Asian Journal of Chemistry Vol. 19, No. 3 (2007), 1714-1722

Depolymerization of Poly (L-lactic acid) under Hydrothermal Conditions

MUHAMMAD FAISAL*†, TAKASHI SAEKI‡, HIDETO TSUJI, HIROYUKI DAIMON*
and KOICHI FUJIE
Department of Ecological Engineering, Toyohashi University of Technology
Tempaku-cho, Toyohashi, Aichi 441-8580, Japan
Tel/Fax: (81)(532)446910; E-mail: daimon@eco.tut.ac.jp; mohdfaisal_99@yahoo.com

Depolymerization of poly (L-lactic acid) was conducted under hydrothermal conditions at the temperature range of 160-350ºC and for a period of 3 h. The results show that the reaction temperature and time affect the extent of depolymerization and optical selectivity. The optimum conditions on depolymerization of poly (L-lactic acid) were attained at 270ºC and 8 min of reaction time. Higher optical purity of L-lactic acid was obtained with a yield of 96 %. A study on the effect of temperature on the optical purity of lactic acid product demonstrated that L-lactic acid was predominant at low range temperature of 250-270ºC. At higher temperature, optical purity was reduced and racemization occured. The experimental results showed that the method was found to be simple and promising for chemical recycling of poly (L-lactic acid) into its monomer.

Key Words: Depolymerization, Poly (L-lactic acid), Optical isomer, Biodegradable, Hydrothermal conditions.

INTRODUCTION

Plastics offered uncountable useful and inexpensive items for modern living and their use in many applications increase every year. However, they are mostly made from irreplaceable fossil fuels. Since many plastics can be produced at low costs, they are often used to make disposable items causing to a significant waste problem. These conventional plastic materials are not easily degraded in the environment because scientists have traditionally sought ways to make them more resistant to heat, light, water, chemical attach, *etc*.

Replacement of these highly biodegradation-resistant and petroleum-based plastics with biodegradable ones, such as poly lactic acid (PLA), has

---

*†Department of Chemical Engineering, Syiah Kuala University, NAD, 23111, Indonesia.

†Research Center for Materials Cycle and Waste Management, National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki, 305-8506, Japan.

been attracting much attention. PLA is a biodegradable polyester and has widespread potential use in medicine, agriculture and packaging applications due to their biocompatibility and biodegradability[1,2]. PLA is synthesized by polymerizing of lactic acid that can be obtained from renewable starch containing resources (*e.g.*, corn, wheat, potato or sugar beat) by fermentation. Thus, global reserve of valuable oil, which is approximated to run dry in the coming decade does not have to be wasted in order to produce plastic. Recently, Cargill Dow LLC has started to operate the PLA plant producing of 140,000 t/year in November 2001. They are planning to increase annual output up to 450,000t in 2010, which will reduce the price of PLA[3].

However, producing plant-based plastics might cause the problems such as competition between the productions of crops for food and raw material for plastic production as the population of the world continues to increase in the future. Apart from this, recent studies showed that the production and process of the plant-based plastics itself consumes more energy than the fossil fuel-based plastics manufacturing[4]. The reuse and recycling of the used plastics is therefore crucial. Moreover, the efficient utilization of renewable resources should be established for the sustainable system.

Consequently, in order to solve these problems and to promote a recycling oriented society, PLA should be recycled into its monomer, lactic acid, instead of disposing it and afterward can reproduce the same polymer. This might promote the development of a recycling oriented society for the efficient utilization of natural resources. Depolymerization of PLA oligomers to produce cyclic dimer (L-lactide) in the presence of catalyst has been reported[5]. However, this method is requiring the catalyst. Moreover, the yield of L-lactide was low at a short reaction time. A hydrothermal treatment, an environmentally friendly recycling process which only uses water is effective for recovery of lactic acid from PLA without addition of any catalysts.

