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Kinetics of Solid Phase Thermal Polycondensation of Aspartic Acid in Evacuated System

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Abstract—Solid phase thermal polycondensation of aspartic acid in evacuated system results in formation of poly(aspartic acid) at 190–207°C and in poly(succinimide) at 210–230°C. Kinetic parameters of formation of poly(aspartic acid) and poly(succinimide) have been determined. The aspartic acid → poly(aspartic acid) → poly(succinimide) polycondensation is accompanied by partial decarboxylation of the monomeric units.

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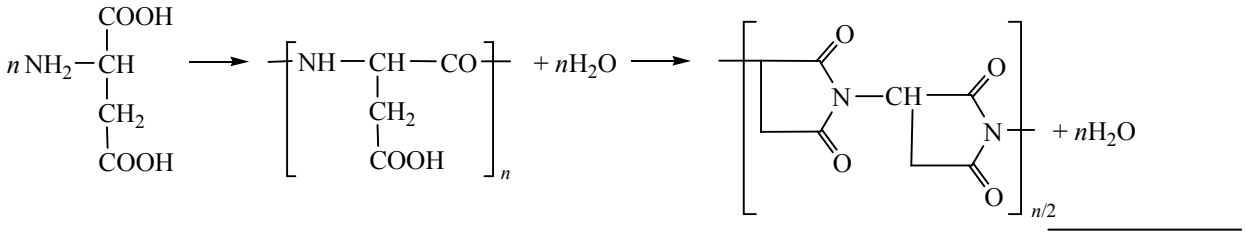
Amino acids are building blocks of the attractive polypeptide-type (co)polymers, rapidly biodegradable in the environment [1–3].

The polypeptides preparation from amino acids, including synthesis of poly(aspartic acid) and poly(succinimide), has been a matter of a number of publications. It has been shown that polycondensation of L-α-aspartic acid results in formation of poly(succinimide) and water at 260°C. In the presence of catalytic amounts of phosphoric acid the same reaction occurs with the same rate at 200°C [4]. From TGA data on dehydration of L-α-aspartic acid, the scheme of the amino acid transformation has been proposed, a sequence of irreversible reactions following the first order kinetic [5].



Subsequent isothermal TGA studies [6, 7] have revealed the complex form of registered derivatographic curves; autocatalytic polycondensation of aspartic acid has been suggested. Autocatalytic character is probably due to special effect of the solid phase matrix on the kinetics of the processes under conditions of fast and irreversible elimination of water vapor by the inert gas flow. It is commonly accepted [3] that the only volatile polycondensation product is water that quickly evaporates from the reaction zone. For example, the conversion of aspartic acid into poly(succinimide) reaches 96% as shown in [4].

This work aimed to determine the rate and to elucidate the mechanism of solid phase thermal polycondensation of aspartic acid in evacuated system at constant volume. The peculiarity of the reported experiments as compared to those described in [5–7] was that the volatile products remained in the reaction zone and thus could be analyzed.

Polycondensation of L-α-aspartic acid at 190–207°C was accompanied by elimination of water vapor and carbon dioxide. The amount of evolving water increased with temperature but did not exceed 0.7 moles

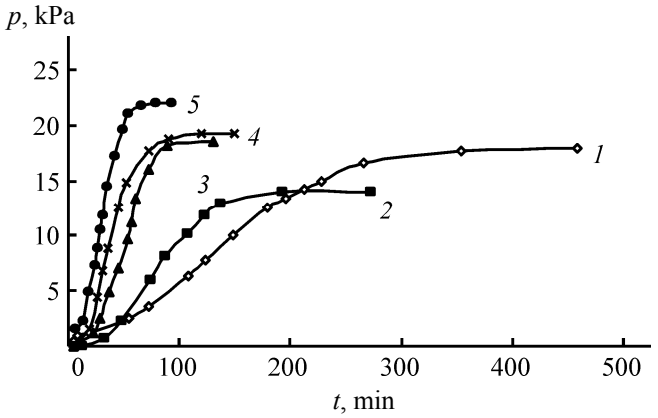


Fig. 1. Kinetic curves of volatile products pressure change during thermal transformation of aspartic acid at (*1*) 190°C, (*2*) 195°C, (*3*) 200°C, (*4*) 205°C, and (*5*) 207°C.

