INTRODUCTION

Poly(L-lactide) has some disadvantages also like poly(lactic acid) (PLA) are inherent brittleness with low toughness [1]. The flexibility, toughness and melt stability of poly(lactic acid) can be improved by some commonly used methods like copolymerization [2,3], by means of blending [4] and by addition of plasticizers [5,6]. For the preparation of aliphatic polyesters, coordination insertion polymerization has most commonly been used as polymerization mechanism. Wide variety of initiators are used for the preparation of poly(L-lactide) like tin alkoxides, aluminium and carboxylates. These initiators are capable of producing stereoregular polymers with controlled molar mass and narrow molar mass distribution [7]. Transesterification reactions and polymerization rate are different in zinc metal as compared to tin octoate initiated polymerization of lactide [8-10]. The polymerization reactions with stannous octoate as initiators are much faster and produce high molecular weight polymers with lower transesterification reactions and no remaining monomer [10]. The kinetics for the synthesis of tin(II) butoxide with tetrahydrofuran as solvent at 20-80 °C or in bulk at 120 °C [11]. The equimolar amount of triphenylphosphine as Lewis base into tin octoate, significantly increase the polymerization rate. Triphenylphosphine is most commonly used as Lewis base because it increases the polymerization rate and speed down the back biting reactions at monomer/initiator ratio greater than 5000 [12].

Gel permeation chromatography is the most commonly used method for the determination of molecular weights of products. The column set can be calibrated with standards of narrow molecular weight distribution or by using universal calibration [12]. The molecular weight sensitive detectors, such as on-line viscosity or light scattering detectors have been used most commonly due the lack of suitable standards for column calibration [13-18]. Gel permeation chromatography method is used to separate polymer samples based on hydrodynamic volume [19].

GPC is a technique to measure molecular weights and molecular weight distributions of polymer samples [20,21].

EXPERIMENTAL

L-Lactide (monomer) purchased was from Sigma Aldrich and recrystallized with dry toluene three times. Triphenylphosphine and stannous octoate were also procured from Sigma Aldrich and used as received without any purification. Chloroform, acetone and methanol were purchased from Ranbaxy Limited and also used as received.

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Differential refractometric detector from Waters, USA was used. Two polystyrene/dinylbenzene linear columns from PSS, Germany were applied. Number and weight average molar mass of samples were calculated by means of DataApex software applying calibration with polystyrene standards. According to the IUPAC terminology, molar mass values obtained by this method are called polystyrene equivalent molar masses. One can also estimate the peak values even for very poorly discriminated peaks, but these values are less exact.

**Polymerization:** Ring opening polymerization of polylactide by using stannous octoate as an initiator and triphenylphosphine as co-initiator have been carried out over a wide range of monomer to initiator ratio. L-Lactide (monomer) was poured in 4-necked round bottom flask and then stannous octoate and triphenylphosphine were added in equimolar proportions into it. Round bottom flask was thermostated with an oil bath at 130 °C (± 0.1 °C). Teflon stirrer was used to stir the reaction mixture. Vacuum was applied at the start of reaction and dry nitrogen gas was allowed to pass through reaction mixture till the end of reaction to maintain the environment dry. The polymerization time was 7-26 h. The obtained polymer was dissolved in chloroform and precipitated with methanol. Product obtained were dried in a vacuum dessicator for 2-3 days.

**RESULTS AND DISCUSSION**

The synthesis of poly(L-lactide) with stannous octoate as an initiator and triphenylphosphine as an accelerator is conducted in bulk. The multiple peaks in some of the GPC chromatograms were observed, which have been attributed to two simultaneously running kinds of ring opening polymerization of L-lactide. One initiated by stannous octoate only and another one initiated by triphenylphosphine-stannous octoate complexes. Since, stannous octoate and triphenylphosphine are taken in equimolar proportions, it is possible that some of triphenylphosphine may not get associated with molecules of stannous octoate at the growing end of polymer chain. The GPC chromatograms of selected samples of poly(L-lactide) are shown in Figs. 1-12. The peaks observed at high retention times likely belong to air dissolved in the sample elution because mobile phase was degassed, as well as to the remains of monomer and polymerization initiators. These peaks do not interfere with the peaks of polymers and were not considered in the molar mass evaluation. The multiple peaks, some of them well visible and other ones represented by bulbs on chromatograms, clearly indicate presence of macromolecules with distinct molar masses. In some samples, even more than two species with different molar masses can be present (Fig. 2, 7 and 12). The plausible explanation of this phenomenon is so far not known.
The plot of lower values of $M_w$ vs. polymerization time is shown in Fig. 13 and the results are shown in Table-1. Similarly, higher $M_w$ values are plotted in Fig. 14 and the results are shown in Table-2.

It is noteworthy that pure triphenylphosphine by itself did not lead to any polylactic acid formation even when the polymerization reaction was carried for much longer time. When the reaction was carried out with only triphenylphosphine and the reaction mass were finally dissolved in chloroform followed by addition of methanol, no precipitate was obtained. FTIR analysis of the reaction mixture also showed presence of only...
monomer. Thus, it is the combination of stannous octoate and triphenylphosphine which gives high molecular weight polylactic acid.

Conclusion

Multiple peaks have been observed in some of the GPC chromatograms of the reaction samples prepared with help of stannous oxide initiator in presence of triphenylphosphine modifier or accelerator. These are ascribed to existence of two independent polymerization processes. In one of them, stannous octoate acts alone while polymerization is simultaneously but independently initiated with the complexes of stannous oxide with triphenylphosphine. To further test this hypothesis, polymerization of lactide will take place in the presence of stannous octoate and triphenylphosphine in the molar ratios of 1:3 and 1:10. It has also been observed that molar mass of resulting polymer increases with time of polymerization and with decreasing ratio of monomer to initiator (M/Io).

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES