2–10 h) [11]. Considering the reaction conditions, these processes are not favourable, especially in technological processes. Additionally, the polymerization process requires a catalyst, for example phosphorus acid, which causes impracticability of PAA e.g., in medicine or pharmacology.

In this paper, we report a new and simple method of obtaining poly(aspartic acid) by using microwave irradiation method, and the next, we present several diversified applications this polymer. First reports about application of this method to production of biopolymers appeared by the end of the 20th century. Harada *et al.* used microwaves to manufacture poly(amino acids) [12]. Since then there has been hardly any research about application microwave in synthesis of polymers of amino acid.

Experimental

Materials

The following materials were used in this work:

- D, L-Aspartic acid, propylene carbonate (Sigma-Aldrich)
- Maleic anhydride, ammonium hydroxide (POCh, Poland)

A new original method of synthesis of PAS from maleic acid and aspartic acid derivatives under microwave irradiation was worked. The process was carried out using a microwave reactor "MicroSYNTH" from Milestone S. R. L. brand by applying 1000 W power. The main advantage of this monomer is its availability and price. Maleic anhydride is almost three times cheaper than aspartic acid and is also a by-product in some processes [13].

The Synthesis of PAA Using Maleic Anhydride

The reaction required a few steps. Firstly, maleic anhydride was hydrolyzed in water to give maleic acid (step I), then it was converted into ammonium derivatives by addition of ammonium hydroxide (step II). The stages I and II require an increased temperature 100°C. In this way, there is possible to obtain ammonium salt or/and

Table 1. Compared reaction parameters in PAA preparation

Substrate	Time of cycle [min]	Temperature [°C]	Power [W]	Colour
Maleic acid ammonium	5	130	200	Colourless
	3	150	250	Pink
	3	170	300	Dark pink
	3	190	350	Dark pink
	3	210	400	Dark pink
	3	230	450	Dark red
Aspartic acid	3	176	380	White
	3	186	380	White
	3	196	380	Light pink
	3	200	380	Light pink
	7	215	390	Light pink
	5	220	390	Light brown
	3	230	390	Brown
	14	230	390	Dark brown

amide of maleic acid. It is not very important which transitional product is formed because polymerization of both gives the same cyclic product, namely anhydropoly(aspartic acid) – APAA (step III). The temperature of polymerization is raised gradually in order to achieve high yield of polycondensation- Table 1. Water from the reaction is removed by means of distillation. Finally, linear PAA is obtained after hydrolysis of its cyclic form at room temperature (step V). The hydrolysis of the APAA leads to poly(aspartates) containing α and β-peptide bonds. It is explained by nucleophilic attack of the hydroxide ions at the C–N bonds (Fig. 1, step V).

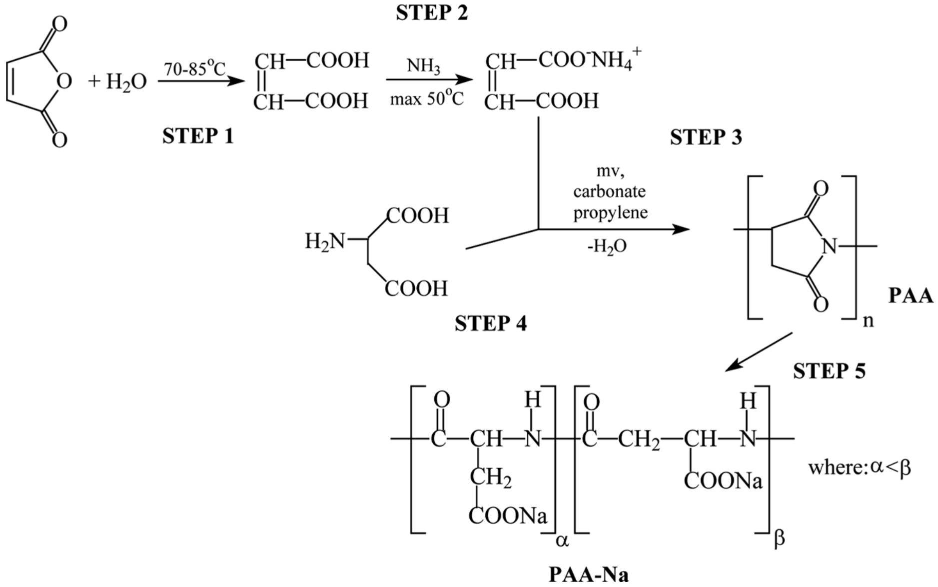

Figure 1. The synthesis of cyclic and linear PAA using maleic anhydride and aspartic acid.

