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Zinc acetate as a catalyst for the bulk ring opening polymerization of cyclic esters and lactide

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ABSTRACT

$Zn(OAc)_2{\cdot}2H_2O$ is found to be an effective bulk polymerization catalyst for the ring-opening polymerization of *rac*-lactide, L-lactide, ε-caprolactone and δ-valerolactone. The propensity of polymerizations can be enhanced by performing them in the presence of appropriate amounts of different alcohols. The major initiation pathway in the polymerization is found to proceed via the activated monomer mechanism and depending on the nature of the alcohol used, polymers with different end groups can be synthesized. These polymerization system constitutes an economical process, employing readily available inorganics such as $Zn(OAc)_2{\cdot}2H_2O$ as catalyst and do not necessitate solvents. The overall system is green and eco friendly.

1. Introduction

The conventional polyolefin synthesis has already manifested its culmination as a consequence of depleting petrochemical feedstock and the non-degradable fate of these commodity polymers. Increased environmental awareness and depleting fossil-fuel resources have made it mandatory to search for new catalytic processes leading to the synthesis of bio-degradable polymers [1,2]. The increasing need to search alternative polymeric materials to those based on non-renewable petroleum resources, along with the desire to produce environmentally benign biodegradable plastics has provided active impetus towards the polymerization of cyclic esters and lactide [3–7]. Aliphatic polyesters have been implicated for biomedical applications such as delivery medium for the controlled release of drugs and biodegradable surgical sutures [8,9]. Polylactones and lactides have potential utility for such applications as a result of their permeability, biocompatibility and biodegradability [10–12]. One of the convenient strategies in synthesizing these polymers is the ring-opening polymerization of the corresponding cyclic lactone monomers, functionally related compounds and lactide [13–15]. Lactide is the cyclic dimer of lactic acid and is produced from annually renewable food resources like corn and sugar-beet through bio-mass fermentation [16,17]. The polymerization of lactide yields poly(lactide) which has emerged recently as a bulk commodity material since it is a environmentally friendly recyclable thermoplastic and is completely bio-degradable [10,12,18–21]. Such polymers are found to possess a bio-compatible nature with living tissue and bioassimilable. As a result, they have found useful applications biomedical and pharmaceutical applications, for example, in resorbable surgical sutures [22–25], drug delivery vehicles [24,25], and artificial tissue matrices [26,27]. Although a multitude of initiators are known for such polymerizations [28–32], the major hurdle regarding the commercialization of such processes is the difficulty in removing catalyst residues and the cytotoxicity associated with such residues, which limit the utility of these polymers in biomedical applications. An attractive process is envisioned to be engineered upon new catalysts that have environmentally benign metals that are constituents in the mammalian anatomy so that the residues are potentially harmless [33].

Among the various mechanistic modes of polymerization, the coordination-insertion ring-opening polymerization is the most popular because of its capability in producing polymers with narrow molecular weight distribution [3,29,34–43]. A large variety of metal complexes containing alkyl [44–48], alkoxide [34–43], carboxylates [49–51] and oxides [52] have been reported to possess good activity. Other metal alkoxides or aryloxides containing main-group as well a transition metals including lanthanides have been reported [3,29]. The medicinal value of such polymers has prompted active research into the synthesis of new catalysts containing biocompatible metals. These include examples from zinc [53–69], magnesium [70], calcium [71] and iron [72].

We have reported recently the use of simple iron and ruthenium chloride catalysts in the synthesis of polylactones [73].

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Here the polymerizations were found to proceed by the activated monomer mechanism [74,75]. We have been able to activate cyclic ester monomers and lactide by simple Lewis acids. Considerable control in the polymerization behavior was noticed in this method. Our contentions were again verified with different catalyst libraries of metal aryloxides of group 4 metals [76]. The key feature that is understood in these research is elaborate ligands on the metal catalyst is not a mandatory feature to facilitate such a process. What is really needed is a suitable initiating group that facilitates the cleavage of the acyl-oxygen bond of the monomer.

Although a multitude of zinc containing initiators have been reported in the recent past [53–69], what is most surprising is no detailed investigations have been reported with zinc acetate which is readily available and is stable under ambient conditions in the presence of oxygen and moisture. However, detailed studies with zinc octoate have been reported recently. Here the polymerization proceeds with coordination-insertion mechanism [77]. Our recent endeavor of having a thorough understanding of the activated monomer mechanism [73,76] initiated these investigations.

2. Experimental

2.1. Materials

L-Lactide (L-LA), *rac*-Lactide (*rac*-LA), ε-caprolactone (CL) and δ-valerolactone (VL) were purchased from Aldrich. L-LA and *rac*-LA were sublimed fresh prior to use. The other monomers were dried over CaH_2 overnight and distilled fresh before the commencement of the respective polymerizations. Benzyl alcohol (BnOH) and isopropanol (*i*-PrOH) used in these studies were purchased from Ranchem India and were used after drying using appropriate procedures. $Zn(OAc)_2{\cdot}2H_2O$ was purchased from Aldrich and used as received.

2.2. Instrumentation and characterization

^{1}H NMR spectra in $CDCl_3$ were recorded on a Bruker 400 MHz instrument. MALDI-TOF measurements were performed on a Bruker Daltonics instrument in dihydroxy benzoic acid matrix. Molecular weights and the polydispersity indices of the polymers were determined by GPC instrument with Waters 510 pump and Waters 410 Differential Refractometer as the detector. Three columns namely WATERS STRYGEL-HR5, STRYGEL-HR4 and STRYGEL-HR3 each of dimensions (7.8 mm × 300 mm) were connected in series. Measurements were done in THF at 27 °C. Number average molecular weights (M_n) and polydispersity (M_w/M_n) (MWD) of polymers were measured relative to polystyrene standards. For LA and CL, molecular weights (M_n) were corrected according to Mark-Houwink corrections [78].

2.3. Typical procedure for bulk polymerization

The procedures given are for polymerizations between the respective monomers and $Zn(OAc)_2{\cdot}2H_2O$ in 200:1 stoichiometric ratio.

For L-LA or *rac*-LA, polymerization, 17.34 μmol of $Zn(OAc)_2{\cdot}2H_2O$ and 0.50 g L-LA or *rac*-LA were taken in a sealed tube. The contents were rapidly stirred at 145 °C. Once the monomer melted completely, rise in viscosity of the polymerization reaction was observed, finally the stirring ceased. The completion of reaction was confirmed by ^{1}H NMR spectroscopy and GC. The contents were dissolved into minimum quantity of CH_2Cl_2 and poured into cold methanol. The polymer precipitated immediately and was isolated by filtration. The filtered product was dried in vacuum until a constant weight was attained.

For, CL polymerization, 23.66 μmol of $Zn(OAc)_2{\cdot}2H_2O$ was used for 0.50 mL of monomer. The polymerization was performed at 100 °C in a sealed tube. Rise in viscosity of the polymerization reaction was observed and finally the stirring ceased. The progress of the polymerization was followed by monitoring the disappearance of the monomer using TLC technique [73,76]. The contents were dissolved into minimum quantity of CH_2Cl_2 and poured into cold methanol. The polymer precipitated immediately and was isolated by filtration. The filtered product was dried in vacuum until a constant weight was attained. Similarly for, VL polymerization, 26.97 μmol of $Zn(OAc)_2{\cdot}2H_2O$ was used for 0.50 mL of monomer. The polymerization was performed at 100 °C and same procedure for work up was followed.

2.4. Typical procedure for bulk polymerization in the presence of BnOH

The procedures given are for polymerizations between the respective monomers and $Zn(OAc)_2{\cdot}2H_2O$ and BnOH in 200:1:5 stoichiometric ratio.

For L-LA or *rac*-LA, polymerization, 17.34 μmol of $Zn(OAc)_2{\cdot}2H_2O$ and 0.50 g L-LA or *rac*-LA along with 87.7 μmol of BnOH were taken in a sealed tube. The contents were rapidly stirred at 145 °C. Once the monomer melted completely, rise in viscosity of the polymerization reaction was observed, finally the stirring ceased. The completion of reaction was confirmed by ^{1}H NMR spectroscopy and GC. The contents were dissolved into minimum quantity of CH_2Cl_2 and poured into cold methanol. The polymer precipitated immediately and was isolated by filtration. The filtered product was dried in vacuum until a constant weight was attained.

For, CL polymerization, 23.66 μmol of $Zn(OAc)_2{\cdot}2H_2O$ was used for 0.50 mL of monomer along with 118.3 μmol of BnOH. The polymerization was performed at 100 °C in a sealed tube. Rise in viscosity of the polymerization reaction was observed and finally the stirring ceased. The progress of the polymerization was followed by monitoring the disappearance of the monomer using TLC technique [73,76]. The contents were dissolved into minimum quantity of CH_2Cl_2 and poured into cold methanol. The polymer precipitated immediately and was isolated by filtration. The filtered product was dried in vacuum until a constant weight was attained. Similarly for, VL polymerization, 26.97 μmol of $Zn(OAc)_2{\cdot}2H_2O$ was used for 0.50 mL of monomer along with 134.85 μmol of BnOH. The polymerization was performed at 100 °C and same procedure for work up was followed.

3. Results and discussion

3.1. Polymerization activity and characteristics

A thorough inspection of the literature reveals that although a multitude of different zinc containing systems have been used for lactide and cyclic ester polymerization [53–69], there have been no detailed investigations carried out with simple and commercially available compounds. We surmised that $Zn(OAc)_2{\cdot}2H_2O$ should be potent towards such polymerizations. There have been a report which prove the viability of metal acetates as suitable catalyst [79]. We envisaged from experience [73,76] that the coordinated H_2O molecule in the catalyst must act as a viable initiator, facilitating the cleavage of the acyl-oxygen bond in these monomers, hence affecting such polymerizations in an effective manner. The use of water as an initiator is known, although claimed to be ineffective towards the enhancement of rate of polymerization and molecular weights of the resulting polymers for catalyst bearing ligating ini-