

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Synthesis and Characterization of Hybrid Biopolymers of L-lactic Acid and 2-Pyrone-4,6-dicarboxylic Acid

Tsuyoshi Michinobu<sup>ab</sup>; Masami Bito<sup>a</sup>; Miki Tanimura<sup>a</sup>; Yoshihiro Katayama<sup>c</sup>; Eiji Masai<sup>d</sup>; Masaya Nakamura<sup>e</sup>; Yuichiro Otsuka<sup>e</sup>; Seiji Ohara<sup>e</sup>; Kiyotaka Shigehara<sup>ab</sup>

<sup>a</sup> Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan <sup>b</sup> Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan <sup>c</sup> Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan <sup>d</sup> Department of Bioengineering, Nagaoka University of Technology, Nagaoka, Niigata, Japan <sup>e</sup> Forestry and Forest Products Research Institute, Tsukuba, Ibaraki, Japan

Online publication date: 26 April 2010

**To cite this Article** Michinobu, Tsuyoshi , Bito, Masami , Tanimura, Miki , Katayama, Yoshihiro , Masai, Eiji , Nakamura, Masaya , Otsuka, Yuichiro , Ohara, Seiji and Shigehara, Kiyotaka(2010) 'Synthesis and Characterization of Hybrid Biopolymers of L-lactic Acid and 2-Pyrone-4,6-dicarboxylic Acid', *Journal of Macromolecular Science, Part A*, 47: 6, 564 – 570

**To link to this Article:** DOI: 10.1080/10601321003742121

**URL:** <http://dx.doi.org/10.1080/10601321003742121>

## PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Synthesis and Characterization of Hybrid Biopolymers of L-lactic Acid and 2-Pyrone-4,6-dicarboxylic Acid

TSUYOSHI MICHINOBU<sup>1,2,\*\*</sup>, MASAMI BITO<sup>1</sup>, MIKI TANIMURA<sup>1</sup>, YOSHIHIRO KATAYAMA<sup>3</sup>, EIJI MASAI<sup>4</sup>, MASAYA NAKAMURA<sup>5</sup>, YUICHIRO OTSUKA<sup>5</sup>, SEIJI OHARA<sup>5</sup> and KIYOTAKA SHIGEHARA<sup>1,2,\*</sup>

<sup>1</sup>Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan

<sup>2</sup>Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan

<sup>3</sup>Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan

<sup>4</sup>Department of Bioengineering, Nagaoka University of Technology, Nagaoka, Niigata, Japan

<sup>5</sup>Forestry and Forest Products Research Institute, Tsukuba, Ibaraki, Japan

Received September 2009, Accepted November 2009

Copolymers of L-lactic acid (LA) and 2-pyrone-4,6-dicarboxylic acid (PDC), a chemically stable metabolic intermediate of lignin, were prepared by dehydrated polycondensation based on stepwise oligomerization followed by post-polymerization *in vacuo*. When the polymerization was performed in the presence of methanesulfonic acid as a catalyst, the molecular weights of the resulting copolymers were sufficiently high. Furthermore, expansion of the polymeric surface area was found to be an important factor in facilitating dehydration and thereby producing high molecular weight polymers. PDC feed ratio significantly affected the molecular weight because of the different polymerization capability from LA. Relationship between the PDC feed ratio and the molecular weight of the resulting polyesters was for the first time demonstrated quantitatively. The obtained copolymers were characterized by <sup>1</sup>H- and <sup>13</sup>C-NMR, IR, and thermal analysis. The high molecular weight copolymers possessed the higher decomposition temperatures than PLLA and their fusible temperature ranges were reasonably expanded.

**Keywords:** Biomass, lignin, polycondensation, polyester, polylactide

## 1 Introduction

Importance of biomass-based renewable plastics has been increasing because construction of carbon-neutral sustainable society is extremely desired (1–8). Poly(L-lactic acid) (PLLA) is one of the most promising candidates for this purpose (9–18). It can be readily prepared from renewable resources of L-lactic acid (LA) by self-condensation (19–21), and its excellent biocompatibility and biodegradability make it an important material in biomedical applications. However, PLLA has several disadvantages such as the lack of mechanical strength and heat resistivity, which are common for most existing biopolymers. Therefore, little success has been achieved on the application studies of PLLA as a substitute of various engineering plastics. For example, PLLA is very brittle at room temperature,

despite the glass transition temperature ( $T_g$ ) well above the room temperature (about 60°C). To overcome these disadvantages, two main approaches have generally been employed. One is blending with thermally stable materials and polymers (22). However, an ideal additive has not yet been found because of the lack of compatibility with PLLA. The other is introduction of (pseudo-) aromatic rings into the polymer main chain via a covalent bond, since aromatic nuclei usually contribute to improvement of mechanical strength and heat resistant properties (23, 24).