The Synthesis of PAA Using Aspartic Acid

Polycondensation of cyclic PAA (Fig. 1, step 4) was realized at the temperature range from 176°C to 230°C, carbonate propylene was used as solution. Water was removed from the system by an azeotropic distillation under normal pressure. In Table 1 the reaction parameters for two ways of obtaining the products are presented comparatively.

Cyclic PAA was precipitated with methanol, washed in water and dried. The reaction efficiency was above 93%. PAA sodium salts has been obtained during the reaction of hydrolysis of cyclic forms of PAA, water solutions of sodium (Fig. 1, step 5). The process of hydrolysis was carried out in solution with pH = 8.5 to 13.0.

Results and Discussion

1) Analysis of PSI

Infrared Spectroscopy (FT-IR). FT-IR spectrum of cyclic PAA (Fig. 2) shows intensive absorption band of stretching vibrations of C=O group cyclic imide ring in the range from $1690\,cm^{-1}$ to $1720\,cm^{-1}$. Strong absorption band of NH stretching vibrations is in the range of $3500–3100\,cm^{-1}$.

Proton Nuclear Magnetic Resonance (^{1}H NMR). ^{1}H NMR spectrum of cyclic PAA in DMSO-d_6 is characterized signals of the methine proton in the range from 4.5 ppm to 5.4 ppm. The methylene is observed at 3.3 and 2.8 ppm.

Carbon Nuclear Magnetic Resonance (^{13}C NMR). ^{13}C NMR spectrum of cyclic PAA in DMSO-d_6 is characterized two carbonyl peaks, which are observed at 173 and 174 ppm, representing the two inequivalent carbonyls of the succinimide repeat unit. The repeat unit methylene and methine are observed at 32 and 47 ppm, respectively [2–4].

Termogravimetric Analysis (TG). TG profile is shown that decomposition process of cyclic PAA proceed in two steps, leaving 35% of residue. TG analysis have

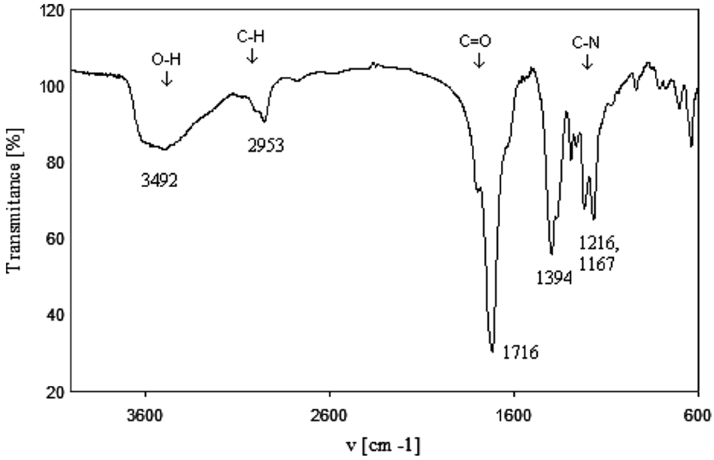

Figure 2. Spectrum of cyclic PAA using aspartic acid as reagent.