In recent years, the use of hydrothermal treatment process of thermal decomposition[6-8], organic syntheis[9, 10] and recovery of useful materials from various organic wastes[11-15] has attracted the interest of many researchers. This technique was also applied to chemical recycling processes such as hydrolysis of polyethylene terephthalate (PET) into ethylene glycol and terephthalic acid[16]. Park *et.al.*[17] showed the ability of supercritical and near-critical water to break down the styrene-butadiene rubber (SBR) into a range of lower molecular weight organic compounds for potential recovery. Thus, water under hydrothermal conditions provides excellent properties (*i.e.* high ion product, low solvent polarity, high solubility for oil, *etc.*) for hydrolysis and offer opportunities to adjust the reaction environment to optimal conditions for the chemical transformation of interest[18].

Recently, preliminary study on recycling of poly (L-lactic acid) (PLLA) at high temperature conditions has been carried out in our laboratory[19]. However, the recycling process was not yet sufficiently optimized and the principal concern on enantiomer selectivity during the high temperature hydrolysis has not been considered. In fact, from the technical applications viewpoint, such discussions should be explored.

In this study, the depolymerization of PLLA was examined in order to obtain L-lactic acid for recycling by taking the full advantage of the unique properties of high temperature water described above. The optimum condition for the recovery of L-lactic acid and the effect of high temperature on the formation of the optical isomer of lactic acid will be discussed. The results obtained will be of great importance for the development of recycling technology and biomass efficiency.

EXPERIMENTAL

All experiments were performed using SUS316 batch reactor (8.2 mL volume, 12.7 mm OD, 10.2 mm ID and 100 mm length). The reaction conditions were over a temperature range of 250 to 350ºC at the corresponding saturated vapour pressures and time ranging from 1 to 30 min. During a typical run, about 0.24 g PLLA (LACTY 5000, Shimadzu Corp., weight average molecular weight (mw) = 4.4×10^5, mw/number average molecular weight (mn) = 2.1, initial fraction of L-lactic acid = 95 %) and 4.8 g of distilled water (weight ratio of 1 : 20) were charged into the reactor. The reactor was then sealed, and then the air inside was replaced by argon gas. Subsequently, the reactor was immersed into the preheated molten salt bath (TSC-B600, Taiatsu Techno) containing a mixture of potassium nitrate and sodium nitrate set at desired temperature. The reaction time was started at this point. At the end of the reaction time, the reactor was removed from the salt bath and quenched immediately by immersing the reactor in a cold water bath to bring them quickly to room temperature, effectively ceasing any occuring reactions. The reaction products were analyzed using an organic acid analyzer (LC-10A, Shimadzu Corp.) with an ion-exclusion column (Shim-Pack SCR-102H, Shimadzu Corp.) and electroconductivity detector (CDD-6A, Shimadzu Corp.). The optical isomer of lactic acid produced was also analyzed using these conditions: analytical column; Sumichiral OQ-5000 (5 μm particle size, 4.6 mm i.d. × 150 mm long, Sumika Chemical Analysis Service Ltd. Japan), column temperature; 30ºC, mobile phase; 1 mM copper (II) sulfate in water, flow rate; 1 mL/min, injection volume 20 μL. The total organic carbon (TOC) was analyzed using TOC analyzer (TOC-VE, Shimadzu Corp.).

RESULTS AND DISCUSSION

The effect of reaction temperature and time on the yields of D- and L-lactic acids under hydrothermal conditions is demonstrated in Fig. 1. The depolymerization efficiency, strongly depends upon the reaction conditions. The products were mostly lactic acid and the amount of lactic acid increased with increasing the reaction temperature up to 300ºC. At short reaction times (0-3 min), the thermal energy of depolymerization was insufficient to produce lactic acid and might result only in the reduction of molecular weight due to the scission of ester group[19]. At reaction times of 3 and 5 min, a significant increase of lactic acid was observed. The yield of lactic acid started to increase and reached around 82, 78 and 97 % at 5 min for reaction temperatures of 280, 290 and 300ºC, respectively. Such rapid degradation at high temperature might occur through random main-chain scission reaction as reported by Gupta *et al.*[20] and Sodergard *et al.*[21]. However, for the reaction time exceeding 5 and up to 0.5 h, the amount of lactic acid produced remained unchanged, indicating the relatively slow depolymerization occured at these conditions. The stability of lactic acid at those conditions was also reported by Li *et al.*[8]. From the results of Fig. 1, the maximum yield of lactic acid was attained at 8 min of reaction time and 270ºC, more than 98 % of PLLA was converted into lactic acid. At this temperature the thermal energy and the ion product of water are sufficiently high for lactic acid recovery. The ion product of water goes through a maximum (*ca.* 10^{-11} $(mol/L)^2$ at about 250-275ºC under a pressure of 4-6 MPa and water density of 0.2-0.3 g/cm^3. A large amount of dissociated ions and a high dielectric constant might also favourable to depolymerization process. High maximum yields of lactic acid (*ca.* 96 and 98 %) were also observed at 20 min of reaction time for the temperatures of 250 and 260ºC, respectively. At the temperature as high as 350ºC, the degradation rate of PLLA was high and small amounts of propionic acid and acetic acid were traced by organic acid analysis (data not shown here). This can be explained by the rapid decomposition of lactic acid at high temperature. Further decomposition of lactic acid might have occured producing carbon monoxide and eventually carbon dioxide[8].