Since biodegradability is one important positive feature of PLLA, the incorporated (pseudo-)aromatic component should also originate from biomass. Fortunately, we have previously succeeded in massive production of a novel pseudo-aromatic molecule, 2-pyrone-4,6-dicarboxylic acid (PDC), from the lignin-bio-metabolic intermediates by transformed bacterium (25). It should be noted that lignin is now an industrial waste, although it is produced on a large scale in paper manufacturing. Thus, its utilization in industry is highly desired from the environmental viewpoint (26, 27). PDC is a small molecule possessing two

\*Address correspondence to: Kiyotaka Shigehara, Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, 184-8588 Tokyo, Japan. Fax: (+81) 42 381 8175; E-mail: jun@cc.tuat.ac.jp

\*\*E-mail: michinobu.t.aa@m.titech.ac.jp.

carboxylic acids (28, 29). Our previous reports demonstrate the ability as a bifunctional monomer for polycondensation and polyaddition. The obtained polyesters, prepared by polycondensation with  $\alpha$ ,  $\omega$ -alkylenediol or bis(2-hydroxyethyl)terephthalate, showed the high PDC content in the polymers and, accordingly, the improved thermal stability (30). However, they lacked the advantageous properties of aliphatic polymers, such as fusibility, elasticity, and high solubility into organic solvents. High solubility into organic solvents was very recently achieved for the linear polymer prepared by using copper(I)-catalyzed azide-alkyne click reaction (31). All these studies revealed that PDC content has significant effects on the polymer properties.

In the present report, we describe the successful preparation of hybrid biopolymers of LA and PDC by direct dehydrated polycondensation. The polymerization conditions were comprehensively investigated by variation of a catalyst, monomer feed ratio, and polymerization time and temperature. The relationship between the PDC feed ratio and the molecular weight of the resulting polymers was described for the first time.

## 2 Experimental

### 2.1 Materials

All reagents were purchased from Kanto Chemical Co., Tokyo Kasei Co., and Wako Chemical Industries Ltd., and used as received unless otherwise stated. L-Lactic acid (LA) was purified before use. 2-Pyrone-4,6-dicarboxylic acid (PDC) was obtained from protococatechuate via the metabolic pathway of *Sphingomonas paucimobilis* SYK-6 as reported previously (25). Bis(2-hydroxyethyl) 2-pyrone-4,6-dicarboxylic acid (BHPDC) was prepared from PDC and 1,2-ethanediol (32).

### 2.2 General Measurements

$^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were measured on a JEOL model AL300 or AL400 spectrometer at 20°C. Chemical shifts are reported in ppm downfield from  $\text{SiMe}_4$ , using the solvent's residual signal as an internal reference. The resonance multiplicity is described as s (singlet) and m (multiplet). Infrared spectra (IR) were recorded on a JASCO FT/IR-4100 spectrometer. Gel permeation chromatography (GPC) was measured on a JASCO system (PU-980, CO-965, RI-930, UV-970, and AS-950) equipped with polystyrene gel columns using chloroform as an eluent at a flow rate of 1.0 ml  $\text{min}^{-1}$  after calibration with standard polystyrene. Thermogravimetric-differential thermal analysis (TG-DTA) was carried out on a Rigaku Thermoplus TG 8120 under nitrogen flow at a heating rate of 10°C  $\text{min}^{-1}$ . Elemental analyses of the polymers were carried out on a Yanaco MT-5 elemental analyzer.

### 2.3 Polymerization

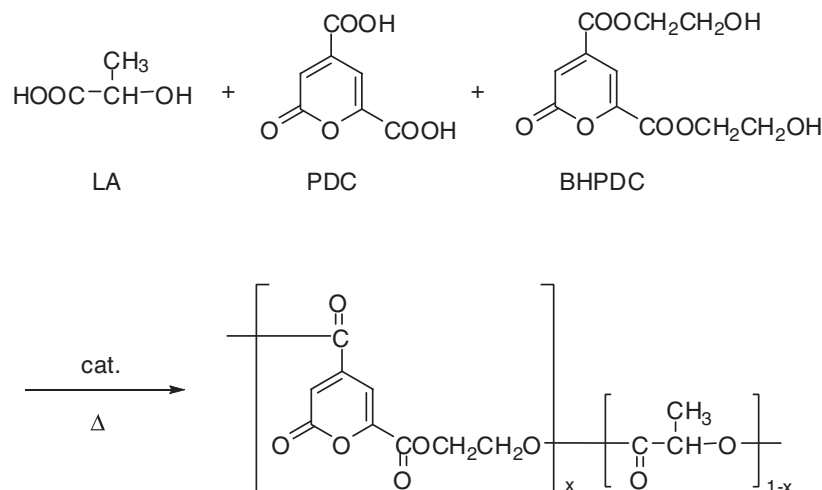
Copolymers of LA and PDC were prepared by the direct polycondensation of LA, PDC, and BHPDC.  $\text{Sb}_2\text{O}_3$  or methanesulfonic acid (MSA) was employed as a catalyst. A mixture of three monomers and a catalyst (0 or 0.3 wt%) was charged in a test tube, and preheated to 120°C to obtain homogeneous molten solutions. The mixture was then reacted at 120°C for 6 h, followed by 180°C for 6 h, affording the oligomers. The oligomers were subjected to post-polymerization at 180°C at 2 mmHg for a given period. In the optimized conditions, further reaction was carried out at 120°C at 2 mmHg for 15 h with a rotation of a test tube or with bubbling nitrogen gas. After cooling to room temperature,  $\text{CHCl}_3$  was added and the solution was precipitated into  $\text{CH}_3\text{OH}$ . The precipitate was collected and purified by repeated reprecipitation from  $\text{CHCl}_3$  into  $\text{CH}_3\text{OH}$  until the small molecular weight fractions are completely removed.

