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Microwave-assisted synthesis of poly(aspartic acid)

RAPID COMMUNICATION

Summary — The reactions of poly(aspartic acid) syntheses were carried out in the microwave reactor. The cyclic form obtained, *i.e.* polysuccinimide [PSI, formula(IV) in Scheme A] was then subjected to alkaline hydrolysis in the presence of NaOH to reach finally the linear form, sodium salt of poly(aspartic acid) (PAspNa) [formula (V) in Scheme A presents its anion]. D,L-aspartic acid being a monomer [formula (III)] was dispersed in propylene carbonate and polimerized without the catalyst at temp. 160—230 °C for 41 min. The polymer obtained was precipitated with non-solvent, filtered and washed first with the same non-solvent and then with distilled water, and dried at room temperature. The effects of weight ratio monomer:solvent and the type of non-solvent on the reaction yield and molecular weight and polydispersity of the product were investigated changing the parameters mentioned.

Key words: poly(aspartic acid), polysuccinimide, microwave radiation.

SYNTEZA POLI(KWASU ASPARAGINOWEGO) Z WYKORZYSTANIEM PROMIENIOWANIA MIKROFALOWEGO

Streszczenie — W reaktorze mikrofalowym przeprowadzono reakcje syntezy poli(kwasu asparaginowego) otrzymując jego cykliczną formę tj. poliimid kwasu bursztynowego [PSI, wzór (IV) na schemacie A], który następnie poddawano alkalicznej hydrolizie w obecności NaOH uzyskując formę liniową będącą solą sodową poli(kwasu asparaginowego) [PAspNa, anion tej soli przedstawia wzór (V) na schemacie A]. Monomer, którym był D,L-kwas asparaginowy [wzór (III)] zdyspergowano w węglanie propylenu i polimeryzowano bez użycia katalizatora w temp. 160—230 °C w ciągu 41 min. Polimer wytrącano dodając nierozpuszczalnik otrzymywanego polimeru, filtrowano i przemywano najpierw tym samym nierozpuszczalnikiem, a później wodą destylowaną, po czym suszono w temperaturze pokojowej. Stosując różny stosunek wagowy monomer:rozpuszczalnik oraz różne nierozpuszczalniki do wytrącania polimeru badano wpływ tych czynników na wydajność reakcji oraz ciężar cząsteczkowy i polidyspersyjność produktu (tabela 1).

Słowa kluczowe: poli(kwas asparaginowy), poliimid kwasu bursztynowego, promieniowanie mikrofalowe.

Poly(aspartic acid)s form a group of amorphous, biodegradable polymers occurring in three structural forms: cyclic — polysuccinimide (PSI) and two linear ones: poly(aspartic acid) with free carboxyl groups (PAspA) or salts with different cations (PAspX, where X represents a cation). PAspA is a very hygroscopic material so is not commonly used and will not be investigated here. As it is shown in Scheme A, PSI [formula (IV) in Scheme A] can be prepared from D,L-aspartic acid [formula (III)] thermally through a polycondensation procedure, optionally in the presence of an acid catalyst, and then through hydrolysis with aqueous alkali metal hydroxide to form a water soluble PAspX salt [formula (V)]. On the other hand, PSI can be prepared from maleic anhydride [formula (I)] through monoammonium maleate [formula (II)], which can reduce the production cost. Microwave radiation has been successfully applied in polymer chemistry and technology [1], among others to syntheses of poly(aspartic acid) and its derivatives [2—4]. Nevertheless the influence of different parameters of such synthesis method on the properties of the polymer obtained is not known.

EXPERIMENTAL

Materials

D,L-aspartic acid was purchased from Xenon (Poland), propylene carbonate was delivered by Fluka (Switzerland), whereas methanol, acetone and isopropanol by POCh (Poland). All substances were of pure grade and used as received.

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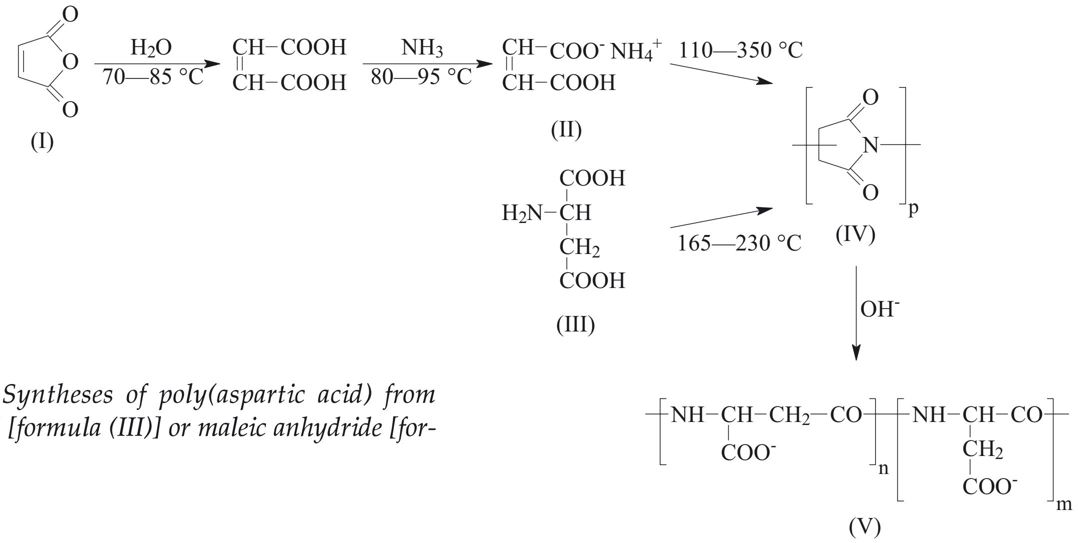

