

Polyaniline Salts as Polymer-Based Solid Acid Catalyst for Low Molecular Weight Poly(lactic acid)

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ABSTRACT: Polymer-based solid acid catalyst, polyaniline (PANI) salt, is used for the first time to synthesize polymer. In continuation of our work to synthesize organic chemicals using PANI-based solid acid catalyst, in this work, polylactic acid is synthesized by the condensation polymerization of lactic acid using PANI salts. PANI salts are characterized by FTIR, FE-SEM, and TGA analyses. Polymerization of lactic acid in xylene solvent at 140°C for 24 h with the use of very low amount of PANI catalysts gave polylactic acid (PLLA) in the order: PANI-MSA (46%) > PANI-TFA (33%) > PANI-Bi(OTf)₃ (27%) > PANI-Cu(OTf)₂ (20%) > PANI-Yb(OTf)₃ (15%). Molecular weights of PLLA synthesized using PANI-MSA and PANI-TFA are found to be 4385 and 4830, respectively. This methodology gives highly crystalline polymer with mushroom cap-like morphology. Advantage of this methodology is the use of easily synthesizable, recyclable, easily handleable, cheaper, and eco-friendly nature of the catalyst. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41147.

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INTRODUCTION

Biocompatible and biodegradable polymers became very important and gained a lot of attention from both biomedical and ecological outlooks in the past decade.¹ The most popular and important biodegradable polymers are aliphatic polyesters^{2–5} such as poly(3-hydroxybutyrate), poly(ϵ -caprolactone), poly(glycolic acid), and poly(lactic acid) (PLA), whereby PLA received the most attention due to its renewable resources,⁶ biodegradation, biocompatibility without poisoning side effect, as well as excellent thermal and mechanical properties, and superior transparency of the processed materials.⁷ The properties of PLA allow a wide range of applications from pharmaceutical and biomedical such as surgical implants, tissue engineering, resorbable surgical sutures, wound closure, textile or packaging and drug controlled release systems, and environmental materials.^{2–5}

PLA can be synthesized by two reaction mechanisms: The first is a commonly commercialized one to ring-open polymerization of the intermediate lactide by step-growth condensation polymerization.⁸ The second one is also a commercialized route, established by Mitsui Chemicals Co. (Japan), wherein lactic acid and catalyst are azeotropically dehydrated in a refluxing, high boiling point, aprotic solvent such as diphenyl ether, under reduced pressure⁹ to obtain PLA with weight-average molecular weight (M_w) greater than 3.0×10^5 . Kazuhiko et al.¹⁰ reported rapid synthesis of PLA by direct polycondensation of lactic acid (LA) using microwave irradiation at 200°C, 30 mmHg for

30 min with various catalysts such as Bronsted/Lewis acids/metals/metal triflates. Among the catalysts, SnCl₂/p-TsOH binary catalyst system gave PLA with molecular weight of 16,000. Bharatkumar et al.¹¹ synthesized PLA with molecular weight of 14,875 using cellulose sulfuric acid in *m*-xylene at 180°C for 24 h.

Low-molecular weight PLA has substandard mechanical properties and even the low molecular weight precondensates is of interest for the preparation of biodegradable glues or lacquers, because the —OH and —COOH end groups allow crosslinking with suitable inorganic or organic multivalent additives.¹²

Our aim is to prepare low-molecular weight polylactic acid. Since polyaniline (PANI) salts are mild polymer-based acid catalyst, in this work, lactic acid is polymerized to low-molecular weight polylactic acid using PANI salts.

EXPERIMENTAL

Instruments and Characterization

Fourier transform infrared (FTIR) spectra of polymer samples were registered on a FTIR spectrometer (Thermo Nicolet Nexus 670, USA) using the KBr pressed pellet technique. Molecular weight of polycarbazole was carried out using matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF MS) instrument (Shimadzu Biotech Axima Performance 2.9.3.20110624: Model Linear, Power: 80, Blanked, P. Ext@4300 (bin 97) UK) using 2,5-dihydroxybenzoic acid matrix. Morphology studies (Micro structural and elemental analyses)

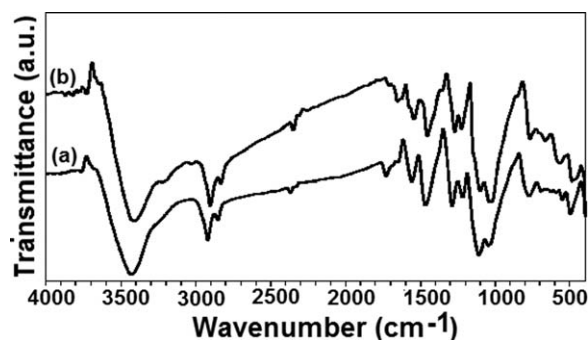


Figure 1. Infrared spectra of (a) PANI-MSA, (b) recycled PANI-MSA.

