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Study on the Polymerization of Aspartic Acid Catalyzed by Phosphoric Acid

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ABSTRACT

The dehydration kinetics of DL- and L-aspartic acid, either in the absence or presence of phosphoric acid, from 323 to 573K were studied with thermogravimetric analysis (TGA), and the polymerization of DL-aspartic acid was studied by a thin-layer polymerization method. The 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 of carboxyl 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 extrapolated onset temperatures of dehydration, the first and the second maximum were obtained by a method similar to the Ozawa–Flynn–Wall method. The results further revealed that the presence of phosphoric acid effectively catalyzed the dehydration of aspartic acid. In the synthesis of polyaspartate, only the product with molecular weight below 5000 was obtained in the absence of phosphoric acid. However, in the presence of phosphoric acid, the product with molecular weight up to 14,000 can be obtained.

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Key Words: Aspartic acid; Dehydration; Thermogravimetric analysis; Polymerization; Polyaspartate.

INTRODUCTION

Thermal polymerization of amino acids was tried for the synthesis of proteins,[1] but only low molecular weight 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 polyaspartate, alkali metal salts of polyaspartic acid, which are very useful chemicals.[2–9] It can be used as: a dispersant to prevent the redeposition of minerals,[2] an inhibitor of scale formation in water treatment,[3–5] a corrosion inhibitor[6,7] and plant nutrient uptake enhancer,[8] a sequestering agent for washing,[9] etc. Polyaspartate has a linear polyamide backbone structure that enables the polymer to biodegrade rapidly and completely.[10,11] Ecotoxicity studies have shown that polyaspartate is nontoxic and biodegradable and does not adversely impact the environment.[10,11]

Polyaspartate can be synthesized by a two-step process. Polysuccinimide is first produced, and then, the polyimide rings in polysuccinimide are hydrolyzed with stoichiometric quantities of base to form polyaspartate. Typically, the resulting polyamide is a copolymer in which the amide bonds are formed from ca. 30% α- and ca. 70% β-hydroxyl groups.[12]

The hydrolysis of polysuccinimide was studied in detail by Mosig et al.[13] The kinetics of the reaction in aqueous slurry was described by a shrinking core model. The reaction was found to be first order with respect to OH^- concentration, and it follows a normal Arrhenius relationship with respect to temperature. In the range of 40–70°C and a pH of 8.0–9.5, the reaction completes within 1 h. Since polysuccinimide can be readily hydrolyzed, the key step of production, molecular weight and the properties of polyaspartate lie in the synthesis of polysuccinimide.

The synthesis of polysuccinimide can be achieved by reacting maleic anhydride with ammonia[14] or by heating mixtures of aspartic acid precursors such as mono and diammonium maleate, maleamic acid, ammonium maleamate, ammonium malate or mixtures of these.[15] However, these processes only produce products with weight average molecular weight less than 4000. Another method for the production of polysuccinimide is thermal polymerization of aspartic acid. But it was reported that this process could also only produce low molecular weight products in the absence of catalyst.[16] In order to increase the molecular weight of the polymer, catalysts such as phosphoric acid must be used.[17,18] However, in those reported processes, organic solvents must be used.

Thermogravimetric analysis (TGA) has found wide application in the investigation of both physical and chemical processes involving mass change. In a series of review papers, Dollimore summaries the literatures of recent years in these fields.[19–21] Since the polymerization of aspartic acid proceeds by dehydration, TGA is a valuable method to follow the course of mass loss by dehydration. However, TGA technique used to be used for the measurement of total mass loss and the starting and ending temperature, but not the rate of mass loss. Making a first derivative of a TGA curve gives a curve, which shows the rate of mass loss. Assuming an overall first-order process, the mass lost (m) at time t is proportional to the amount of reacted substrate and the following kinetic equations are obtained:

$$\frac{1}{m_T}\frac{dm}{dt} = Ze^{-E/RT}\left(\frac{m_T - m}{m_T}\right) = \frac{d\alpha}{dt} = Ze^{-E/RT}(1 - \alpha) \tag{1}$$

$$k = Z\exp(-E/RT) \tag{2}$$

where m_T is the total mass lost, E is the activation energy, R is the gas constant, Z is the Arrhenius pre-exponential factor, T is the absolute temperature, $\alpha = m/m_T$ is the degree of conversion, and k is the Arrhenius rate constant.

According to the Ozawa–Flynn–Wall method,[22] the extrapolated start of the dehydration process and the maximum of the mass loss are the points of constant degree of conversion. Therefore, by introduction of the linear heating rate β into Eq. (1) and combination with Eq. (2), the temperature of the start or temperature of the maximum of mass loss obtained from the several derivative TGA curves with different β values can be used for the determination of kinetic parameters from equation

$$\log\beta = aT^{-1} + b \tag{3}$$

When $\log\beta$ vs. $1/T$ is plotted, the straight line with the slope $a = -0.4567E/R$ and the reciprocal $b = -2.315 + \log(ZE/R)$ should be obtained. Therefore, the activation energy E is calculated from

$$E = -2.19R\frac{d\log\beta}{dT^{-1}} \tag{4}$$

Values of E and pre-exponential factor Z (calculated from reciprocal b) can be used to calculate the rate constant of reaction given by the Arrhenius equation (Eq. 2).

In this work, we studied the kinetics of aspartic acid dehydration by TGA and the synthesis of polyaspartate through solid thin-layer polymerization of aspartic acid, either in the absence or presence of phosphoric acid without organic solvents, followed by base hydrolysis. The thin-layer polymerization method was used because it well presents the reaction in a TGA sample cell in which the samples were also packed as a thin layer.

EXPERIMENTAL

Materials

L-aspartic acid was biochemical reagent (>97%). DL-aspartic acid and phosphoric acid (85%) were all analytical grade. All these reagents were used without further purification.

TGA Measurements

Thermogravimetric measurements were carried out using a TGA apparatus: SHIMADZU model TGA-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 50 cm^3/min. Samples (5.0 ± 0.1 mg) of pure aspartic acid were heated from room temperature to 573K in a silica pan with linear heating rates ($\beta = 2.5-20K/min$). For those runs with phosphoric acid as catalyst (H_3PO_4: aspartic acid = 1:10, mol), aspartic acid was first impregnated with an aqueous solution of H_3PO_4 (85%). The slurry formed was left at room temperature for 12 h, and then dried to constant mass at 353K under stirring. It was confirmed that after drying, all the water evaporated and H_3PO_4 was left in the sample. Then, 5.3 ± 0.1 mg sample (containing 5 mg aspartic acid) prepared in this manner were used for thermogravimetric measurements. Derivative TGA curves were obtained directly from TGA data using the software in the working station. All the measurements were repeated at least three times.

Thin-Layer Polymerization of Aspartic Acid

10 g aspartic acid either in the presence or absence of phosphoric acid with a thin-layer in a stainless steel pan was placed in an oven in the flow of nitrogen at 473–503K for 1–6 h. The samples thus formed were thoroughly washed with deionized water, and after drying hydrolyzed with 0.1 M NaOH solution at pH = 8.5. The mass-average molecular weight was determined by measurement of viscometry of aqueous solution using poly(acrylic acid) as standard with Mark–Houwink coefficients $K = 0.0506\ ml/g$ and $\alpha = 0.656$.[23]

RESULTS AND DISCUSSION

Kinetics of Aspartic Acid Dehydration

TGA curves of aspartic acid dehydration, either in the presence or absence of phosphoric acid, for various heating rate β are presented in Fig. 1. In the absence of phosphoric acid, the dehydration process begins around 480K (Fig. 1(a) and (b)). In the presence of phosphoric acid, the dehydration process begins at much lower temperatures, around 420K (Fig. 1(c) and (d)). The extrapolated onset (T_e) and end temperatures of mass loss are defined in Fig. 1(a). The mass losses at $\beta = 2.5K/min$ 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 phosphoric acid, the mass losses of DL-aspartic acid and L-aspartic acid are only 25.5% and 25.7%, 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 phosphoric acid, the mass losses are 23.7% and 23.9% for DL-aspartic acid and L-aspartic acid, respectively. Deducting the phosphoric