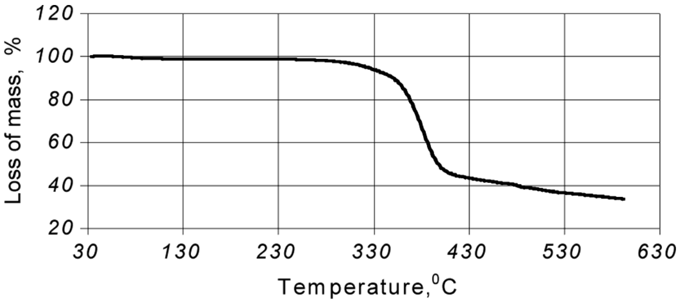

Figure 3. TG curve of PAA.

been showed, that PAA is resistant to temperatures 230°C. Figure 3 is shown TG curves of PSI.

2) Application of Cyclic and Linear of Poly(Aspartic Acid)

a) Modification of HD-polyethylene using poly(aspartic acid) for total artificial joints. Owing to its toxicity and biodegradability to amino acids, poly(aspartic acid) has already established its position in the field of medical engineering. This polymer is characterized by high thermal stability (300°C) and could be safely used to modify PEHD. The first experiments have shown that addition of poly(aspartic acid) results in an improvement of mechanical and tribologic properties comparing to the pure PE [14,15].

Modification of HD PE using PAA in amount of 5 and 10 mass % were carried out. The components were added into granulated polyethylene and this mixture was used to manufacture paddles by injection processing. The results of mechanical properties are shown in Table 2.

Degradation of Modified Polyethylene. As poly(aspartic acid) degrades easily, analyses of modified polyethylene samples under degradation conditions were carried out. The samples were kept to physiological NaCl solution at 70°C for 30 days. After removing the extracts mechanical analyses were performed. The results are shown in Table 3 and Figure 4.

In spite of that after 30 days of incubation hardness and abrasion resistance of analyzed samples have decreased by their values were still higher than those of polyethylene without modification. However, for some samples durability after incubation was better than before.

Table 2. Mechanical properties of HD PE modified whit PAA

Sample	Hardness [N/mm^2]	Abrasion [mm^2/m]	Tensile strength [MPa]	Young module [MPa]	Elongation at break [%]
PEHD	11.10	2.19	21.74	1.14	10.40
PEHD + 5% PAA	13.10	1.62	20.51	1.13	10.96
PEHD + 10% PAA	15.06	2.09	19.11	1.11	10.49

Table 3. Mechanical properties of HD PE modified PAA after 30 days of incubation

Sample	Hardness [N/mm^2]	Abrasion [mm^2/m]	Tensile strength [MPa]	Young module [MPa]	Elongation at break [%]
PE HD	11.01	2.24	22.04	1.06	12.39
	12.42	1.83	22.38	1.00	10.94
	12.60	2.25	21.06	1.11	10.03

The pH measurements of physiological NaCl solution have indicated that after 48 hours of incubation the value of pH change from 6 to 3. during this time the most abundant degradation products, probable oligomers, were passed through into solution. Later, in the next 28 days the value of pH decreased much slower. After 30 days in vitro tests mass loss of all samples was observed to occur higher for samples containing 5 and 10% of PAA was a results of mowing into solution of some decomposition products or migration of a modifying agent.

b) Linear of PAA as addition to cement – correction of cement prolix, reduction of "make-up water" amount in cement mixtures. We have studied the influence of sodium polyaspartate on rheological properties flow of Portland cement depends on pH salt and amount water in cement mixtures. We also performed investigations of the influence addition of sodium polyaspartate with pH = 11.20 on the amount of water in cement mixture at different ratio water/cement- Table 4. Addition of PAA salt to cement is (0.35–0.40 w/w %) results in obtaining a plasticized cement, characterized by good flow properties.