Experiments at lower temperatures have also been carried out. The results shown in Fig. 2 explained that a significant amount of lactic acid could also be obtained, however long reaction time was required for complete hydrolysis of PLLA. The crystalline residues were observed at temperature up to 180ºC even after 1 h of reaction time indicating that the depolymerization process was not yet completed.

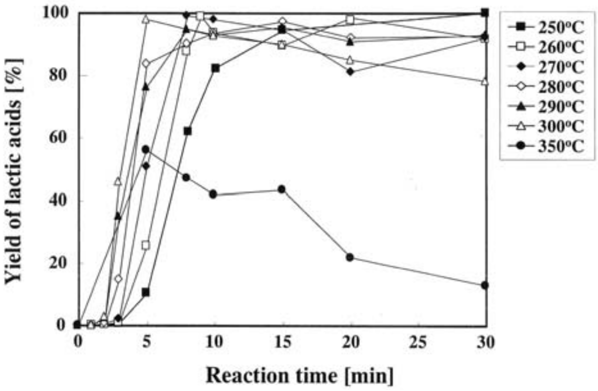

Fig.1 Effect of reaction time on the yield of lactic acid at 250-350ºC

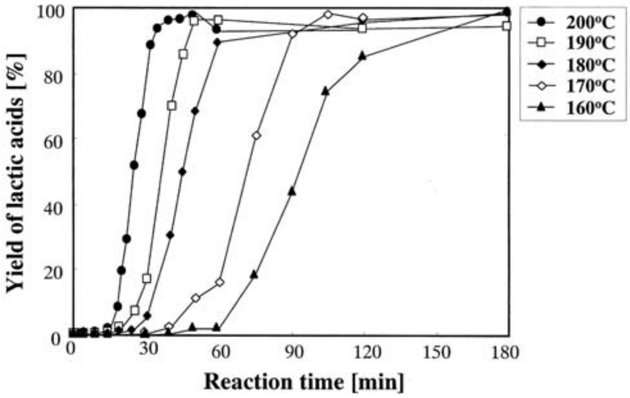

Fig. 2. Effect of reaction time on the yield of lactic acid at 160-200ºC

Effect of reaction temperature and time on the optical isomer selectivity

Fig. 3 shows the effect of reaction time on the formation of L-lactic acid at various temperatures. At low range temperatures of 250-300ºC and short reaction times such as 3-5 min, the formation of L-lactic acid was dominant, and thus comparable with that of D- and L-lactic acid (Fig. 1). As can be seen, at reaction time up to 8 min, the yield of L-lactic acid increased with reaction time excluding for the temperature of 350ºC. Rapid formation of L-type (*ca.* 83 %) was also observed at 5 min for the temperature of 300ºC and yield of L-lactic acid was then decreased with increasing the reaction time. In contrast, the different behaviour was observed for reaction temperature of 250ºC, where the yield of L-lactic acid continued to increase with reaction time up to 0.5 h. These findings indicated that the formation of L-lactic acid is favoured at lower temperatures. Fig. 4 demonstrates the course of the selectivity of L-lactic acid at the conditions employed in this work.

