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THERMAL DECOMPOSITION OF SOLID STATE POLY(β-*L*-MALIC ACID)

S. Fujishige[*]

Tokyo Kasei University, Kaga 1-18, Itabashi, Tokyo 173-8602, Japan

Abstract

Thermal decomposition process of solid state poly(β-*L*-malic acid) was traced by DSC combined with FT-IR. Melting temperature of this partially crystallized polymer was detected at 46–60°C. The thermal decomposition initiated at ca 185°C accompanied by an evolution of gaseous products. In contrast to the cleavage reaction in the aqueous polymer solutions which gives *L*-malic acid and corresponding dimer of *L*-malic acid, the solid state poly(β-*L*-malic acid) decomposed at above the decomposition temperature giving not the constituent *L*-malic acid but fumaric acid at the first stage of the reaction then, maleic and maleic anhydride.

Keywords: DSC, FT-IR, fumaric acid, *L*-malic acid, maleic acid, maleic anhydride

Introduction

A biological synthetic route for poly(*L*-malic acid) has recently been developed by Nagata *et al*. [1] and the molecular structure of the polymer produced by *Aureobasidium sp.* A-91 was elucidated as poly(β-*L*-malic acid) by ^{1}H- and ^{13}C-NMR spectroscopy applied to the hydrolytic cleavage products of the polymer in aqueous solution [2, 3].

It was found that the cleavage reaction was accelerated on heating the aqueous polymer solutions but racemization does not take place during the course of the cleavage of poly(β-*L*-malic acid) via both hydrolytic reactions either autocatalytic or chemically (alkali) induced hydrolysis. DSC starting at room temperatures up to 330°C on this solid state polymer sample showed neither glass transition temperature nor melting temperature below the decomposition temperature starting at 185°C accompanying a remarkable endothermic reactions [3].

In this paper, a thermal decomposition process of this solid state poly(β-*L*-malic acid) was traced by FT-IR spectroscopy applied on a very little amount of the reaction products recovered from DSC cells after every stage of DSC operations. In contrast to those of hydrolytic cleavage in aqueous polymer solutions, major products of thermal decomposition of the solid state poly(β-*L*-malic acid) were not malic acid but a mixture composed of maleic acid, maleic anhydride and fumaric acid.

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[*] Author for correspondence: E-mail: fujisige@tokyo-kasei.ac.jp

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Experimental

Fractionally precipitated from aqueous methanol solution, poly(β-*L*-malic acid) having average molecular mass of 10 000 (evaluated by ^{13}C-NMR) was used. Other chemicals used as the reference materials both for FT-IR and DSC were *L*-malic acid (*m.p.*: 100°C, dec. at 140°C), *D,L*-malic acid (*m.p.*: 128.5°C, dec. at 150°C), fumaric acid (*m.p.*: 290°C, subl. at 200°C), maleic acid (*m.p.*: 137–138°C, dec. at 135°C to fumaric acid) and maleic anhydride (*m.p.*: 53°C, *b.p.*: 200°C) as purchased from Wako Pure Chemicals Co. DSC was recorded using Seiko's DSC220C+SSC5200 System. This polymer is so hygroscopic that almost all operations must be done under argon gas. A half of the samples for DSC were carefully sealed in aluminum pans and another half of the samples were subjected to the DSC operations filled in aluminum open cells in order to allow free release of reaction products during the course of heating for DSC. During the DSC operations, constant feeds of argon gas into the furnace were maintained to prevent not only water absorption but also coagulation of the reaction products evolved. All samples were recovered from those aluminum pans after each DSC operations to prepare KBr disks for further experiments by FT-IR on Horiba's FT-210.

In parallel to the above, a hand made glass tube of 60 cm long and 8 mm diameter, as schematically shown in Fig. 1, was used to obtained much more amount of reaction products as a simulation of the thermal decomposition of poly(β-*L*-malic acid). Under argon gas, ca 0.2 g of the polymer sample was fed into the bottom of the tube and was subjected to heat treatment at 140°C for 2 h or at 240°C for 4 h for thermal decomposition. After 4 h at 240°C, the solid state polymer sample decomposed completely and gave well separated four zones depending on the molecular characteristics of the reaction products, respectively as shown in Fig. 1. These reaction products were also examined by FT-IR and DSC.