$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.33–1.67 (m,  $-\text{CH}_3$ ), 4.20–4.24 (m,  $-\text{CH}_2\text{CH}_2-$ ), 5.02–5.09 (m,  $-\text{C}(=\text{O})\text{CH}(\text{CH}_3)\text{O}-$ ), 7.10 (s, pyrone  $\epsilon\text{H}$ ), 7.42 ppm (s, pyrone  $\gamma\text{H}$ );  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 17.05 ( $-\text{CH}_3$ ), 63.38 ( $-\text{CH}_2\text{CH}_2-$ ), 66.11 ( $-\text{CH}_2\text{CH}_2-$ ), 69.27 ( $-\text{C}(=\text{O})\text{CH}(\text{CH}_3)\text{O}-$ ), 108.98 (pyrone  $\epsilon\text{C}$ ), 124.02 (pyrone  $\gamma\text{C}$ ), 142.28 (pyrone  $\delta\text{C}$ ), 148.79 (pyrone  $\phi\text{C}$ ), 158.42 (pyrone  $\delta\text{C}-\text{C}(=\text{O})$ ), 162.18 (pyrone  $\phi\text{C}-\text{C}(=\text{O})$ ), 169.79 (pyrone  $\beta\text{C}$ ), 174.54 ppm ( $-\text{C}(=\text{O})\text{CH}(\text{CH}_3)\text{O}-$ ); IR (liquid film)  $\nu$  3068, 2995, 2359, 1757, 1642, 1564, 1456, 1383, 1362, 1265, 1185, 1131, 1092, 1046, 869, 756  $\text{cm}^{-1}$ .

## 3 Results and Discussion

In synthesizing polyesters of L-lactic acid (LA) and 2-pyrone-4,6-dicarboxylic acid (PDC) by polycondensation, the stoichiometric balance between carboxylic acid and hydroxyl functionalities is important for an increase in the molecular weight. LA is a self-condensed monomer possessing both a carboxylic acid group and a hydroxyl group, whereas PDC is a dibasic acid possessing two carboxylic acid groups. Therefore, a new diol comonomer was necessary in the same molar amount as PDC to maintain the stoichiometry. To avoid the reduction of biomass content, bis(2-hydroxyethyl) 2-pyrone-4,6-dicarboxylic acid (BHPDC) was designed and prepared from PDC and 1,2-ethanediol in an excellent yield (32). A three component polycondensation was performed with a different LA/PDC ratio under various conditions (Scheme 1). General procedure is based on the oligomerization at 120°C for 6 h and then at 180°C for 6 h, followed by post-polymerization *in vacuo* for an additional period.

First, the effect of a catalyst was studied under the conditions of the post-polymerization at 180°C for 8 h, and the catalyst efficiency was judged by the molecular weight of the resulting polyesters. Since the previous studies suggested that a higher PDC feed ratio leads to insoluble and



**Sch. 1.** Synthesis of copolymers of LA and PDC.

infusible gels (30), the PDC feed ratio was maintained at <10 mol%. When the polymerization was performed at 9.1 mol% PDC feed ratio in the absence of a catalyst, only soluble oligomer with the number average molecular weight ( $M_n$ ) of 1100 and the relatively large polydispersity ( $M_w/M_n$ ) of 2.3 was obtained (Table 1, run 1). PDC was expected to become a catalyst because of the strong acidity, but this result fully negates the possibility. Decreasing the PDC content to 6.3 mol% and further to 4.8 mol% did not improve the result (Table 1, run 2 and 3). However, use of a catalyst (0.3 wt%) definitely improved the  $M_n$  values and decreased the polydispersity of the resulting polymers. Reaction yields were also slightly higher in the presence of the catalysts. It turned out that methanesulfonic acid (MSA) is a better catalyst than  $\text{Sb}_2\text{O}_3$ . Polymerization in the presence of  $\text{Sb}_2\text{O}_3$  and MSA provided the copolymers with the maximum  $M_n$  of 3800 and 4300, respectively (Table 1, run 5 and 9). Furthermore importantly, MSA can be readily removed in the purification process. Other strong acids such as sulfuric acid were also examined as a catalyst, but they resulted in discoloration of the reaction mixtures and never improved the polymerization efficiency.

Next, polymerization conditions were optimized by changing the post-polymerization time at 180°C as a parameter (Table 2). Prolonged polymerization time tended to increase the molecular weight of the resulting polymers. However, longer polymerization time lead to a dramatic increase in the viscosity and the subsequent partial deposition or gelation occurred in the case of a higher PDC content. Thus, a lowering of PDC feed ratio to <9.1 mol% was necessary for the post-polymerization time of 8 h to obtain homogeneously melt polymers at 180°C. Similarly, PDC feed ratio was maintained to be <6.3 mol% for 10 h and <3.2 mol% for 15 h. Effects of the post-polymerization time were studied for the polymerizations at the same PDC feed ratio. For example, at the PDC feed ratio of 4.8 mol%, the  $M_n$  value increased from 3300 to 3800 with the increasing post-polymerization time from 8 h to 10 h (Table 1, run 6 vs Table 2, run 2). A similar increase in the  $M_n$  value was demonstrated for further prolongation of the post-polymerization time from 10 h to 15 h (Table 2, run 3 vs run 6 and run 4 vs. run 7). However, the  $M_n$  value was almost saturated at about 6000 and, therefore a significant improvement was found to be difficult. These results suggest

**Table 1.** Effect of catalyst on copolymerization of LA, PDC, and BHPDC<sup>a</sup>

Run	LA/PDC/BHPDC	PDC feed ratio × (%)	Catalyst	Yield (%)	$M_n^b$	$M_w/M_n^b$
1	20/1/1	9.1	—	87.3	1100	2.3
2	30/1/1	6.3	—	87.4	1200	2.6
3	40/1/1	4.8	—	86.8	1300	2.6
4	20/1/1	9.1	$\text{Sb}_2\text{O}_3$	88.7	2400	1.7
5	30/1/1	6.3	$\text{Sb}_2\text{O}_3$	90.1	3800	1.8
6	40/1/1	4.8	$\text{Sb}_2\text{O}_3$	88.4	3300	1.7
7	20/1/1	9.1	MSA	89.5	3100	1.9
8	30/1/1	6.3	MSA	90.6	3700	1.8
9	40/1/1	4.8	MSA	89.3	4300	1.7

<sup>a</sup>Post-polymerization at 180°C and 2 mmHg for 8 h.

**Table 2.** Effect of polymerization time on copolymerization of LA, PDC, and BHPDC<sup>a</sup>

Run	LA/PDC/BHPDC	PDC feed ratio × (%)	Polym. time (h)	Yield (%)	$M_n^b$	$M_w/M_n^b$
1	30/1/1	6.3	10	88.1	3500	1.7
2	40/1/1	4.8	10	86.1	3800	1.8
3	60/1/1	3.2	10	81.4	3900	1.7
4	80/1/1	2.4	10	79.2	4500	1.8
5	100/1/1	2.0	10	80.3	6800	1.8
6	60/1/1	3.2	15	89.1	4700	1.8
7	80/1/1	2.4	15	86.3	5600	1.8
8	100/1/1	2.0	15	85.9	6000	1.6
9	80/1/1	2.4	19 <sup>c</sup>	82.1	8200	1.2
10	100/1/1	2.0	19 <sup>c</sup>	83.8	8600	1.2

<sup>a</sup>In the presence of Sb<sub>2</sub>O<sub>3</sub> (0.3 wt%) as a catalyst, post-polymerization at 180°C and 2 mmHg.

<sup>b</sup>Determined by GPC (CHCl<sub>3</sub> eluent, polystyrene standard).

<sup>c</sup>Post-polymerization at 180°C for 4 h followed by at 120°C for 15 h with a rotation of a test tube.

that polymerization rate becomes extremely slow at the  $M_n$  of about 6000, probably because of the increased viscosity and thereby prevented dehydration as well as the equilibrium attainment of polymerization and depolymerization. To solve these problems, the next optimization of the post-polymerization conditions was attempted. First, in order to prevent depolymerization, the post-polymerization temperature was decreased to 120°C. This change did not decrease the  $M_n$  values, indicating the sufficient activation at this temperature. Second, the surface area of the resulting polymers was expanded to facilitate dehydration. An attempt of bubbling nitrogen gas directly into the melt polymers was unsuccessful. In contrast, inclination and rotation of a test tube provided a good result and finally increased the  $M_n$  values to >8000 (Table 2, run 9 and 10).