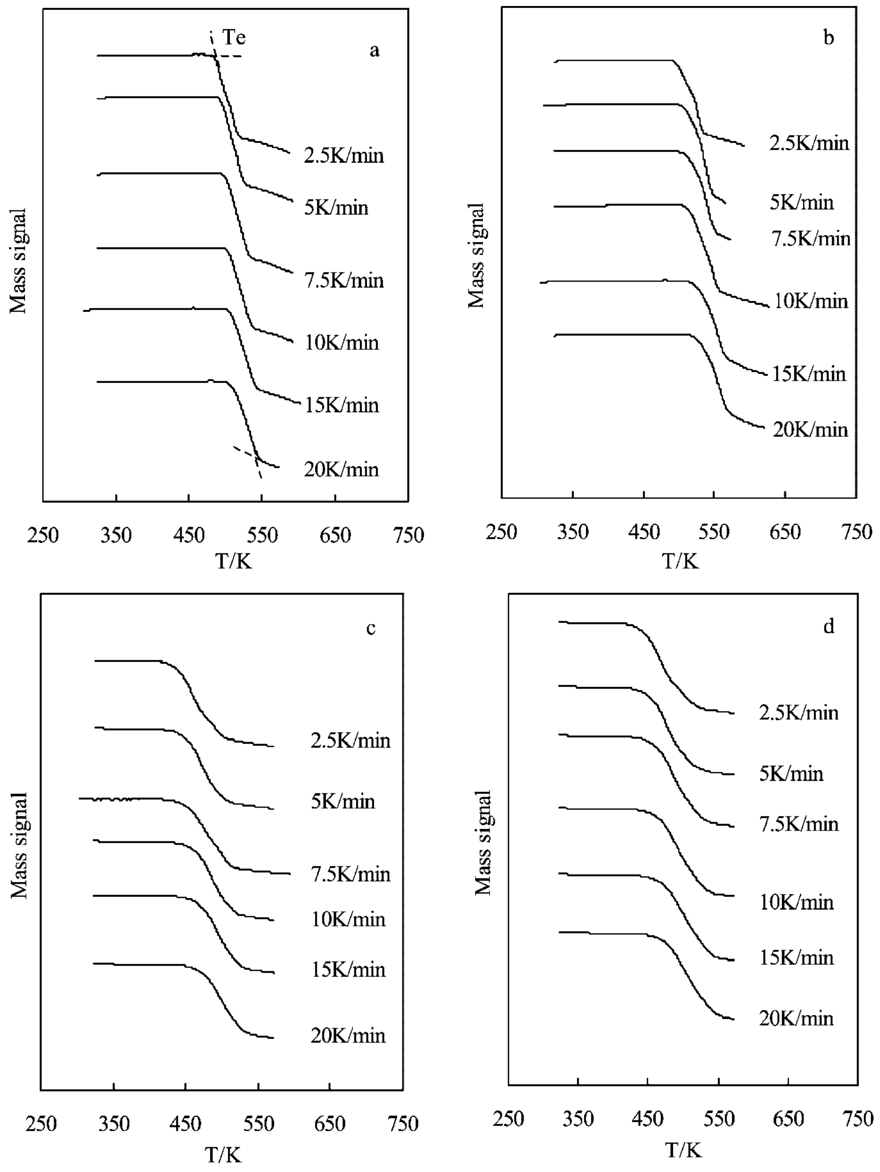


Figure 1. TGA curves of (a) DL-aspartic acid; (b) L-aspartic acid; (c) DL-aspartic acid with 10 mol% H_3PO_4, and; (d) L-aspartic acid with 10 mol% H_3PO_4.

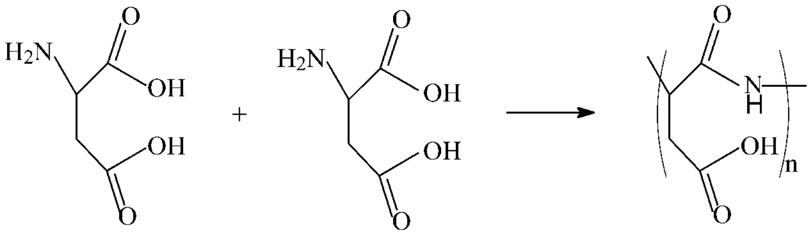
acid, the mass losses are 25.6% for DL-aspartic acid and 25.8% for L-aspartic acid, similar to those in the absence of phosphoric acid, indicating that phosphoric acid did not evaporate, but stayed in the product. Although the boiling point of 85% phosphoric acid in water is 431K, after drying of the aspartic acids impregnated with 85% phosphoric acid to constant mass at 353K, all the water evaporated, but H_3PO_4 was left in the samples as

Table 1. Mass loss of aspartic acid at $\beta = 2.5$K/min.