of the polymer samples were carried out with a Hitachi S-4300 field emission scanning electron microscopy (FE-SEM) (Tokyo, Japan). The sample was mounted on a carbon disc with the help of double sided adhesive tape and sputter-coated with a thin layer of gold to prevent sample charging problems. Thermogravimetric analyses (TGA) of polymer samples were carried out using TA Instruments (TGA Q500 V20.8, USA) from ambient to 700°C under nitrogen atmosphere at a heating rate of 10°C/min. ¹H- and ¹³C-NMR spectra of all the products in CDCl₃ with TMS as internal standard were taken using Avance-500/Inova-400 instruments.

Synthesis of Polyaniline Base by the Aqueous Polymerization Pathway

PANI base was prepared by aqueous polymerization pathway via our earlier reported procedure.¹³ In a 250-mL round-bottomed flask, 60 mL of water were charged and 9.6 mL of HCl were added slowly with stirring. To this mixture, 1 mL of aniline was added and the solution was kept under constant stirring at ambient temperature. To this solution, 40 mL of an aqueous solution containing sodium persulfate (3.3 g) was added for 15–20 min duration. The reaction was allowed to continue for 4 h at 25–30°C. The precipitated PANI salt powder was filtered, washed with distilled water, followed by acetone. PANI salt (1 g) thus synthesized was stirred in 100 mL aqueous sodium hydroxide solution (1M) for 4 h at ambient temperature. The PANI base powder was filtered, washed with excess water, finally with acetone, and dried the sample in oven at 50°C till a constant weight.

Synthesis of Polyaniline Salts

PANI base (1 g) was added to 100 mL of aqueous solution containing methanesulfonic acid (MSA) (1M)/trifluoromethanesulfonic acid (TFA) (0.1M)/Bi(OTf)₃ (0.1M)/Yb(OTf)₃ (0.1M)/Cu(OTf)₂ (0.1M) for 4 h, filtered, washed with excess water, finally with acetone, and dried at 50°C to a constant weight.

Synthesis of Polylactic Acid Using Polyaniline Salts

In a typical reaction, 8 g of L-(+)-lactic acid (LLA), 0.2 g of PANI catalyst, and 200 mL xylene were added to a 500-mL round-bottom flask equipped with a magnetic stirrer, and the reaction mixture was refluxed. The water was azeotropically distilled off using a Dean–Stark assembly. The reaction was continued at 140°C for 24 h under nitrogen gas flow. Catalyst was removed by filtration. Polymer was precipitated with methanol and the polymer was dried under vacuum at room temperature for 24 h.

RESULTS AND DISCUSSION

Catalyst Characterization

PANI salt was prepared by oxidizing aniline using sodium persulfate oxidant in the presence of hydrochloric acid, followed by dedoping of PANI-hydrochloride salt (PANI-HCl) to polyaniline base (PANI) and subsequent redoping with MSA, TFA, or metal triflates.

FTIR Spectra of Polyaniline Salts

FTIR spectra of PANI-MSA, PANI-TFA, PANI-Bi(OTf)₃, PANI-Yb(OTf)₃, and PANI-Cu(OTf)₂ are recorded from 4000 to 400 cm⁻¹ and the spectra are very nearly the same with that of the reported IR spectrum for PANI SALT.^{13–16} As a representative system, FTIR spectrum of PANI-MSA is shown in Figure 1. It shows major characteristics peaks of PANI salt, i.e., at 3430 cm⁻¹ (N–H str.), 3230 cm⁻¹ (NH⁺—indicative of doping), 2920 and 2850 cm⁻¹ (C–H str. of acid dopant), 1560 cm⁻¹ (C=C str., quinonoid ring), 1470 cm⁻¹ (C=C str., benzenoid ring), 1290 cm⁻¹ (C–N str., quinonoid ring), 1220 cm⁻¹ (C–N str., benzenoid ring), 1110 cm⁻¹ (electronic vibrational band), 1050 cm⁻¹ (S=O str. of SO₃H group), and 790 cm⁻¹ (1,4-disubstituted benzene). Infrared spectrum of recycled PANI-MSA [Figure 1(b)] shows peaks similar to that of the as-synthesized PANI-MSA [Figure 1(a)].

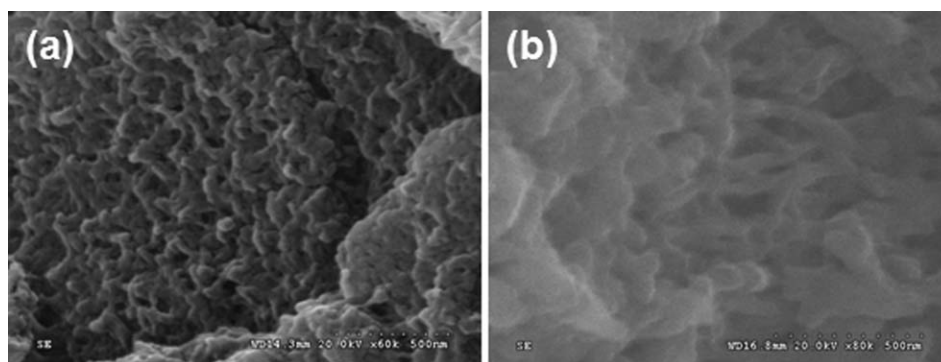


Figure 2. FE-SEM images of (a) PANI-MSA and (b) recycled PANI-MSA.

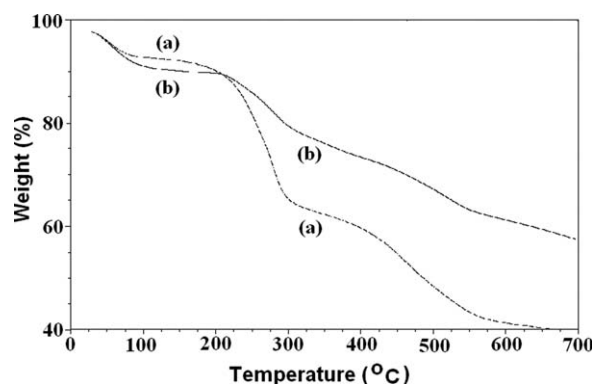


Figure 3. TGA thermograms of (a) PANI-MSA and (b) recycled PANI-MSA.

FE-SEM of PANI-MSA

Morphological structures of PANI salts were carried out by scanning electron microscopy and are shown in Figure 2. As-synthesized PANI-MSA shows nanofiber network morphology [Figure 2(a)] and recycled PANI-MSA shows nanofiber network morphology with more space inside the network [Figure 2(b)] compared to PANI-MSA morphology [Figure 2(a)] due to solvent effect. Energy dispersive X-ray analysis (EDAX) of as-synthesized PANI-MSA indicates the presence of sulfur (~7%) and this result is due to the presence of sulfonic acid group as dopant on PANI chain. EDAX of recycled PANI-MSA also showed the presence of sulfur (~5%).

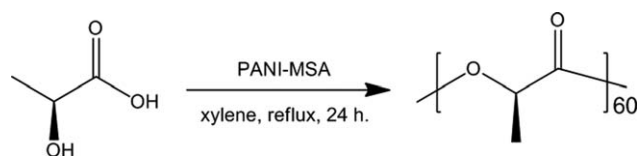
Thermogravimetry of PANI-MSA

TGA thermogram of as-synthesized and recycled PANI-MSA are shown in Figure 3. TGA thermogram shows three steps weight loss process, first step weight loss is due to moisture present on PANI sample and in the second step, polymer undergoes degradation. TGA thermogram shows that as-synthesized PANI-MSA is stable up to 165°C and the stability increases to 210°C for recycled PANI-MSA.

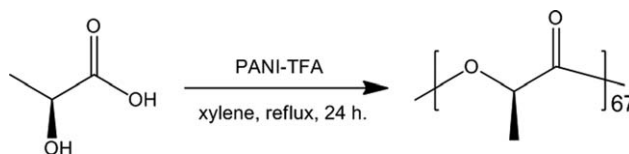
Polymerization of Lactic Acid Using Polyaniline-Based Solid Acid Catalysts

In continuation of our work on the use of conjugated conducting polymers as reusable catalysts for carrying out organic transformations,¹⁷ in this article, we carried out the synthesis of polylactic acid by employing PANI salt as polymeric solid acid catalyst for the first time.

Bulk condensation polymerization of lactic acid was carried out using PANI-MSA catalyst (2.5 wt % with respect to lactic acid) under reflux temperature in organic solvents such as chloroform (60°C), acetonitrile (80°C), benzene (80°C), and xylene (140°C) for 24 h. Among the solvents used, only xylene solvent favored the formation polylactic acid. Hence, various PANI catalysts were



Scheme 1. Synthesis of PLLA using PANI-MSA catalyst.