The aforementioned optimized polymerization conditions were applied to the catalytic system of MSA, which was proven to be a better catalyst than Sb<sub>2</sub>O<sub>3</sub> for the polymerization of LA and PDC (vide supra). As expected, the  $M_n$  of the resulting copolymers was dramatically increased in particular at a low PDC feed ratio. When a PDC feed ratio is <3.8 mol%, the molecular weight increase was significant and the polydispersity became very narrow. For example, the  $M_n$  value reached 23300 at the PDC feed ra-

tio of 2.4 mol% (Table 3, run 7). This value is more than twice larger than that of the copolymer obtained by using Sb<sub>2</sub>O<sub>3</sub> as a catalyst (Table 2, run 9) and at the same time the record value of soluble PDC polyesters prepared so far.

Relationship between PDC feed ratio and the  $M_n$  values of the obtained copolymers was summarized and the data were plotted with respect to the polymerization conditions. As shown in Figure 1, the  $M_n$  values tended to increase with the decreasing PDC feed ratio under all the conditions. This result indicates that the polymerization capability of PDC is lower than that of LA. An abrupt molecular weight increase was observed at the PDC feed ratio of about 5 mol% when MSA was employed as a catalyst. In contrast, although the post-polymerization was performed without a rotation of a test tube, a slight increase in the molecular weight barely started at the PDC feed ratio of about 3 mol% in the case of Sb<sub>2</sub>O<sub>3</sub> catalyst. This difference again highlights the superior catalytic activity of MSA over Sb<sub>2</sub>O<sub>3</sub>.

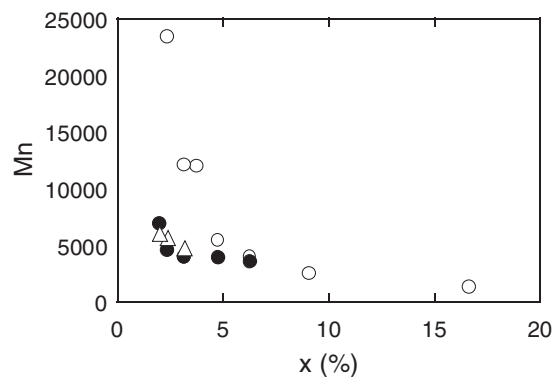
The obtained copolymers were soluble into common organic solvents, such as CHCl<sub>3</sub> and THF, and unambiguously characterized by <sup>1</sup>H and <sup>13</sup>C-NMR, IR, and thermal analysis. All obtained polymers showed the same or at least very similar spectra dependent on the PDC

**Table 3.** Effect of monomer feed ratio on copolymerization of LA, PDC, and BHPDC<sup>a</sup>

Run	LA/PDC/BHPDC	PDC feed ratio × (%)	Yield (%)	$M_n^b$	$M_w/M_n^b$
1	10/1/1	17	88.0	1200	2.7
2	20/1/1	9.1	82.1	2400	2.2
3	30/1/1	6.3	86.9	3900	2.7
4	40/1/1	4.8	85.6	5300	2.7
5	50/1/1	3.8	88.0	11900	1.2
6	60/1/1	3.2	87.9	12000	1.2
7	80/1/1	2.4	87.8	23300	1.4

<sup>a</sup>In the presence of MSA (0.3 wt%) as a catalyst, post-polymerization at 180°C and 2 mmHg for 4 h followed by at 120°C and 2 mmHg for 15 h with a rotation of a test tube.

<sup>b</sup>Determined by GPC (CHCl<sub>3</sub> eluent, polystyrene standard).

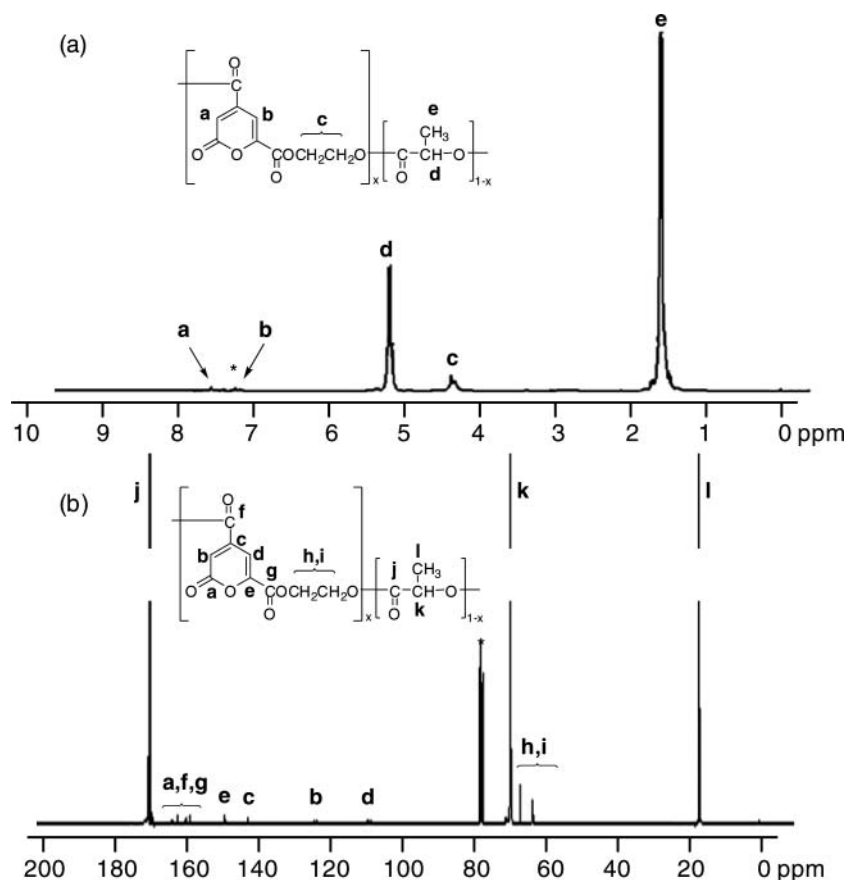


**Fig. 1.** Relationship between PDC feed ratio ( $x$ ) and the molecular weight ( $M_n$ ) of the copolymers, prepared in the presence of  $Sb_2O_3$  for 10 h at 2 mmHg (●) (Table 2, Run 1-5), in the presence of  $Sb_2O_3$  for 15 h at 2 mmHg ( $\Delta$ ) (Table 2, Run 6-8), and in the presence of MSA for 19 h at 2 mmHg (○) (Table 3).

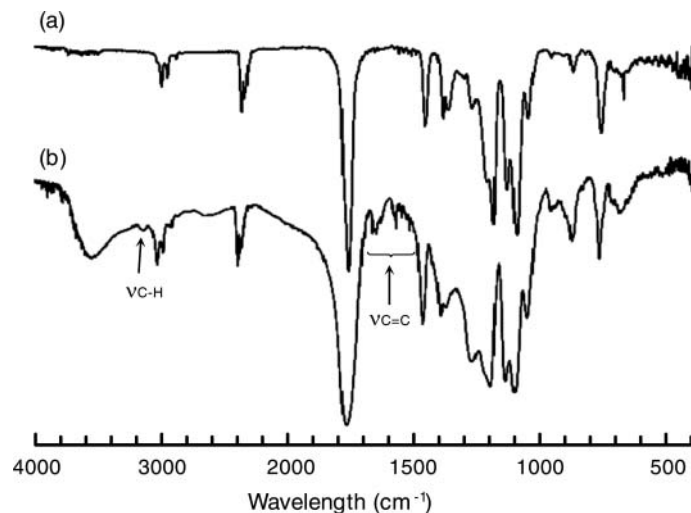
content. Copolymers with a higher PDC content showed the stronger peaks ascribed to PDC moiety. By using this feature, the actual PDC content in the copolymers was estimated. For example,  $^1H$ - and  $^{13}C$ -NMR spectra of the copolymer prepared at the PDC feed ratio of 2.4 mol%

(Table 3, run 7) are shown in Figure 2. In addition to the intense peaks of PLLA, very weak but well-defined peaks ascribed to PDC and BHPDC moieties appeared. In the  $^1H$  NMR spectrum, two weak single peaks ascribed to the pyrone ring were observed in the aromatic region (Figure 2a). Careful integration of the PDC peaks and the comparison with the methine peak of PLLA at  $\sim 5.1$  ppm revealed that the PDC content in this copolymer is 1.4 mol%. Elemental analysis also supported the  $^1H$ -NMR result. The PDC content of this copolymer, calculated from the C and H contents, was 1.5 mol%. All these results again suggest the low polymerization ability of PDC as compared to LA.

Because of the low PDC content, IR spectra showed little difference between PLLA and the obtained copolymers. However, new peaks attributable to the  $C=C$  stretching vibration of the diene moiety of PDC finally appeared at 1642 and 1564  $cm^{-1}$  after the repeated accumulation of the copolymer prepared at the high PDC feed ratio of 9.1 mol% (Fig. 3b). At the same time, a weak and rather broad peak at 3068  $cm^{-1}$  can be assigned to the  $C-H$  stretching vibration of the diene moiety. Other noticeable changes include a broadening of ester-derived peaks but the distinction between the pyrone ring and aliphatic main chain was not possible.

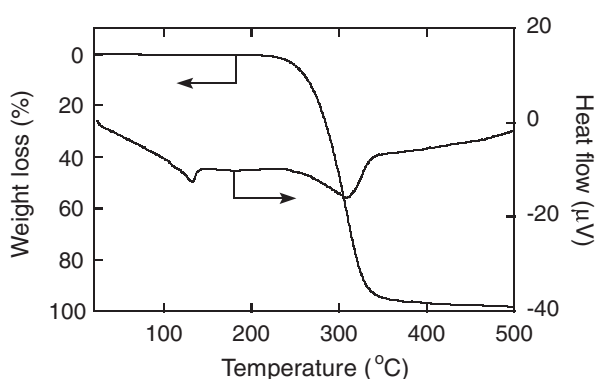


**Fig. 2.** (a)  $^1H$ -NMR and (b)  $^{13}C$  NMR spectra of LA-PDC copolymer prepared at the monomer feed ratio of LA/PDC/BHPDC = 80/1/1 in the presence of MSA for 19 h at 2 mmHg (in  $CDCl_3$  at 20°C). The residual solvent peak is marked.



**Fig. 3.** IR spectra of (a) PLLA and (b) LA-PDC copolymer prepared at the monomer feed ratio of LA/PDC/BHPDC = 20/1/1 in the presence of MSA for 19 h at 2 mmHg.

Thermal properties of the obtained copolymers were investigated by thermogravimetric-differential thermal analysis (TG-DTA) at a heating rate of  $10^{\circ}\text{C min}^{-1}$  under nitrogen atmosphere. PLLA is a crystalline polymer with a melting point of about  $170^{\circ}\text{C}$  and a decomposition temperature of about  $270^{\circ}\text{C}$  (33). All copolymers prepared under the conditions of Table 2, run 1–8, which corresponds to the  $M_n$  ranging from 3500 to 6800, displayed the decomposition temperature of  $258\text{--}267^{\circ}\text{C}$ . However, the copolymers prepared under the optimized conditions, providing a larger  $M_n$  value of  $>8000$ , showed the slightly higher decomposition temperatures of  $275\text{--}276^{\circ}\text{C}$  than PLLA. Figure 4 depicts the representative TG curve of the copolymer with an  $M_n$  of 8600 (Table 2, run 10). A small amount of PDC content did not cause a significant decomposition at lower temperature. DTA curve exhibits the clear melting



**Fig. 4.** Thermogravimetric-differential thermal analysis (TG-DTA) of LA-PDC copolymer prepared at the monomer feed ratio of LA/PDC/BHPDC = 100/1/1 in the presence of  $\text{Sb}_2\text{O}_3$  for 15 h at 2 mmHg.

point at  $132^{\circ}\text{C}$  (Fig. 4). It should be noted that the previously prepared PDC polymers were completely infusible and could not be processed. For the first time, the combination with PLLA resulted in the fusible PDC polymer. The significantly decreased melting point as compared to that of PLLA expands the fusible temperature range and, accordingly, enables to prepare various films for further mechanical analysis and practical applications, which are currently pursued in our laboratory.

## 4 Conclusions

We have successfully prepared the soluble high molecular weight biopolymers of LA and PDC. Based on the rational design to keep the stoichiometric balance of the functional groups as well as high biomass content, three-component polycondensation between LA, PDC, and BHPDC was examined. Optimization of various parameters in the polymerization conditions revealed that MSA is the best catalyst and that the molecular weight of the resulting copolymers increases with the decreasing amount of PDC. By using this knowledge, the PDC copolymer showing the record highest molecular weight ( $M_n$ ) of 23300 was finally obtained when the PDC content was 1.4–1.5 mol%. These high molecular weight copolymers are soluble in common organic solvents and also thermally stable with the higher decomposition temperature than that of PLLA. Moreover, their expanded fusible temperature range will facilitate the extensive studies on the mechanical and degradable properties in the film states. Combined features of LA and PDC are expected to compensate each shortcoming and provide highly valued biopolymers.

## Acknowledgments

This work was supported, in part, by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan, and General Sekiyu Research Promotion. We thank Prof. S. Kajita (Tokyo University of Agriculture and Technology) for useful discussion.

## References

- Steinbuechel, A., Doi, Y. and Hofrichter, M. *Biopolymers*, Wiley-VCH: Weinheim, Vol. 3, 2003.
- Kamm, B., Gruber, P. R. and Kamm, M. *Biorefineries-Industrial Processes and Products*, Wiley-VCH: Weinheim, 2006.
- Gross, R.A. and Kalra, B. (2002) *Science*, 297(5582), 803–807.
- Mecking, S. (2004) *Angew. Chem., Int. Ed.*, 43(9), 1078–1085.
- Ragauskas, A.J., Williams, C.K., Davison, B.H., Britovsek, G., Cairney, J., Eckert, C.A., Frederick, W.J., Hallett, J.P., Leak, D.J., Liotta, C.L., Mielenz, J.R., Murphy, R., Templer, R. and Tschaplinski, T. (2006) *Science*, 311(5760), 484–489.
- Nishio, Y. (2006) *Adv. Polym. Sci.*, 205, 97–151.

7. Williams, C.K. (2007) *Chem. Soc. Rev.*, 36(10), 1573–1580.
8. Gandini, A. (2008) *Macromolecules*, 41(24), 9491–9504.
9. Hartmann, M.H. *Biopolymers from Renewable Resources*, Kaplan, D.L., Ed. Springer: Berlin, 367–411, 1998.
10. Vert, M. *Encyclopedia of Biomaterials and Biomedical Engineering*, Wnek, G.E., Bowlin, G.L., Eds. Marcel Dekker: New York, 1254–1263, 2004.
11. Zhang, J.F. and Sun, X. *Biodegradable Polymers for Industrial Applications*, Smith, R. Ed. Woodhead Publishing: Cambridge, 251–288, 2005.
12. Huang, S.J. *Handbook of Biodegradable Polymers*, Bastioli, C. Ed. Rapra Technology: Shrewsbury, 287–301, 2005.
13. Iwata, T. and Doi, Y. (1999) *Macromol. Chem. Phys.*, 200(11), 2429–2442.
14. Agrawal, A.K. and Bhalla, R. (2003) *J. Macromol. Sci. Polym. Rev.*, C43(4), 479–503.
15. Vink, E.T.H., Rabago, R., Glassner, D.A., Spring, B., O'Connor, R.P., Kolstad, J. and Gruber, P.R. (2004) *Macromol. Biosci.*, 4(6), 551–564.
16. Tsuji, H. (2005) *Macromol. Biosci.*, 5(7), 569–597.
17. Dorgan, J.R., Braun, B., Wegner, J.R. and Knauss, D.M. (2006) *ACS Symp. Series*, 939, 102–125.
18. Gupta, B., Revagade, N. and Hiborn, J. (2007) *Prog. Polym. Sci.*, 32(4), 455–482.
19. Mehta, R., Kumar, V., Bhunia, H. and Upadhyay, S.N. (2005) *J. Macromol. Sci. Polym. Rev.*, C45(4), 325–349.
20. Nakano, K., Kosaka, N., Hiyama, T. and Nozaki, K. (2003) *Dalton Trans.*, 21, 4039–4050.
21. Takasu, A., Narukawa, Y. and Hirabayashi, T. (2006) *J. Polym. Sci. Part A: Polym. Chem.*, 44(18), 5247–5253.
22. Kai, W., Zhao, L., Zhu, B. and Inoue, Y. (2006) *Macromol. Rapid Commun.*, 27(2), 109–113.
23. Kaneko, T., Tran, H.T., Shi, D.J. and Akashi, M. (2006) *Nature Mater.*, 5(12), 966–970.
24. Kaneko, T. (2007) *Chem. Rec.*, 7(4), 210–219.
25. Otsuka, Y., Nakamura, M., Shigehara, K., Sugimura, K., Masai, E., Ohara, S. and Katayama, Y. (2006) *Appl. Microbiol. Biotechnol.*, 71(5), 608–614.
26. Funaoka, M. (1998) *Polym. Int.*, 47(3), 277–290.
27. Yoshida, T., Lu, R., Han, S., Hattori, K., Katsuta, T., Takeda, E.I., Sugimoto, K. and Funaoka, M. (2008) *J. Polym. Sci. Part A: Polym. Chem.*, 47(3), 824–832.
28. Michinobu, T., Bito, M., Yamada, Y., Katayama, Y., Noguchi, K., Masai, E., Nakamura, M., Ohara, S. and Shigehara, K. (2007) *Bull. Chem. Soc. Jpn.*, 80(12), 2436–2442.
29. Bito, M., Michinobu, T., Katayama, Y., Otsuka, Y., Nakamura, M., Ohara, S., Masai, E. and Shigehara, K. (2008) *Trans. Mater. Res. Soc. Jpn.*, 33(4), 1165–1168.
30. Michinobu, T., Hishida, M., Sato, M., Katayama, Y., Masai, E., Nakamura, M., Otsuka, Y., Ohara, S. and Shigehara, K. (2008) *Polym. J.*, 40(1), 68–75.
31. Michinobu, T., Inazawa, Y., Hiraki, K., Katayama, Y., Masai, E., Nakamura, M., Ohara, S. and Shigehara, K. (2008) *Chem. Lett.*, 37(2), 154–155.
32. Hishida, M., Shikinaka, K., Katayama, Y., Kajita, S., Masai, E., Nakamura, M., Otsuka, Y., Ohara, S. and Shigehara, K. (2009) *Polym. J.*, 41(4), 297–302.
33. Baiardo, M., Frisoni, G., Scandola, M., Rimelen, M., Lips, D., Ruffieux, K. and Wintermantel, E. (2003) *J. Appl. Polym. Sci.*, 90(7), 1731–1738.