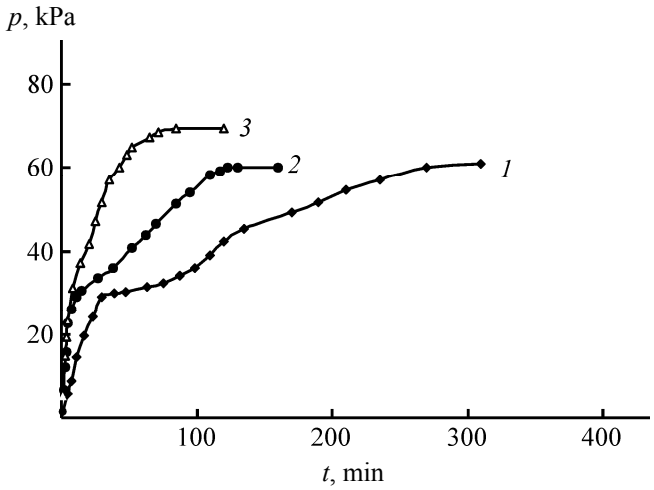


Fig. 2. Kinetic curves of volatile products pressure change during thermal transformation of aspartic acid at (*1*) 210°C, (*2*) 220°C, and (*3*) 230°C.

per 1 mole of aspartic acid. The amount of carbon dioxide was below 0.03 mol/mol. At higher temperatures (210–230°C), the amount of evolving water increased from 1.8 to 1.95 mol/mol, and that of carbon dioxide rose from 0.08 to 0.13 mol/mol.

Figure 1 represents the kinetic curves of the volatile products pressure in the gas phase during thermal conversion of aspartic acid at 190–207°C. Polycondensation of aspartic acid resulted in formation of poly (aspartic acid). In the IR spectrum of the solid product of polycondensation, the absorption bands assigned to the amide group vibrations were observed: ν(C=O) 1608 cm^{-1}, 1710 cm^{-1} and ν(NH) 1530 cm^{-1} [3, 8]. The bands of the imide group vibrations [that could have resulted from formation of poly(succinimide)] were absent. The amount of water in the gaseous products along with the spectral data confirmed formation of poly(aspartic acid). The same solid product was formed under the conditions of continuous removal of water and carbon dioxide from the reaction zone. Formation of small fraction of carbon dioxide was ascribed to partial decarboxylation of poly(aspartic acid) units.

At 210–230°C, the kinetic curves of the products pressure showed a sharp bend (Fig. 2) dividing the plot into two parts. The initial stage corresponded to polycondensation with formation of poly(aspartic acid), as confirmed by spectral analysis of the solid phase. From the data plotted in Fig. 1 and Fig. 2 (initial part), the kinetic parameters of poly(aspartic acid) formation were calculated (see table). The Arrhenius dependence of the reaction rate constants (k_1) on temperature (Fig. 3) held over the whole temperature range of 190–230°C. It supported the two-stage sequential transformation of aspartic acid to poly-(aspartic acid) and further to poly(succinimide).

$$\text{Aspartic acid} \xrightarrow{k_1} \text{Poly(aspartic acid)} \xrightarrow{k_2} \text{poly(succinimide)}.$$

Poly(succinimide) was only formed at the later stage of polycondensation at 210–230°C, the corresponding part of the kinetic curves were to the right of the bend (Fig. 2). From the highest pressure of the gaseous products at 210–230°C, the effective rate constants (k_2) and the activation parameter of the second polycondensation stage, transformation of poly (aspartic acid) into poly(succinimide), were calculated