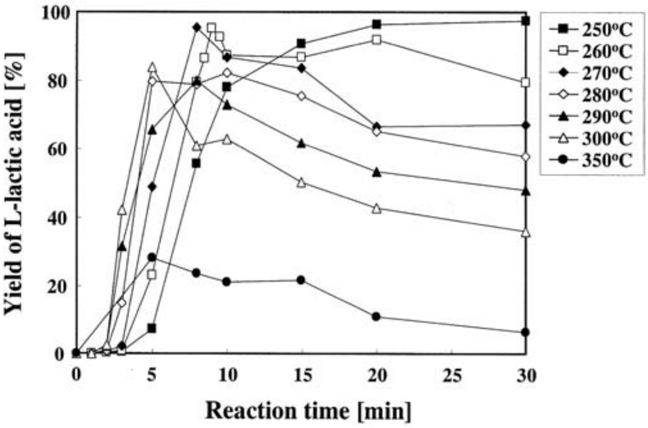

Fig. 3. Effect of reaction time on the yield of L-lactic acid at various temperatures

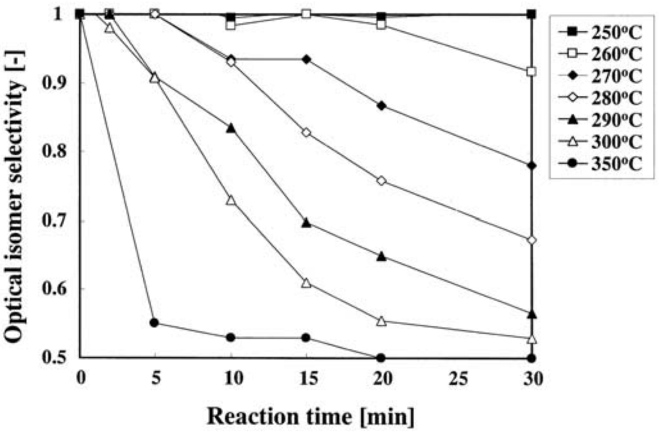

Fig. 4. Course of enantiomer selectivity to L-lactic acid at various temperatures

The L fraction of lactic acid was calculated on the basis of the inital L-fraction in the sample, *ca.* 95 %. It as can be seen that the selectivity value for L-lactic acid at short reaction time up to 5 min in the temperature range of 240-280ºC were found at around 1 indicating the insignificance change in optical purity occured during depolymerization. Moreover, the selectivity of L-lactic acid remained unchanged for a period of 0.5 h at the temperatures of 240 and 250ºC, respectively. These findings suggest that the degradation of PLLA at these conditions results in only L-lactic acid and water-soluble oligomers. The selectivity of L-lactic acid decreased to 0.95, 0.91 and 0.92 within 5-10 min for reaction temperatures of 290, 280 and 270ºC, respectively. As expected, at a higher temperature, the selectivity decreased gradually with reaction time. For instance, at 300ºC and 20 min of reaction time, the selectivity was reduced to 0.55 indicating the recemization occured resulting in the partial loss of optical activity. In other words 45% of L-enantiomer was converted to D-lactic acid. This result reflects that L-lactic acid changed into D-lactic acid at high temperature and thus consistent with our previous study[22]. It seems that the ester groups of PLLA were cleaved to form L-lactic acid, then the formed L-lactic acid changes into D-lactic acid at high temperature and long reaction time. Two mechanisms of the recemization of lactic acid are considered; at low temperature, PLLA is hydrolyzed to yield lactic acid and heat induces on the formation of D-lactic acid. At high temperature, the recemization at symmetric carbon atoms of PLLA can occur through radical-homolysis and enolization resulting in formation of D-lactic acid[23].

These findings reveal that the temperatures ranging from 250-280ºC are most favorable for high yield of L-lactic acid. The highest maximum selectivity of L-lactic acid was attained in this experiment at around 260-270ºC and 8-10 min.

Carbon balance

The PLLA degradation process was also investigated by TOC measurements. Fig. 5 demonstrates the effect of time and temperature on the course of TOC reduction. The value 1 means the theoretical TOC value when all of the PLLA chains are depolymerized completely to produce lactic acid, water-soluble oligomers and other organic acids. A significant increase of the TOC with increasing reaction temperature and time was found as expected. As can be seen in Fig. 4, at 8-15 min of reaction times and temperatures of 250-300ºC, the amount of TOC achieved a maximum and reached a theoretical value suggested that all of the PLLA chains were degraded into its monomer water-soluble oligomers and other organic acids and thus comparable with the results of lactic acid formed in the Fig. 1. The TOC value then remained unchanged even when the reaction was continued for 0.5 h, which was in contrast with the lactic acid formation (excluding the result at 250ºC). These occured presumably due to the formation of low molecular carboxylic acids (from lactic acid) such as acetic acid which is considered one of the most refractory organic intermediates[24]. As expected, at higher temperature of 350ºC, TOC decreased significantly with reaction time exceeding 5 min. The suggests that volatile carbon such as CO_2, CO and CH_4 were formed by thermal decomposition of lactic acids through decarboxylation and the dehydration route of decomposed compounds[8].

Effect of ratio sample to water

To obtain additional information concerning the deploymerization of PLLA, further experiments on the effect of ratio of sample (PLLA) to water were also carried out with different charges ratios ranging from 1:1 to 1:100 (PLLA:water). Experiment was performed at 250ºC for reaction time up to 30 min and obtained results are shown in Fig. 6. The results show that the amount of water charged into reactor influenced the yield of lactic acid. The yield of lactic acid increased with the charge ratio of PLLA to water when compared at the same reacton time. However, as can be seen, there was no significant difference in the yield of lactic acid for ratios of 1:100 to 1:20, in which the yield of lactic acid approached 100 % for the reaction time exceeding 10 min. Therefore, it can be concluded that in practical application the ratio of 1:20 is suitable for depolymerizaton of PLLA. At the ratio of up to 1:10, small amount of un-reacted materials (residues in solid phase) of PLLA was observed, even when the reaction was continued for 0.5 h. Probably, at this condition the small amount of water produced an insuficient amount of OH radical for degradation of PLLA. In contrast, the reaction extents of PET hydrolysis slightly decreased with the charge ratios of PET to water when was hydrolyzed[25] at high temperature water up to 265ºC.

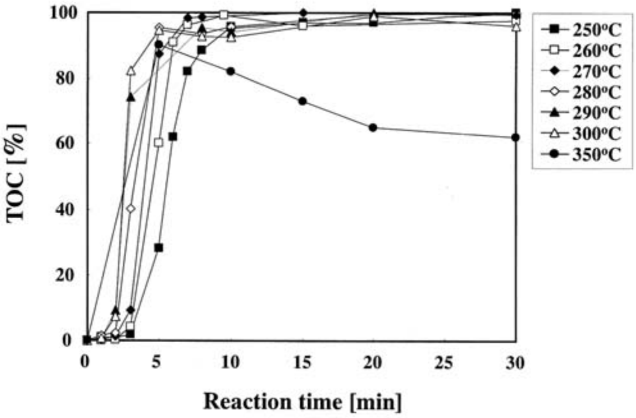

Fig. 5. Course of TOC at various conditions

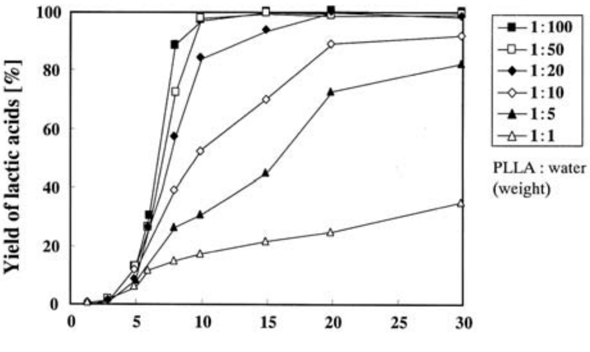

Fig. 6. Effect of charge ratio sample to water on the yield of lactic acid at 250ºC

Conclusion

The depolymerization efficiency strongly depends upon the operating conditions of temperature, reaction time and ratio of sample to water. The organic compounds were recovered mainly consist of lactic acid. Our observation shows that the depolymerization of PLLA to lactic acid appears predominant at lower temperatures, while at the higher temperatures were favourable to thermal degradation formed lactic acid into other low molecular weight organic compounds. As suggested in the present study, the hydrothermal process has been found to affect the optical isomer of lactic acid. At low temperatures, it was observed that recovered monomer mainly consist of L-lactic acid. The mechanism proposed in the discussion might suggest the suitable reaction conditions on the formation of L-lactic acid with high optical purity. At the temperature of 270ºC and reaction time of 8 min, the highest yield of L-lactic acid (96 %) was recoverable.

ACKNOWLEDGEMENTS

The authors are grateful to the Japan Society for the Promotion of Science (Research for the Future Program) and the 21st Century COE Program at the Toyohashi University of Technology (Ecological Engineering for Homeostatic Human Activities) for their financial support of this research.

REFERENCES

1. E. Chiellini and R. Solaro, *Adv. Mater.*, **8**, 303 (1996).
2. M.H. Hartmann, in ed.: D.L. Kaplan, Biopolymers from Renewable Resources, Springer, Berlin, Germany, Ch. 15, p. 367 (1998).
3. M.A. Verespej, Industry Week, Dec. 11 (2000).
4. T.U. Gerngross and S.C. Slater, *Sci. Am.*, **2**, 36 (2000).
5. M. Noda and H. Okuyama, *Chem. Pharm. Bull.*, **47**, 467 (1999).
6. M. Goto, T. Nada, S. Kawajari, A. Kodama and T. Hirose, *J. Chem. Eng. (Japan)*, **30**, 813 (1997).
7. M. Goto, T. Nada, A. Ogata, A. Kodama and T. Hirose, *J. Supercrit. Fluids*, **13**, 227 (1998).
8. L. Li, J.R. Portela, D. Vallejo and E.F. Gloyna, *Ind. Eng. Chem. Res.*, **38**, 2599 (1999).
9. P.E. Savage, *Chem. Rev.*, **99**, 603 (1999).
10. R.L. Holliday, B.Y.M. Jong and J.W. Kolis, *J. Supercrit. Fluids*, **12**, 255 (1998).
11. K. Kang, A.T. Quitain, H. Daimon, R. Noda, N. Goto, H. Hu and K. Fujie, *Can. J. Chem. Eng.*, **79**, 65 (2001).
12. A. Shanableh, *Wat. Res.*, **34**, 945 (2000).
13. H. Daimon, K. Kang, N. Sato and K. Fujie, *J. Chem. Eng. (Japan)*, **34**, 1091 (2001).
14. A.T. Quitain, M. Faisal, K. Kang, H. Daimon and K. Fujie, *J. Hazard. Mater.*, **93**, 209 (2002).
15. A.T. Quitain, N. Sato, H. Daimon and K. Fujie, *Ind. Eng. Chem. Res.*, **40**, 5885 (2001).
16. K. Arai and T. Adschiri, *Fluid Phase Equilib.*, **158**, 673 (1999).
17. Y. Park, J.N. Hool, C.W. Curtis and C.B. Roberts, *Ind. Eng. Chem. Res.*, **37**, 1228 (1998).
18. N. Akiya and P.E. Savage, *Ind. Eng. Chem. Res.*, **40**, 1822 (2001).
19. H. Tsuji, H. Daimon and K. Fujie, *Biomacromolecules*, **4**, 835 (2003).
20. M.C. Gupta and V.G. Deshmukh, *Colloid Polym. Sci.*, **260**, 514 (1982).
21. A. Sodergard and J.H. Nasman, *Ind. Eng. Chem. Res.*, **35**, 732 (1996).
22. M. Faisal, T. Saeki, H. Daimon and K. Fujie, *Asian J. Chem.*, **18**, 248 (2006).
23. H. Tsuji, I. Fukui, H. Daimon and K. Fujie, *Polym. Degrad. Stab.*, **81**, 501 (2003).
24. Z.Y. Ding, M.A. Frisch, L. Li and E.F. Gloyna, *Ind. Eng. Chem. Res.*, **35**, 3257 (1996).
25. C. Kao, B. Wang and W. Cheng, *Ind. Eng. Chem. Res.*, **37**, 1228 (1998).

(*Received*: 31 January 2006; *Accepted*: 9 October 2006) AJC-5170