

High molecular weight of polylactic acid (PLA): A Review on the effect of initiator

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Abstract

This article reviews various initiator used to synthesize high molecular weight (MW >10,000 g/mol) of polylactic acid (PLA) through ring-opening polymerisation (ROP) of lactide. ROP has been chosen as the best method in producing PLA. On the other hand, stannous octoate (Sn(Oct)₂) has been reported as the best catalyst used for ROP method. Many researchers have studied that polymerisation rate with the presence of only Sn(Oct)₂ as catalyst is slow compared to polymerisation of lactide with the presence of initiator. An initiator is also favourable in producing high molecular weight of PLA as it can initiate the synthesis of PLA. Therefore, this review focus on ROP method catalysed by Sn(Oct)₂ using different solvent as initiator. Among groups of initiators being reviewed are hydroxyl, carboxylic acid, aldehyde, aliphatic polyester and organophosphorus compound. Most of the studies applied in nitrogen atmosphere with a temperature range of 125 to 200 °C, while only one study in vacuum condition. Duration of the polymerisation time is between 1 to 24 hours. Based on the review, alcohol (hydroxyl group initiator) has been reported as the best initiator to produce high molecular weight of PLA. This functional group act as co-initiator molecule that reacts with Sn(Oct)₂, forming the initiating stannous alkoxide linkage. The linkage is necessary to propagate monomer addition and hence increase the MW.

Article Info

<https://doi.org/10.24191/mjct.v4i1.12906>

Article history:

Received date: 17 March 2021

Accepted date: 23 April 2021

Published date: 30 April 2021

Keywords:

Lactide
Polylactic Acid
Polymerisation
Initiator
Molecular Weight

1.0 Introduction

Around 140 million tons per year, lots of plastic trash disposal ends up as solid waste disposal. Solid waste disposal and dumping on land or ocean leads to long-term contamination in soils and water environment. (Hu et al., 2016; Motta & Duek, 2014). Plastics severely can cause environmental problems as they are based on synthetic polymers which are not biodegradable (Lee & Hong, 2014; Chamas et al., 2020). Even though recycling and energy recovery have been implemented to a limited extent in reducing plastic waste, these efforts are still inadequate to handle an increasing volume of plastics used by the society (Mezzasalma et al., 2017). Therefore, replacement of biodegradable polymers, obtained from sustainable sources, from non-biodegradable polymers emerges as an encouraging solution to environmental waste (Dubey et al., 2016). One of biodegradable polymers that is in high demand is PLA, since it has many good properties that can suit in various application especially

in biopolymer production field. Being a biodegradable polymer, PLA undergoes a transformation into natural material in form of water, carbon dioxide, and composite. If treated with organic waste and by microorganisms in the environment, they can become compost.

The main routes in synthesizing polylactic acid are by polycondensation, ROP and enzymatic polymerisation. Many researchers have concluded that the most common and suitable synthesizing method in producing high molecular weight of PLA is through ROP compared to the other two (Hu et al., 2016). In applying ROP method, stannous octoate (Sn(Oct)₂) was found to be the best catalyst used.

In addition, certain initiator such as carboxylic acid decomposes at elevated temperatures and this can influence the rate of ring-opening polymerisation and promoting side reactions. Also, higher molecular weight distribution of PLA is affected by inadequate dispersion of initiator/monomer during polymerisation. Different parameters of the reaction produce different

characteristics of PLA as the parameters shows high influenced on the PLA characteristics produced.

2.0 Polylactic Acid (PLA)

PLA is an aliphatic thermoplastics polyester produced from renewable sources, which is one of the most attractive biodegradable polymers (Garlotta, 2019). PLA has its own unique properties which make it suitable for different applications (Mishra et al., 2015). Lactic acid has two stereo-isomers, namely L-lactic acid and D-lactic acid. From these isomers, several polymer products can be synthesized, among others are poly(L-lactic acid) PLLA, and poly(D-lactic acid) PDLA (Lee & Hong, 2014; Geueke, 2014).

PLA is usually known for its biocompatibility, good processability and biodegradability. The degradation rates and isomeric composition are affected by the physical and mechanical properties of polymers. The properties of PLA generally are depending on the molecular mass, degree of crystallinity and the ratio of co-monomers (Wilfred et al., 2018; Jamshidian et al., 2010). Other than that, PLA also is an eco-friendly biodegradable synthetic polyester. It is a linear thermoplastic polymer having high tensile strength, high modulus, high melting point, good barrier properties (gas, water and oxygen), good transparency and mechanical strength (Geueke, 2014; Singh & Anthony, 2016; Tsuji, 2005). PLA is very brittle where only 10% of elongation is expected before breaking. However, it has a strong resistance (Muller et al., 2017).