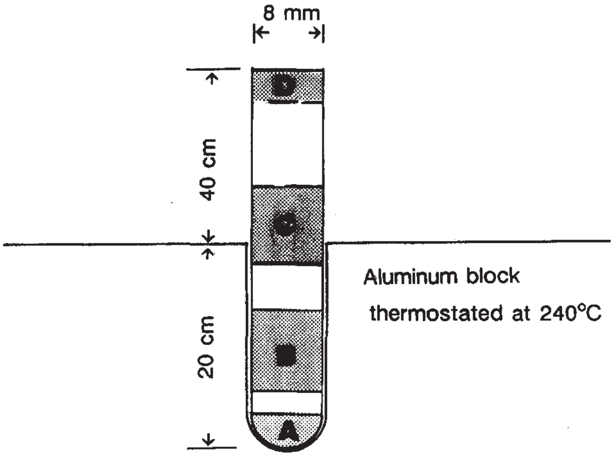

Fig. 1 Glass tube oven for thermal decomposition of solid state poly(β-*L*-malic acid) to collect reaction products to be analyzed by FT-IR

Results and discussion

After each DSC operations, it was noted that all sealed cells were apparently expanded so much suggesting some high pressure evolved during the course of thermal decomposition of the polymer. Typical examples are shown in Figs 2a as compared to that measured in open cells, b. A small but distinct endothermic peak appeared at 40–60°C was assigned to be the melting temperature of this polymer because there was no such peak in our previous experiments on freeze-dried fresh sample [3] and this type of peak, and X-ray diffraction patterns of the same sample also, disappeared after a heat treatment at 140°C for 2 h as shown in Fig. 2c. In Fig. 2b, a sharp endothermic peak appeared at 260°C is not yet assigned while the peak appeared at 290°C is assigned to that of fumaric acid. In Figs 2c and d, DSC of the polymer once pre-treated at 140°C for 2 h is compared to that of *L*-malic acid used as a reference material pre-treated once at the same condition to the polymer. Marked endothermic peak appeared at around 250–260°C might be attributed to that of the decomposition of chain structure of the polymer releasing one mole of water from each sites of connection of the repeating units of poly(β-*L*-malic acid), respectively followed by transformation of the reaction products into fumaric acid.

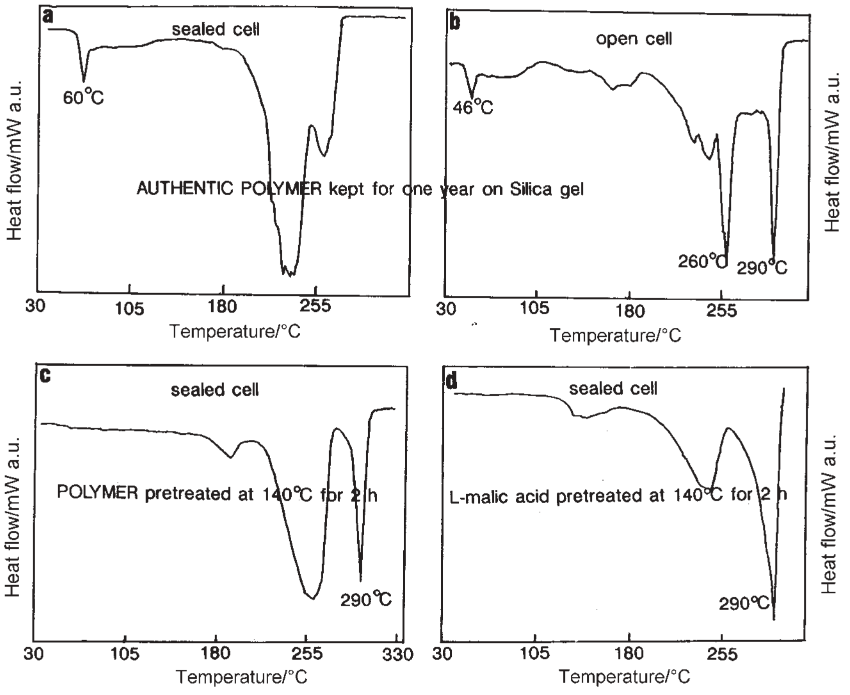

Fig. 2 DSC of solid state poly(β-*L*-malic acid) recorded under different conditions

In Fig. 3, IR spectrum of the authentic polymer is compared to that of the polymer sample thus pre-treated at 140°C for 2 h and of the *L*-malic acid as reference material in-

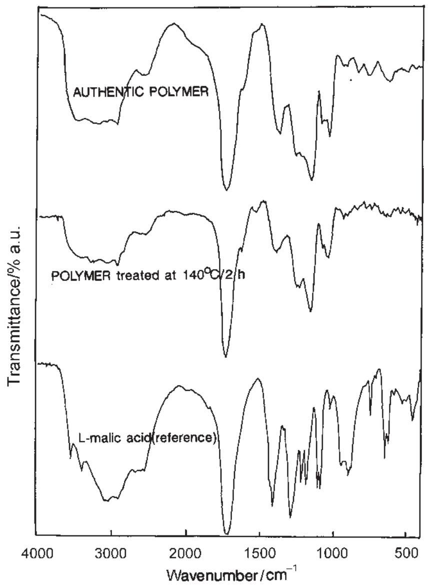

Fig. 3 IR spectra of poly(β-*L*-malic acid) as compared to that of *L*-malic acid (KBr disk)

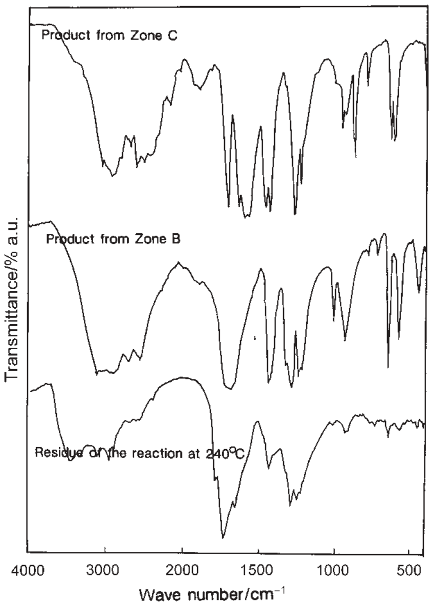

Fig. 4 IR spectrum of the residue after thermal decomposition of solid state poly(β-*L*-malic acid) at 240°C for 4 h as compared to those reaction products trapped inside of the glass tube oven at Zone B and Zone C, respectively (KBr disk)

dicating no significant difference was detected between the two polymer samples. In Fig. 4, IR spectrum of the decomposed residue collected from the bottom of the glass tube oven, Zone A is compared to that of mid layer, Zone B composed mainly of fumaric acid and to that of the third layer from the bottom, Zone C composed of maleic acid. The reaction products at the top layer, Zone D was confirmed as maleic anhydride.

Conclusions

It was found that, after 4 h at 240°C, solid state poly(β-*L*-malic acid) completely decomposed not into the constituent *L*-malic acid but into fumaric acid. Based on these facts, a reaction mechanism of the thermal decomposition of solid state poly(β-*L*-malic acid) is explained as follows: the elemental process does occur when the solid state polymer heated above the decomposition temperature, the polymer releases one mole of water from each connecting sites of the repeating units of *L*-malic acid, respectively to give corresponding amount of fumaric acid depending on the thermal conditions.

References

1 N. Nagata, T. Nakahara and T. Tabuchi, Biosci. Biochem., 57 (1993) 638.
2 S. Fujishige, R. Morita, J. R. Brewer, N. Nagata, N. Nakahara and T. Tabuchi, Makromol. Chem. Rapid Commun., 14 (1993) 163.
3 N. Nagata, N. Nakahara, T. Tabuchi, R. Morita, J. R. Brewer and S. Fujishige, Polymer J., 25 (1993) 585.
4 S. Cammas, Ph. Guerin, J. P. Giraut, E. Holler, Y. Gache and M. Vert, Macromolecules, 26 (1993) 4681.