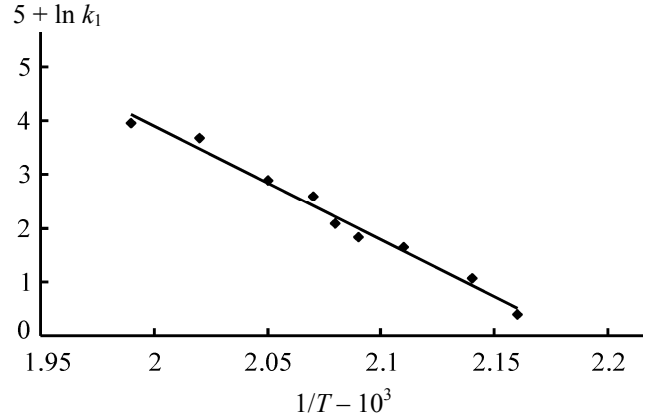


Fig. 3. Determination of the activation parameter of aspartic acid polycondensation to poly(aspartic acid).

Kinetic parameters of thermal transformation of aspartic acid

Reaction	T, °C	$k_1\times10^3$, min^{-1}	Reaction	T, °C	$k_2\times10^3$, min^{-1}
Aspartic acid	190	7.0	Poly(aspartic acid)	210	9
$\downarrow k_1$	195	19.5	$\downarrow k_2$	215	10
Poly(aspartic acid)	200	34.5	Poly(succinimide)	222	20
E 187±12 kJ mol^{-1}	205	42.4	E 191±33 kJ mol^{-1}	230	55
ln k_0 44±3	207	54.2	ln k_0 43±8		
	210	90.3			
	215	121.1			
	222	267.1			
	230	349.1			

(see table). In the IR spectrum of final product obtained at 210–230°C, the characteristic absorption bands assigned to the imide ring stretching were observed at [ν(C=O)] 1672, 1700, and 1705 cm^{-1}; [ν(C–N)] 1270, 1393, and 1727 cm^{-1} [8–10]. MALDI-TOF MS analysis of the final product evidenced the formation of poly(succinimide). In the registered mass spectrum (Fig. 4), several series of signals with the spacing of 97 Da [corresponding to mass of poly (succinimide) unit] were observed. The proposed end groups structure is shown in Fig. 4 as well (sodium cations originated from the salt used for ionization). The molecular mass value of the polymer did not exceed 4000 Da.

In [6, 7] it was stated that the only result of thermal conversion of aspartic acid was polycondensation to poly(succinimide) with stoichiometric elimination of two moles of water per one mole of aspartic acid. Noteworthily, TGA could give the loss of mass but not the composition of the volatile phase. Our experimental data suggested the following mechanism of thermal transformation of aspartic acid at 190–230°C.

Over the whole studied temperature range, the first stage of polycondensation was transformation of aspartic acid to poly(aspartic acid), as confirmed by IR and kinetic data. The rate of poly(aspartic acid) conversion into poly(succinimide) is an order of magnitude lower

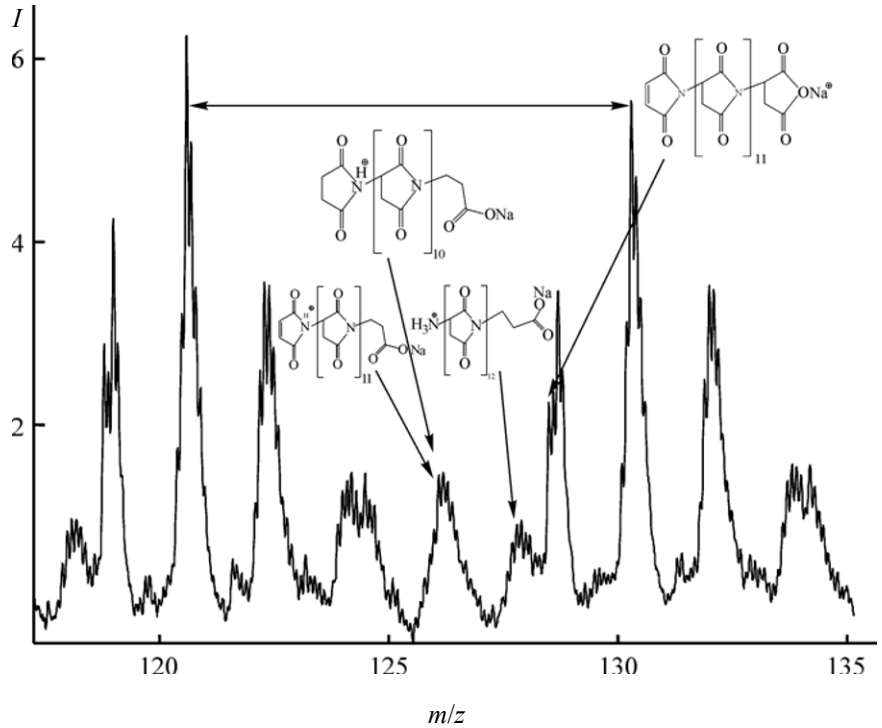
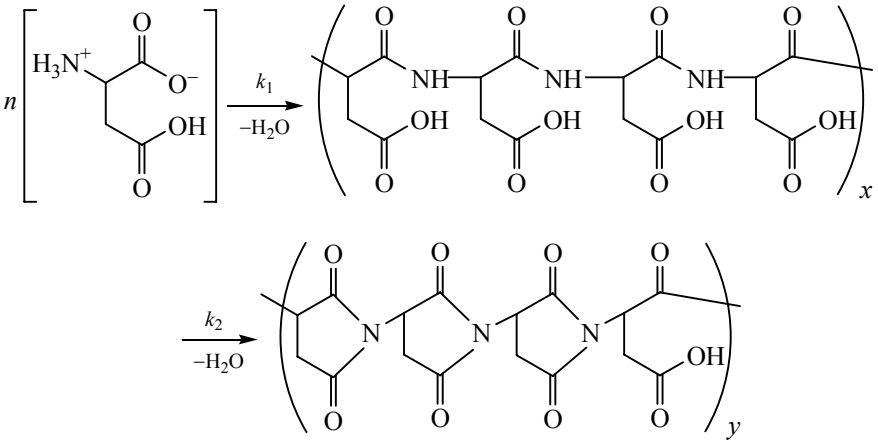


Fig. 4. Magnified fragment of poly(succinimide) MALDI-TOF spectrum (1000–1400 Da).



than that of the first stage (see table). Therefore, separate evaluation of effective rate constants of the both stages was possible at 210–230°C. Decarboxylation contributed to the increase of total volatile products pressure, thus, the determined rate constants were effective values related to combination of two parallel processes: polycondensation and decarboxylation, at the both stages of the process. Decarboxylation was confirmed by MS (signals assigned to macrocations with the structures are shown in Fig. 4). Aspartic acid polycondensation product depended on the reaction temperature. At $T < 207$°C, polycondensation stopped at formation of poly(aspartic acid) containing peptide units formed via dehydration. Above 207°C (210–230°C and higher), aspartic acid was converted to poly(succinimide). The rate-limiting stage of the process was dehydration leading to formation of imide cycles in the polymer.

EXPERIMENTAL

Crystalline aspartic acid (Merck KGaA, Germany) containing ³99.4% of the main substance was used. IR spectra were recorded with Shimadzu IR-Prestige-21/FTIR-8400S spectrometer. The composition of gaseous products was identified with Trace GC Ultra/DSQII chromato-mass spectrometer. The gaseous products pressure at the temperature of experiment as well as at room temperature allowed for accurate quantitative determination of the evolved carbon dioxide and water. MALDI-TOF analysis was performed using Bruker Microflex LT in the linear regime. 2,5-Dihydroxybenzoic acid was used as matrix, and sodium trifluoroacetate was an ionizing agent.

The rate of thermal conversion of aspartic acid was determined by compensation method, according to increase of the pressure of the volatile substances formed in the course of the reaction at constant volume [11]. One-shot glass reactors equipped with the membrane were used. To a reactor (≈38 cm^3), 36–40 mg of the aspartic acid was loaded, and the system was evacuated to the residual pressure of 0.02 mm Hg. Then, the reactor was placed in thermostat heated to the desired temperature. The moment of reaching the target temperature was accepted as the start of thermally induced transformation. The rate constants were calculated from the kinetic equation of the first order reaction.

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