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TG STUDY ON THE KINETICS OF THE POLYMERIZATION OF ASPARTIC ACID CATALYZED BY SODIUM BISULFATE

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Abstract

The polymerization kinetics of *DL*- and *L*-aspartic acid, either in the absence or presence of sodium bisulfate were studied with thermogravimetric analysis. The results revealed that the polymerization of both types of aspartic acids proceeds through the dehydration in two steps, the loss of one water molecule in each step, and the presence of sodium bisulfate effectively catalyzed the polymerization.

Keywords: aspartic acid, polyaspartate, polymerization, sodium sulfate, thermogravimetric analysis

Introduction

Thermal polymerization of amino acids was tried for the synthesis of proteins [1], but only low molecular mass products were obtained and most of the common amino acids could not be incorporated into the protein polymers. However, recently it has been found that thermal polymerization method can be used for the synthesis of polyaspartates, which are very useful chemicals [2, 3]. It can be used as: a dispersant to prevent the redeposition of minerals [4], an inhibitor of scale formation in water treatment [5], a corrosion inhibitor [6] and plant nutrient uptake enhancer [7], etc. Ecotoxicity studies have shown that polyaspartate is nontoxic and does not adversely impact the environment [8].

Polyaspartate can be synthesized by a two-step process. First, polysuccinimide is produced by polymerization of aspartic acid and then, the polyimide rings in polysuccinimide are hydrolyzed with stoichiometric quantities of base to form polyaspartate. The hydrolysis of polysuccinimide was studied in detail by Mosig *et al*. [9]. It was reported that the direct polymerization of aspartic acid in the absence of catalysts could only produce low molecular mass products [10]. In order to increase the molecular mass of the polymer, catalysts such as sodium bisulfate must be used [11]. However, no detailed assessment of the kinetics has been undertaken. In the present work, we studied the kinetics of aspartic acid polymerization and the catalytic effects

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of sodium bisulfate by TG. The results would be very useful for the process design and the prediction of the process conditions.

Experimental

Materials

L-aspartic acid was biochemical reagent (>97%). *DL*-aspartic acid and sodium bisulfates were all analytical grade. All these reagents were used without further purification.

TG measurements

Thermogravimetric measurements were carried out using a Shimadzu TG-50 thermogravimetric analyzer with a working station (TA-50WSI) for collecting data. The apparatus was calibrated with a high-purity indium standard. Experiments were performed in a nitrogen flow of 20 $\text{cm}^3\ \text{min}^{-1}$. Samples (5.5±0.1 mg) of pure aspartic acid were heated from room temperature to 573 K in a silica pan with linear heating rates (β=2.5–20 K min^{-1}). For those runs with sodium bisulfate as catalyst ($NaHSO_4$:aspartic acid=1:10 mol), aspartic acid was first impregnated with an aqueous solution of $NaHSO_4$. The slurry formed was left at room temperature for 12 h, and then dried to constant mass at 353 K under stirring. Then, 6.0±0.1 mg sample (containing 5.5 mg aspartic acid) prepared in this manner were used for thermogravimetric measurements. Derivative TG curves were obtained directly from TG data using the software in the working station. All the measurements were repeated at least three times.

Results and discussion

TG curves of aspartic acid dehydration, either in the presence or absence of sodium bisulfate, for various heating rate β are presented in Fig. 1. In the absence of sodium bisulfate, the dehydration process begins around 480 K (Fig. 1a and 1b). In the presence of sodium bisulfate, the dehydration process begins at much lower temperatures, around 450 K (Fig. 1c and 1d). The mass losses at β=2.5 K min^{-1} were determined by the extrapolated end temperatures and summarized in Table 1. The theoretical mass loss of aspartic acid can be up to 27%. However, in the absence of sodium bisulfate, the mass losses of *DL*-aspartic acid and *L*-aspartic acid are only 25.4 and 25.6%, respectively. This means that the mass loss was not completed. In fact, above the extrapolated end temperature the mass still decreases gradually, indicating that dehydration continues, but at much lower rate. In the presence of sodium bisulfate, the mass losses are 23.6 and 23.9% for *DL*-aspartic acid and *L*-aspartic acid, respectively. Deducting the sodium bisulfate, the mass losses are 25.8% for *DL*-aspartic acid and 26.1% for *L*-aspartic acid, only 0.4 or 0.5% higher than those in the absence of sodium bisulfate, indicating that sodium bisulfate did not evaporate, but mainly stayed in the product after polymerization.

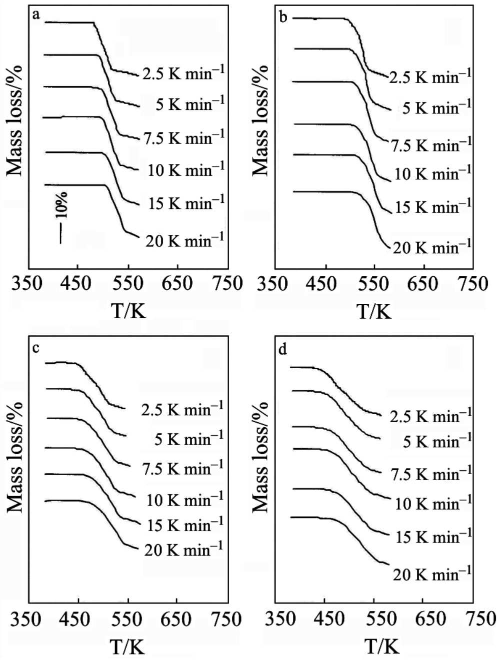
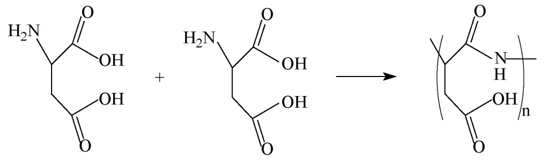


Fig. 1 TG curves of a – *DL*-aspartic acid; b – *L*-aspartic acid; c – *DL*-aspartic acid with 10 mol% $NaHSO_4$, and d – *L*-aspartic acid with 10 mol% $NaHSO_4$

Table 1 Mass loss of aspartic acid at β=2.5 K min^{-1}

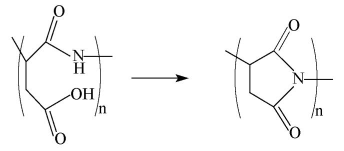
Samples	Measured mass loss/%	Mass loss excluding $NaHSO_4$/%
DL-aspartic acid	25.4±0.2	–
L-aspartic acid	25.6±0.2	–
DL-aspartic acid+$NaHSO_4$	23.6±0.2	25.8±0.2
L-aspartic acid+$NaHSO_4$	23.9±0.2	26.1±0.2

Making a first derivative of the TG data in Fig. 1 gives the derivative TG (DTG) curves as shown in Fig. 2. It can be seen that DTG curves of both *DL*-aspartic acid and *L*-aspartic acid present two peaks, the low temperature peak (peak 1) and the high temperature peak (peak 2). The two peaks in derivative TG curves were obviously not caused by the different enantiomers because *L*-aspartic acid also showed two peaks. The polymerization process only involves dehydration of two molecules of water. This was verified by the total mass loss (see above) and FTIR of the final product (1708, 1771 cm^{-1} for imide group). The two peaks can be ascribed to two steps of dehydration: first, the loss of one water molecule through the reaction of an amino group of one aspartic acid molecule and a hydroxyl group of another aspartic acid molecule, forming the amide bonds Eq. (1),



Scheme 1

and second, the loss of another water molecule through amide hydrogen and another hydroxyl group, leading to the formation of succinimide Eq. (2),