Samples	Measured mass loss (%)	Mass loss excluding H_3PO_4 (%)
DL-aspartic acid	25.5 ± 0.2	/
L-aspartic acid	25.7 ± 0.2	/
DL-aspartic acid + H_3PO_4	23.7 ± 0.2	25.6 ± 0.2
L-aspartic acid + H_3PO_4	23.9 ± 0.2	25.8 ± 0.2

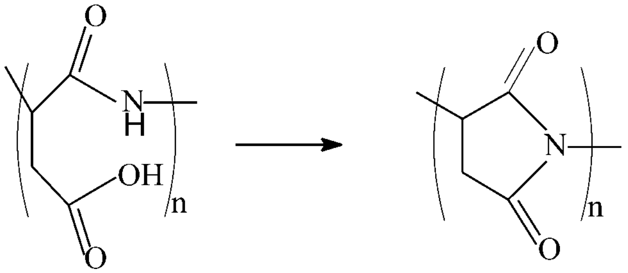
described in the part of experimental. The polymerization temperature is much higher than the boiling point of 85% phosphoric acid. The results that after polymerization phosphoric acid still stayed in the final product suggest that phosphoric acid might strongly interact first with the aspartic acids, then with the polymerization product, and did not evaporate.

From TGA curves only one mass loss step can be differentiated. Making a first derivative of the data in Fig. 1 gives the derivative TGA curves as shown in Fig. 2. It can be seen that derivative TGA curves of both DL-aspartic acid and L-aspartic acid present two peaks. The two peaks in derivative TGA 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 of carboxyl groups of another aspartic acid molecule, forming the amide bonds (Eq. (5)),



(5)

and second, the loss of another water molecule through amide hydrogen and another hydroxyl group, leading to the formation of succinimide (Eq. (6)),



(6)

In all cases, the low temperature peak overlapped with the high temperature peak, showing that the second step starts before the first step is finished. In the absence of