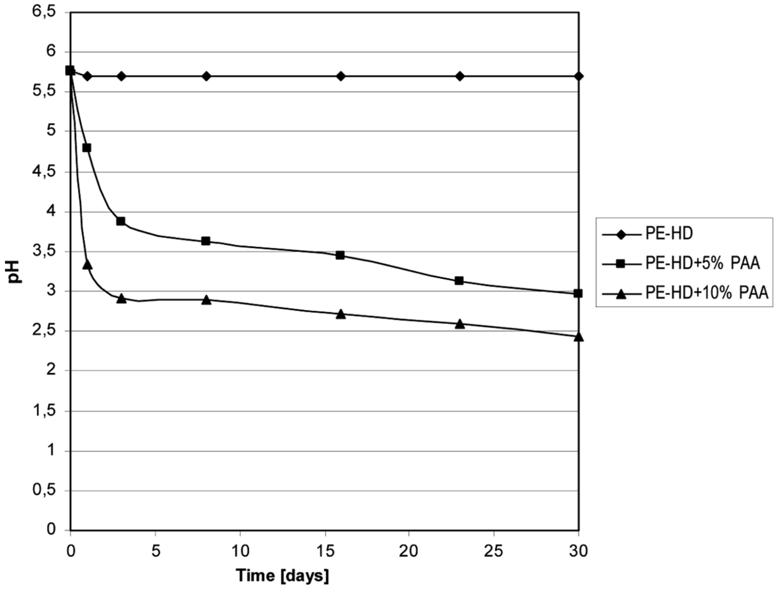

Figure 4. Change of pH values of solution after 30 days of incubation.

Table 4. Relation of cement mixtures flow to water/cement ratio of linear PAA

Water/cement	0.40	0.36	0.35
Flow [cm]	72	50	46

Addition of sodium polyaspartate with pH = 11.20 causes maximum reduction of water (12.5%, w/c = 0.35) with preservation of appropriate consi-stency. Sodium salt of PAA with pH = 11.20 causes the best cement flow (an increase from 48 to 112 cm in relation to standard sample) and makes it possible to decrease the amount of water in cement water by 12.5%.

C) Linear PAA as carrier from metals – prepare catalysts. Complex of sodium salt PAA with cobalt(II) or copper(II) acetate was carried out by mixing of 1.00 g of PAA-Na with corresponding amount of metal acetate in water (Fig. 5).

It in this way a catalyst:was obtained

– PAA-Na + cobalt acetate – **PAA-Co**
– PAA-Na + copper acetate – **PAA-Cu**

Further, it was applied for oxidation reactions of aliphatic and aromatic hydrocarbons that were carried out in the presence of molecular oxygen at the atmospheric pressure.

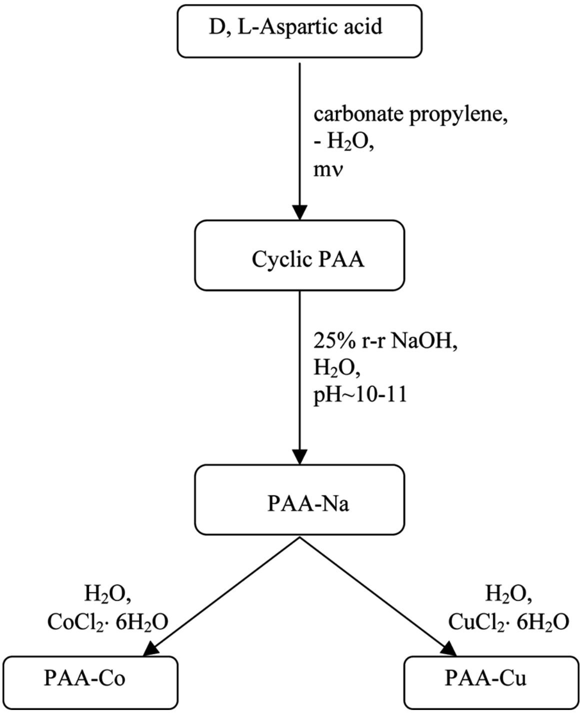

Figure 5. Synthesis of poly(aspartic acid)-based catalysts.

The complex of sodium salt PAA with cobalt or copper are very effective in oxidizing of alkenes under mild conditions. We obtained ketone and epoxide as a products reaction of alkene oxidation.

Conclusion

Our work is focused on evaluation of the influence of microwave irradiation on the PAA properties. Optimization of the process conditions results in shortening of the reaction time (about 1 hour) without using the catalyst. The optimization results also in increasing of yield comparing to the conventional method. Polymer obtained in such a way is characterized by high purity which is of crucial importance in e.g., biomedical applications.

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