Scheme A. Syntheses of poly(aspartic acid) from aspartic acid [formula (III)] or maleic anhydride [formula (I)]

Synthesis of poly(aspartic acid)

Series of reactions were carried out. 10 g of aspartic acid in propylene carbonate as a solvent was placed in Milestone START Labstation multimode microwave reactor equipped with aseotropic condenser, magnetic stirrer and IR temperature sensor, in 100 or 250 ml two-necked flasks. The reactions were carried out without catalyst in propylene carbonate solutions at a temperature range of 160 to 230 °C during 41 min. Monomer:solvent weight ratios ranged from 1:5 to 1:2. A dark bronze solution of PSI in propylene carbonate as a final product was received. The polymer was precipitated with acetone, methanol or isopropanol (non-solvents; 150 ml) [6], or their mixtures with distilled water (1:1 v/v; 200 ml). The precipitate was filtered, washed with 20 ml of non-solvent and then with 500 ml of distilled water and dried at room temperature.

PAspNa was prepared by hydrolysis of PSI. The 0.10 g of polymer was put into beaker and 10 ml of distilled water was added. Mixture was titrated with 10 % NaOH solution to pH = 10—11. Next the solution was heated at temperature *c.a.* 90 °C for 30 min to complete hydrolysis.

Methods of analyses

Received polymer samples were characterized with use of Fourier transform infrared spectroscopy (FT-IR) with attenuated total reflectance (ATR) method using a PerkinElmer Spectrum 100 apparatus.

The structures were also analyzed using ^1H NMR spectra for samples dissolved in D_2O or DMSO-d_6 recordered on Mercury — 300 MHz "Varian" type spectrometer.

The molecular weights and polydispersity indexes of samples were determined by gel permeation chromatography using Knauer Smartline GPC apparatus (POLYSEP-GFC-P 4000 column for water soluble polymers, flow rate 0.5 ml/min, 35 °C, calibration curve for PEG

Table 1. Parameters of PSI syntheses and properties of PAspNa obtained by PSI hydrolysis

Sample	Flask volume, cm^3	Monomer:solvent weight ratio	Non-solvent	Yield of PSI synthesis, %	$Mp^{b)}$ of PAspNa	Polydispersity index of PAspNa
1	250	1:5	acetone	45	6200	4.09
2	100		acetone	60	18100	2.17
3			acetone:water	$77^{a)}$	27200	1.84
4			methanol	67	14100	2.67
5			methanol:water	$73^{a)}$	44800	1.13
6			isopropanol	$69^{a)}$	40400	1.22
7			isopropanol:water	80	20900	2.12
8		1:4	methanol	88	13700	2.23
9		1:3		$99^{a)}$	44800	1.14
10		1:2		96	15300	2.22

a) Fractions with lower molecular weight are also observed and included in yield calculation.
b) M_p — molecular weight corresponding to maximum of GPC peak.

standards). Molecular weights and polydispersity determinations were performed only for PAspNa, because PSI is insoluble in water.

RESULTS AND DISCUSSION

Syntheses parameters and properties of polymer samples obtained are listed in Table 1. It was found that decrease in monomer:solvent weight ratio resulted with an increase in the yield (from 45 % to 99 %). Another important factor is a non-solvent used in the precipitation of a polymer. It was observed that application of methanol influenced polymer particle size supporting the precipitation and filtration processes (Table 1).