Scheme 2. Synthesis of PLLA using PANI-TFA catalyst.

tried out for the polymerization of lactic acid in xylene solvent at reflux condition (Schemes 1 and 2). Conversion of polylactic acid (percentage with respect to weight of lactic acid) using PANI catalyst follows the order PANI-MSA (46%) > PANI-TFA (33%) > PANI-Bi(OTf)₃ (27%) > PANI-Cu(OTf)₂ (20%) > PANI-Yb(OTf)₃ (15%). In PANI-MSA salt, PANI is a long chain polymer and MSA is acid dopant. This acid dopant plays a role as acidic catalyst in the polymerization reaction of lactic acid. The catalytic activity of acid catalyst was higher compared to that of metal salts because of the easily available proton for the reaction in acidic catalyst.

Reusability of the PANI-MSA catalyst was verified for polymerization of lactic acid for 24 h in xylene under reflux condition. Recyclability was checked by separating the catalyst from the reaction mixture by filtration followed by purification using chloroform and used in the reaction again. This procedure was carried out for three cycles and obtained the product in 45, 39, and 33 % respectively. After the recyclability experiment, the catalyst was analyzed by infrared (Figure 1), SEM analyses (Figure 2), and TGA analyses (Figure 3). A similar result was obtained for the catalysts before and after the reaction. The above results indicate that there is only a negligible change in the activity of the catalyst.

Formation of polylactic acid (PLLA) was authenticated by FTIR, ¹H-NMR, and ¹³C-NMR spectral results.¹¹ Molecular weight of PLLA synthesized using PANI-MSA and PANI-TFA were found out by MALDI-TOF-MS using 2,5-dihydroxy benzoic acid matrix and are shown in Figure 4. Molecular weight of PANI-MSA and PANI-TFA are 4385 and 4830 respectively (Schemes 1 and 2).

X-ray diffraction pattern of PLLA is shown in Figure 5 and it shows peaks at $2\theta = 12.1^\circ, 14.6^\circ, 16.5^\circ, 18.8^\circ, 20.5^\circ, 22.1^\circ, 23.7^\circ, 24.8^\circ, 26.9^\circ, 28.9^\circ,$ and 31.0° with corresponding d -spacing 7.3, 6.0, 5.4, 4.7, 4.3, 4.0, 3.8, 3.6, 3.3, 3.1, and 2.9 respectively, indicates the crystalline nature.¹⁸

SEM image of PLLA is shown in Figure 6. SEM image was taken at lower magnification and it shows mushroom cap-like morphology with a length of 9–13 μm and width of 7–12 μm .

CONCLUSIONS

PANI salt was successfully used as polymer-based solid acid reusable catalyst for the synthesis of polymer, low molecular weight polylactic acid, for the first time. Polymerization of lactic acid with the use of very low amount of PANI-MSA catalyst gave PLLA in 46% yield with molecular weight of 4385. This methodology gave highly crystalline polymer with mushroom cap-like morphology. This work may open of new research in the near future.