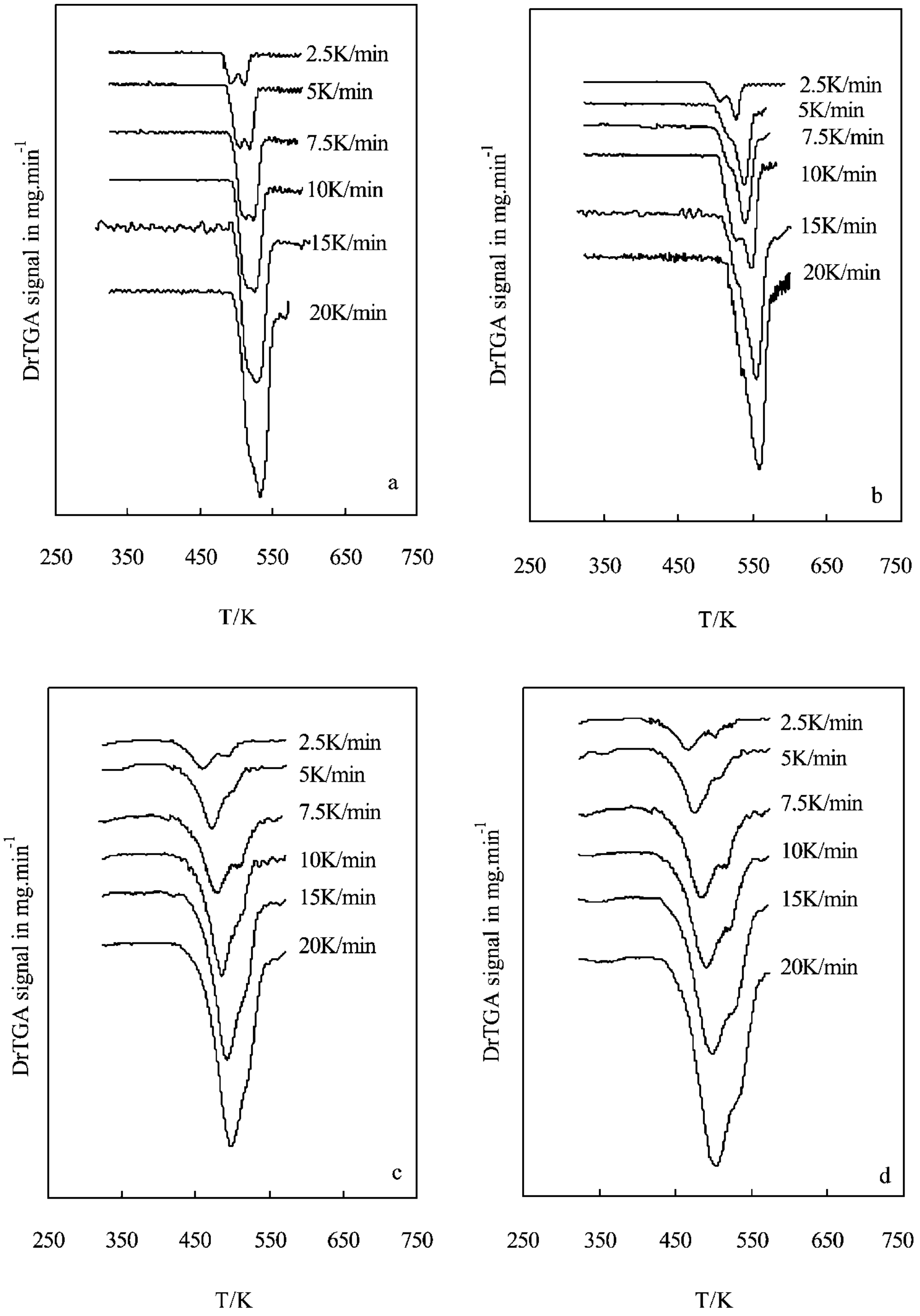


Figure 2. Derivative TGA curves (DrTGA) of (a) DL-aspartic acid; (b) L-aspartic acid; (c) DL-aspartic acid with 10 mol% H_3PO_4; and (d) L-aspartic acid with 10 mol% H_3PO_4.

phosphoric acid, the low temperature peak of DL-aspartic acid is roughly the same size as the high temperature peak, but for L-aspartic acid, the low temperature peak is smaller than the second one. However, in the presence of phosphoric acid, the high temperature peak of both DL-aspartic acid and L-aspartic acid becomes much bigger than the first one. Thus, the results indicate that phosphoric acid catalyzes the first step of 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 phosphoric acid, which is stronger acid than aspartic acid, the hydroxyl group may be freed, and therefore, the dehydration is facilitated. That might be why phosphoric acid catalyzed the dehydration.

The extrapolated onset temperatures (T_e) and temperatures of maximum mass loss (T_{p1} and T_{p2}) were determined from each derivative TGA curves using the software in the working station of the TGA instrument. An increase of the heating rate β results in a shift of temperatures T_e, T_{p1}, and T_{p2} and this phenomenon is used here as the basis for the calculation of the kinetic parameters. Since phosphoric acid stayed in the product after dehydration, its influence on the calculation of the kinetic parameters can be omitted. The straight line plots of Eq. (3) for T_e, T_{p1}, and T_{p2} are shown in Fig. 3. At high β, the small peaks (T_{p1}, in the absence of phosphoric acid or T_{p2} in the presence of phosphoric acid) were difficult to determine. Therefore, only those values at low β were used for the calculation. The parameters a and b of Eq. (3) with standard deviations, square regression coefficients R^2 and calculated kinetic parameters: activation energies E_a and pre-exponential factors Z are listed in Table 2. Errors of activation energies were calculated from the standard deviations of Eq. (3). In order to compare the dehydration 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.

In the kinetic calculations, it was assumed that the water loss was evolved immediately after dehydration. In fact, firstly, the dehydration temperature is much higher that the boiling point of water; secondly, all the activation energies in Table 2 are much higher than that of diffusion, which is usually less than $40\,\mathrm{kJ\,mol^{-1}}$. All these suggest that the water be evolved immediately as soon as it was produced.

Since the polymerization temperature is much lower than the melting point of aspartic acid (611K for DL- and 597K for L-aspartic acid), the polymerization reaction occurs at the solid state. The good linearity of the plots with R^2 near to unity confirms the assumption that the reaction is first order. Table 2 shows that the activation energies of the start and the second step dehydration of DL-aspartic acid are a bit higher than those of L-aspartic acid, but the pre-exponential factors are also higher than those of L-aspartic acid. Thus, the rate constants of DL-aspartic acid at 473K for the start, 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 crystal lattice of amino acids is held together by strong electrostatic forces, between positively and negatively charged functional groups of neighboring molecules. The different enantiomers may exist in different crystal lattice. In the present study, DL-aspartic acid was synthesized by chemical method, existed in the form of monoclinic prisms. While L-aspartic acid was produced by biochemical method, existed in the form of

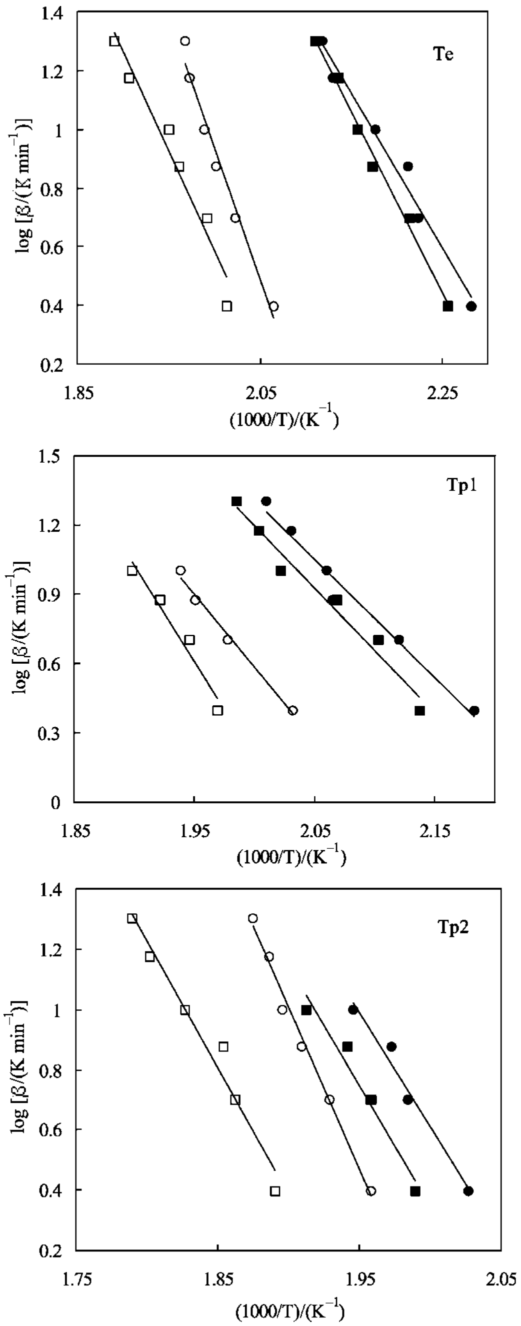


Figure 3. Plots of Eq. (3) obtained for temperatures of (a) extrapolated start of dehydration (T_e,); (b) first maximum of mass loss (T_{p1}); and (c) second maximum (T_{p2}). Circles: DL-aspartic acid without (unfilled) and with 10 mol% H_3PO_4 (filled). Squares: L-aspartic acid without (unfilled) and with 10 mol% H_3PO_4 (filled).

Table 2. Parameters *a* and *b* of Eq. 9 with standard deviations (σ_a and σ_b), square regression coefficients R^2, and calculated kinetic parameters: activation energy E_a, pre-exponential factor *Z*, and rate constant of dehydration k at 473K.