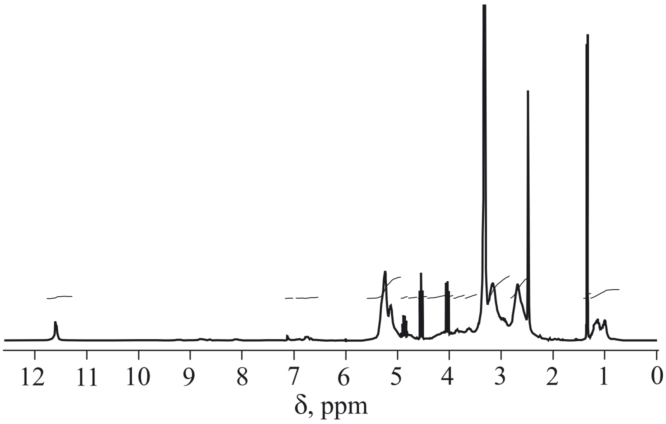

Fig. 2. ^{1}H NMR spectrum of polysuccinimide (PSI) in DMSO-d_6

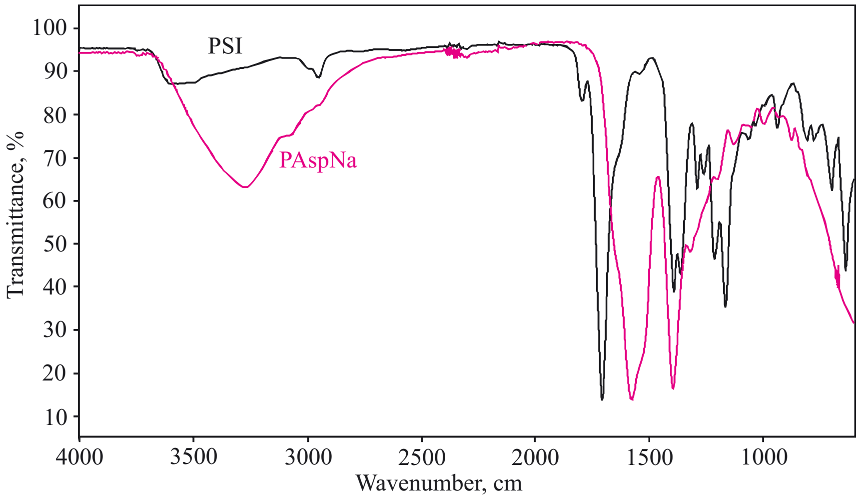

Fig. 1. FT-IR spectrum of polysuccinimide (PSI) and poly(sodium aspartate) (PAspNa)

Structure of the polymer obtained was determined with use of spectroscopic methods. FT-IR spectrum of PSI presented in Figure 1 shows a doublet at 1790—1690 cm^{-1} from imide ring which is very characteristic. Stretching vibrations from N-H at 3700—3100 cm^{-1} (wide band), as well as at 1400 cm^{-1} and 1450—1350 cm^{-1} from C=O are visible in both, cyclic and linear forms of poly(aspartic acid)s. But the main difference is a doublet at 1570—1650 cm^{-1} from amide group in poly(sodium aspartate) (PAspNa) received in hydrolysis process of PSI (Fig. 1) [2, 6—8].

^{1}H NMR spectrum of PSI presented in Figure 2 shows the shifts at 5.3—5.1 ppm from methine protons as well as at 3.2 and 2.7 ppm from methylene protons in imide rings. At 1.4—1.0 ppm the signals from propylene carbonate built-in to polymer backbone and very weak signals at 5.0—4.0 ppm from opened ring units of PSI are observed. In spectrum of PAspNa shown in Figure 3 the signals at 4.7—4.4 from methine protons and at 2.7—2.5 ppm from methylene protons are observed. Moreover, at 3.7—3.3 and 1.0 ppm the signals from propylene glycol received in PSI chain scission during hydrolysis process are presented (Fig. 3) [2, 9—11].

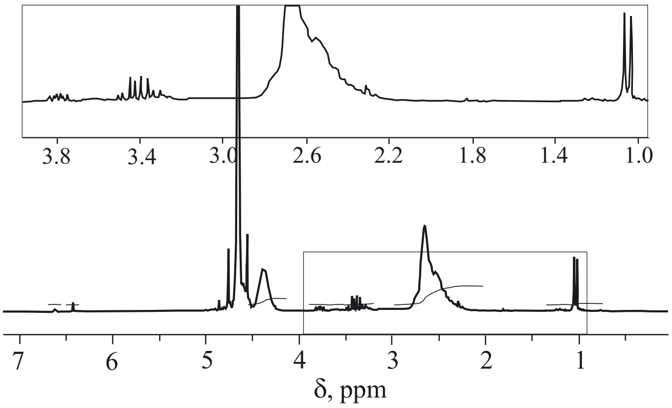

Fig. 3. ^{1}H NMR spectrum of poly(sodium aspartate) (PAspNa) in D_2O

CONCLUSIONS

It has been found that the change of only one reaction parameter (monomer:solvent weight ratio, non-solvent type, flask volume) significantly influenced the yield and molecular weight of polymer synthesized. Because of rapid boiling of reaction mixture, application of larger flask resulted in remaining of unreacted monomer on glass surface. Increase in the amount of solvent affects the viscosity of polymer solution causing problems with precipitation and filtration (particles agglomeration and filter pores blocking). It was also found that all non-solvents exhibited different properties in the precipitation process. Therefore the most optimal parameters for the polymerization reaction of 10 g of aspartic acid are: 100 cm^3 flask, monomer:solvent weight ratio = 1:3 and methanol used as a non-solvent.

Structures of poly(aspartic acid) backbones, low branching degrees and previously investigated thermal stability (up to temp. 250 ^oC) [3] of the samples synthesized at various conditions were very similar.

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