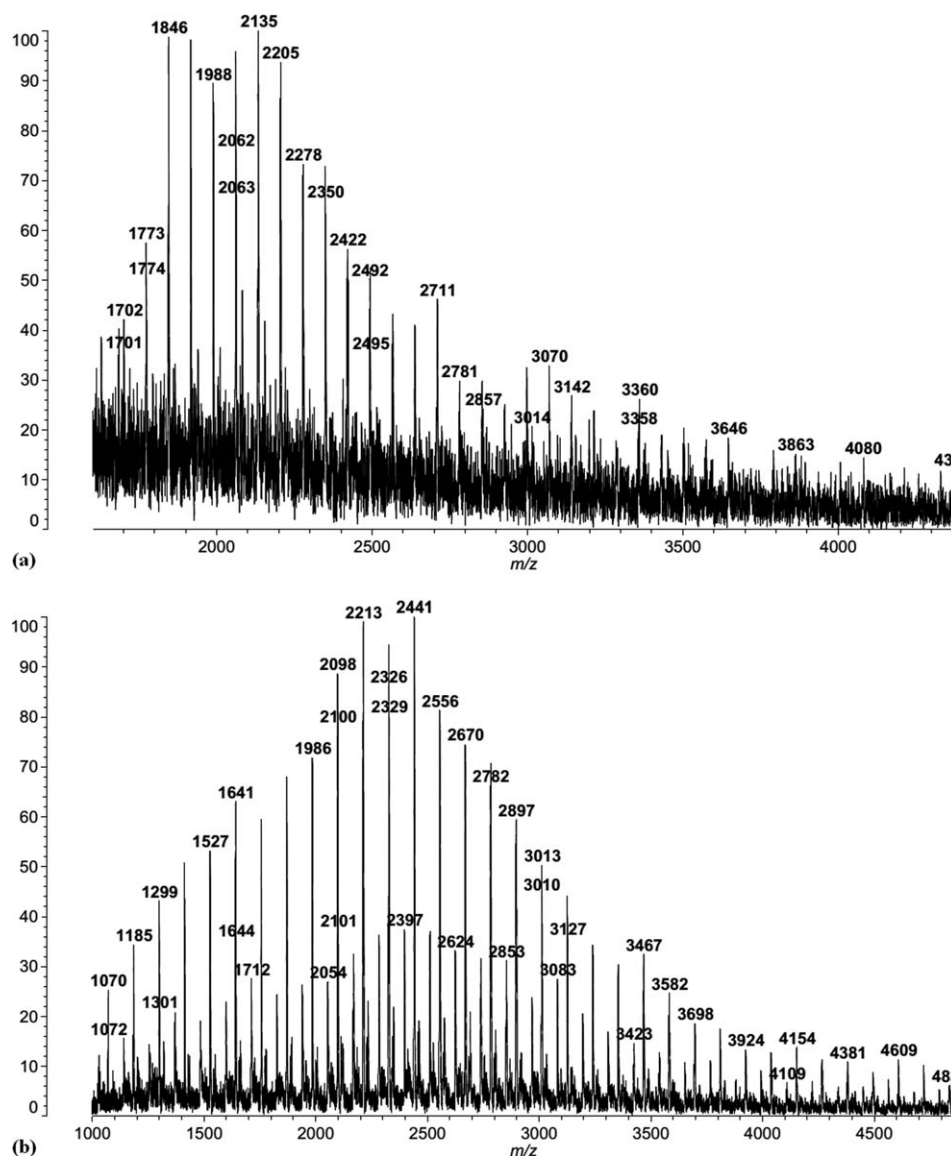


Figure 4. (a) MALDI-TOF mass spectrum of PLLA using PANI-MSA catalyst. (b) MALDI-TOF mass spectrum of PLLA using PANI-TFA catalyst.

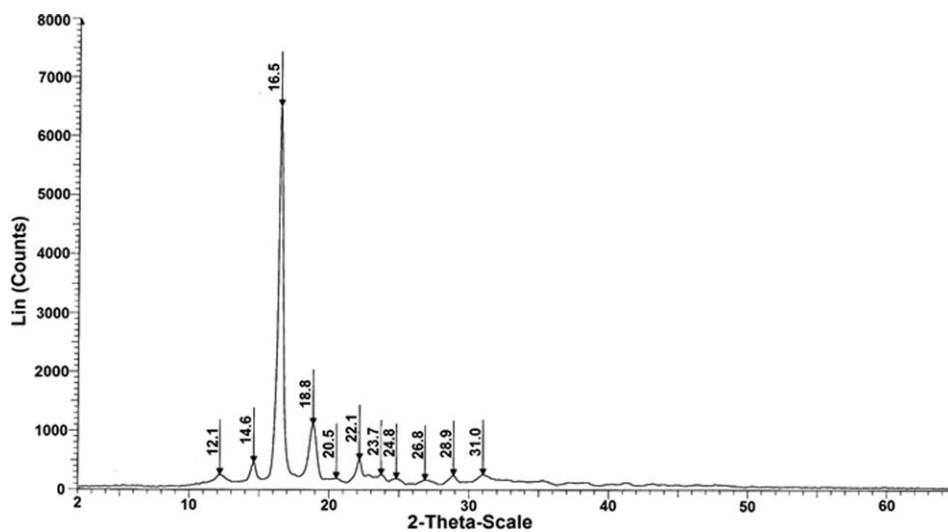


Figure 5. XRD pattern of PLLA.

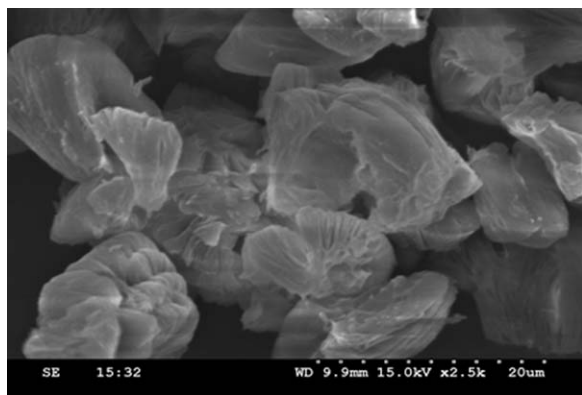


Figure 6. SEM image of PLLA.

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