	a	σ_a	b	σ_b	R^2	E_a/kJ/mol	Z/min^{-1}	K 473K/min^{-1}
DL-aspartic acid								
Start	-8.40×10^3	0.55	17.71	1.13	0.9891	152.9 ± 10.0	5.84×10^{15}	7.52×10^{-2}
First peak	-6.33×10^3	0.10	13.25	0.20	0.9913	115.3 ± 1.8	2.67×10^{11}	4.93×10^{-2}
Second peak	-1.08×10^4	0.10	21.49	0.19	0.9928	196.2 ± 1.8	2.70×10^{19}	5.74×10^{-3}
L-aspartic acid								
Start	-6.85×10^3	0.19	14.27	0.38	0.9608	124.6 ± 3.5	2.58×10^{12}	4.43×10^{-2}
First peak	-8.35×10^3	0.26	16.86	0.50	0.9690	151.9 ± 4.7	8.34×10^{14}	1.39×10^{-2}
Second peak	-8.56×10^3	0.15	16.62	0.27	0.9769	155.8 ± 2.7	4.64×10^{14}	2.91×10^{-3}
DL-aspartic acid with 10 mol % H_3PO_4								
Start	-5.47×10^3	0.30	12.90	0.82	0.9730	99.6 ± 5.5	1.35×10^{11}	1.37
First peak	-5.12×10^3	0.04	11.56	0.10	0.9833	93.3 ± 0.7	6.64×10^{9}	0.334
Second peak	-7.48×10^3	0.13	15.56	0.27	0.9841	136.1 ± 2.4	4.57×10^{13}	4.27×10^{-2}
L-aspartic acid with 10 mol % H_3PO_4								
Start	-6.07×10^3	0.17	14.11	0.38	0.9903	110.6 ± 3.1	2.00×10^{12}	1.23
First peak	-5.51×10^3	0.12	12.21	0.25	0.9751	100.3 ± 2.2	2.80×10^{10}	0.234
Second peak	-7.85×10^3	0.16	16.04	0.32	0.9728	142.9 ± 2.9	1.32×10^{14}	2.19×10^{-2}

rhombic leaves. The slightly higher temperature needed for the dehydration of L-aspartic acid than DL-aspartic acid might be ascribed to the different synthetic methods or the different form of crystal lattice. This needs to be studied further.

The presence of phosphoric acid effectively decreases 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 start, the first and the second step dehydration of DL-aspartic acid in the presence of phosphoric acid are 18, 6.8, and 7.4 times higher than those in the absence of phosphoric acid, respectively. These results demonstrate that phosphoric acid catalyzes not only the first step dehydration, but also the start and the second step of the dehydration. Again, this can be explained by the liberation of the hydroxyl of carboxyl groups by phosphoric acid. It can liberate the hydroxyl of the first carboxyl group, and of course, the one of the second carboxyl group.

Polysuccinimide is formed through the dehydration of aspartic acid. Therefore, the molecular weight 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 weight of the polymers. Therefore, the dehydration kinetic results can not be used for the predication of molecular weights of the final products. Since the overlapping of the two peaks in the derivative TGA 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 phosphoric acid at different temperatures are

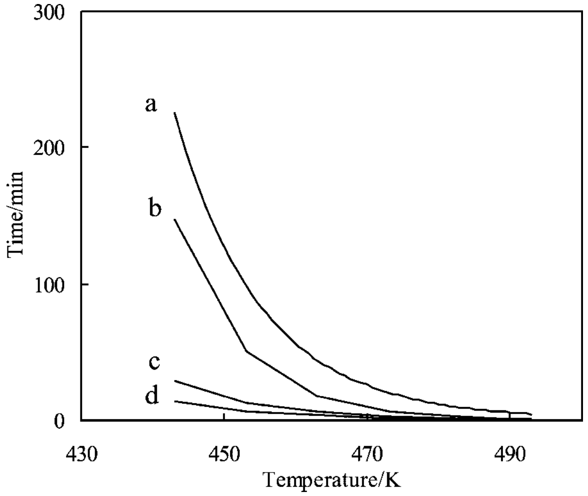


Figure 4. Calculated time needed for the complete dehydration of aspartic acid versus temperatures using the kinetic parameters of the second maximum. (a) L-aspartic acid; (b) DL-aspartic acid; (c) L-aspartic acid with 10 mol% H_3PO_4; and (d) DL-aspartic acid with 10 mol% H_3PO_4.