Scheme 2

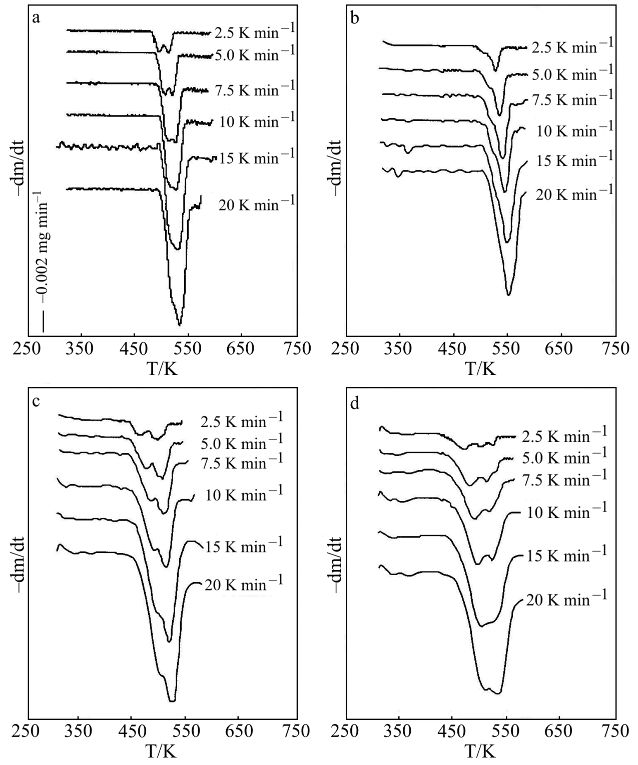


Fig. 2 DTG curves of a – *DL*-aspartic acid; b – *L*-aspartic acid; c – *DL*-aspartic acid with 10 mol% $NaHSO_4$ and d – *L*-aspartic acid with 10 mol% $NaHSO_4$

In all cases peak 1 overlapped with peak 2, showing that the second step starts before the first step is finished. In the absence of sodium bisulfate, peak 1 of *DL*-aspartic acid is roughly the same size as peak 2, but for *L*-aspartic acid, peak 1 is smaller than the peak 2. In the presence of sodium bisulfate, peak 2 of *DL*-aspartic acid becomes bigger than peak 1, while for *L*-aspartic acid the two peaks are almost the same size. Figure 2 shows that all the extrapolated onset temperatures (T_e) and temperatures of maximum mass loss of peak 1 (T_{p1}) and peak 2 (T_{p2}) in the presence of sodium bisulfate are lower than those in the absence of the catalyst, indicating that sodium bisulfate catalyzes the dehydration.

Aspartic acid is an acidic amino acid. It exists in dipolar form (also called zwitterion) in which the amino group is protonated ($-NH_3^+$) and the carboxyl group is dissociated ($-COO^-$). In this form, the hydroxyl group potential for dehydration would be difficult to be deleted. Therefore, high temperature is needed for the dehydration. In the presence of sodium bisulfate that is stronger acid than aspartic acid, the hydroxyl group may be freed, and therefore, the dehydration is facilitated. That might be why sodium bisulfate catalyzed the dehydration.

The kinetic parameters were evaluated according to the Ozawa–Flynn–Wall method [12–15], employing the logarithmic expression:

$$\log\beta = -\frac{0.4567(E/R)}{T} - 2.315 + \log(ZE/R) \tag{3}$$

where β and T are the heating rate and temperature, respectively, and R is the gas constant.

Since sodium bisulfate stayed in the product after polymerization, its influence on the calculation of the kinetic parameters can be omitted. The kinetic parameters are listed in Table 2. In order to compare the polymerization rates, the rate constants at 473 K for all the four samples were calculated from corresponding E_a and Z values and these are also listed in Table 2. Table 2 shows that the activation energy of the second step dehydration of *DL*-aspartic acid is a bit higher than that of *L*-aspartic acid, but the pre-exponential factor is also higher than that of *L*-aspartic acid. Thus, the rate constants of *DL*-aspartic acid at 473 K for the first and the second steps are higher than those of *L*-aspartic acid, indicating that the dehydration of *L*-aspartic acid is a bit more difficult than *DL*-aspartic acid. The reason why different temperatures were required for the dehydration of different enantiomers needs to be studied further.

Table 2 Kinetic results of aspartic acid polymerization determined by TG

		R^2	E/ kJ mol^{-1}	Z/ min^{-1}	k(473 K)/ min^{-1}
DL-aspartic acid	T_{p1}	0.9938	127.8	6.23E+13	0.469
	T_{p2}	0.9690	201.5	9.47E+20	0.052
L-aspartic acid	T_{p1}	0.9899	150.3	5.06E+15	0.125
	T_{p2}	0.9970	149.4	1.09E+15	0.034
DL-aspartic acid+$NaHSO_4$	T_{p1}	0.9786	90.5	2.31E+10	2.32
	T_{p2}	0.9916	135.1	2.72E+14	0.320
L-aspartic acid+$NaHSO_4$	T_{p1}	0.9868	93.6	3.74E+10	1.69
	T_{p2}	0.9843	132.4	8.67E+13	0.209

The presence of sodium bisulfate effectively decreased the activation energies, the pre-exponential factors and therefore the rate constants of both *DL*-aspartic acid and *L*-aspartic acid. For example, the rate constants of the first and the second step dehydration of *DL*-aspartic acid in the presence of sodium bisulfate are 5.0 and 6.2 times higher than those in the absence of sodium bisulfate, respectively. These results further demonstrate that sodium bisulfate catalyzes the dehydration of aspartic acid.

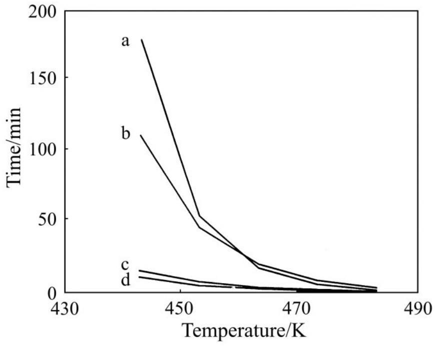


Fig. 3 Calculated time needed for the complete dehydration of aspartic acid at different temperatures using the kinetic parameters of the second maximum

Polysuccinimide is formed through the dehydration of aspartic acid. Therefore, the molecular mass of the final products would depend on the extent of the dehydration. Since the mass loss before the extrapolated end temperatures is lower than the theoretical amount and the dehydration process continues slowly above the extrapolated end temperatures, the final dehydration process might decide the molecular mass of the polymers. Therefore, the polymerization kinetic results can not be used for the predication of molecular masses of the final products. Since the overlapping of the two peaks in the derivative TG curves, the kinetic values may be deviated from the specific reactions to some extent. Nevertheless, the present kinetic results would still be very useful for the prediction of the process conditions. According to the results in Table 2, using the kinetic parameters of the second peaks, the time needed for the complete dehydration of aspartic acid either in the absence or presence of sodium bisulfate at different temperatures are calculated and shown in Fig. 3. From Fig. 3 it can be calculated that for *DL*-aspartic acid, the dehydration process may need 53 min at 453 K, or 8.4 min at 473 K, but in the presence of 10 mol% sodium bisulfate, only 6 or 1.4 min is needed at 453 and 473 K, respectively. The kinetic results may also be very useful for the process design.

Conclusions

TG results revealed that the dehydration of both type aspartic acids proceeds in two steps: the first step might be the loss of one water molecule through the reaction of an amino group of one aspartic acid molecule and a hydroxyl group of another aspartic acid molecule, forming amide bonds, and the second step might be the loss of another water molecule through the amide hydrogen and another hydroxyl group, leading to the formation of succinimide ring. The kinetic parameters of the first and the second maximum were obtained by a method similar to the Ozawa–Flynn–Wall method. The rate constants of *DL*-aspartic acid are higher than those of *L*-aspartic acid, indicating that the dehydration of *L*-aspartic acid is a bit more difficult than *DL*-aspartic acid. The TG results further revealed that the presence of sodium bisulfate effectively catalyzed the dehydration of aspartic acid.

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