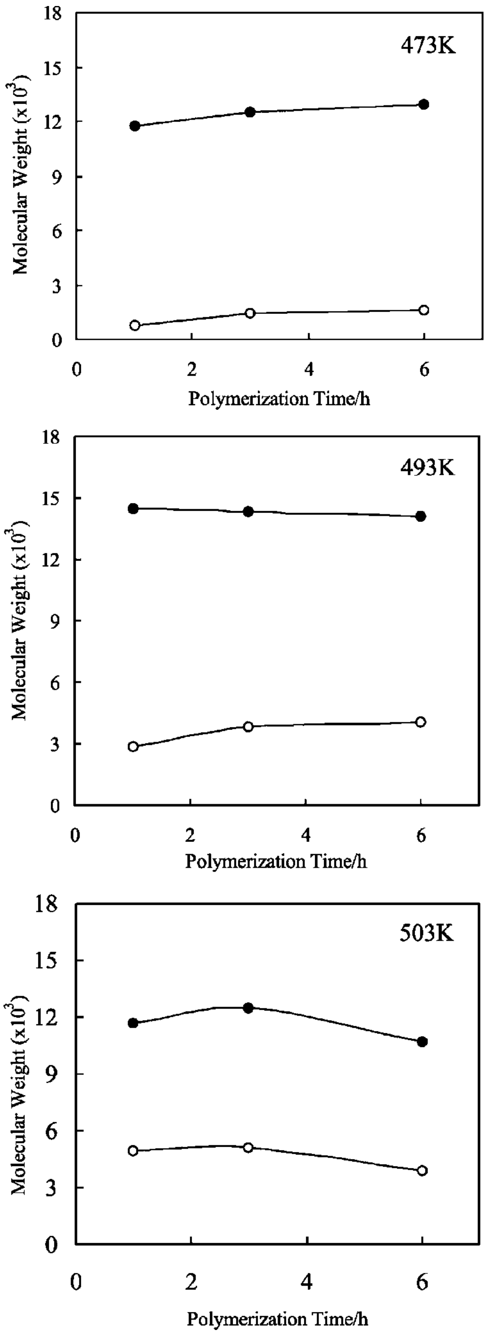


Figure 5. Polymerization of DL-aspartic acid at different temperatures. (○) in the absence of H_3PO_4; (●) in the presence of 10 mol% H_3PO_4.

calculated and shown in Fig. 4. From Fig. 4, we can calculate that for DL-aspartic acid, the dehydration process may need 102 min at 453K, or 20 min at 473K, but in the presence of 10 mol% phosphoric acid, only 8 min or 2 min is needed at 453K and 473K, respectively. The kinetic results may also be very useful for the process design.

Synthesis of Polyaspartate

Figure 5 shows the weight average molecular weight of sodium polyaspartate synthesized by thermal polymerization of DL-aspartic acid at different temperatures. In all cases, the conversions were near to completeness and therefore were not given. At 473K, the molecular weight of polyaspartate is only around 1000. With the increase of polymerization time, the molecular weight increases slightly, indicating that dehydration process still proceeds slowly, which agrees with the TGA results. At 493K, the molecular weight increased to around 4000. With the further increment of polymerization temperature to 503K, the molecular weight increased to 5000. However, at this temperature, with the prolonging of the polymerization time, molecular weight decreased gradually. This might be due to the decomposition of the polymerization product, polysuccinimide. In fact, at high polymerization temperatures, the final products become much darker than those obtained at lower polymerization temperatures. With long polymerization time at higher temperatures, there must be decomposition.

In the presence of phosphoric acid, the molecular weight of the products increased markedly. The molecular weight of around 13,000 and 14,000 were obtained at 473K and 493K, respectively. However, with the further increment of polymerization temperature to 503K, the molecular weight decreased to around 12,000, and with increasing polymerization time, the molecular weight further decreased gradually. Again, this might be caused by the decomposition of polysuccinimide.

The synthesis results further demonstrate the catalytic effect of phosphoric acid. It promotes not only the dehydration rate, but also the molecular weight of the final polymer products. In the absence of phosphoric acid, the end groups of the polymer, amino ($-NH_2$) and carboxyl ($-COOH$), might have lower chance to react with each other. In the presence of phosphoric acid, which does not evaporate in the polymerization process as indicated by TGA results, but exists in the liquid state, it may further promote the reaction of the end amino and carboxyl groups of lower molecular weight polymers, and therefore increased the molecular weight of the final products. The catalytic effect of phosphoric acid needs to be studied further.

CONCLUSION

TGA 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 of carboxyl 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 extrapolated onset temperatures of dehydration, 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 TGA results further revealed that the presence of phosphoric acid effectively catalyzed the dehydration of aspartic acid. In the synthesis of polyaspartate, the product with molecular weight below 5000 was obtained in the absence of phosphoric acid. However, in the presence of phosphoric acid, the product with molecular weight up to 14,000 can be obtained.

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