PLA always considered as the most promising and generally known biopolymer among numerous biopolymers because of its ideal properties such as light, low processing temperature, good printability, no environmental pollution and can be transformed into different forms (Hu et al., 2016).

Apart from that, the mechanical properties and degradation rate of PLA are adjustable and controllable in order to adjust the molecular weight by choosing different forms of polymetric and moulding methods to satisfy its requirement in producing high quality of PLA (Gong et al., 2017). PLA films showed higher values of tensile strength compared to polystyrene (PS) but lower than polyethylene (PET) (Jamshidian et al., 2010).

PLA becomes one of the most favourable biopolymers due to its preferred chemical structure and physical properties mainly regarding its biodegradability which make it suitable in various area

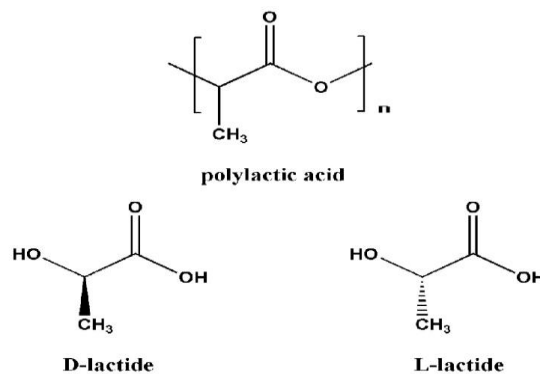


Fig. 1: Polylactic acid chemical structure (Lee & Hong, 2014)

of applications such as biomedical, food packaging, drug deliveries industries and tissue engineering (Kim et al., 2017; Azimi et al., 2014). PLA was approved by the US Food and Drug Administration as far back as in 1970s. Since then, it had been widely utilised in sutures, clips, drug delivery devices, and in food packaging applications (Cheng et al., 2009). Therefore, it is significant to better understand the characteristics of PLA, for both consumers and biomedical applications due to its biocompatibility and bioresorbability (Valentina et al., 2017; Lasprilla et al., 2012).

In addition, the applications of PLA are not totally based on its biodegradability nor due to it is made of renewable sources. But it is actually because PLA are efficiently work and cost at low price even though it is providing excellent properties. It is difficult to produce material which apply all the properties required for an application. However, PLA with its diversification had proved to be useful in many applications. This can be done by simple modification of its physical and chemical structure from its single polymer (Lopes et al., 2014).

3.0 Polylactic acid synthesis

Generally, there are three main routes to synthesis PLA from lactide which are polycondensation, ring-opening polymerisation (ROP) and enzymatic polymerisation (Lee & Hong, 2014; Jamshidian et al., 2010; Lasprilla et al., 2012). In addition, the most common methods applied in synthesizing PLA are direct polymerisation and ring-opening polymerisation (Avinc & Khoddami, 2016). Niaounakis (2013) has stated that low molecular weight of PLA usually synthesized by condensation polymerisation while high molecular weight of PLA usually synthesized by ring-opening polymerisation with the addition of

catalyst such as oxides of zinc, stannous, chlorides of zin and tin (ii) octanoate.

3.1.1 Direct Polycondensation

Polycondensation is one of the formation processes of polymer by linking small molecules (monomers) and accompanied by elimination of by products such as water or alcohol. This reaction involves a solvent at high vacuum and temperature, where water is being removed at the end of the process. In general, this is the least expensive route. However, it is difficult to achieve high production rates in a solvent-free system (Motta & Duek, 2014; Lee & Hong, 2014; Dubey et al., 2016).

There are two types of polycondensation method which are direct polycondensation, melt and solid-state polycondensation (Mishra et al., 2015; Moon et al., 2001). Generally, low quality and low molecular weight of polymer is produced during polycondensation due to its difficulty in removing by products completely from the highly viscous reaction mixture (Hu et al., 2016; Motta & Duek, 2014; Cardoso et al., 2013; Khan et al., 2013).

Liu et al. (2013) reported that high molecular can be obtained by using direct polycondensation followed by chain extending with hexamethylene diisocyanate (HDI). HDI is non-toxic and can be used as chain extender. Hence, it can control the degradation time of polylactic acid. It is also known that this addition is the simplest and most effective way of controlling the degradation time. The direct condensation of LLA was initially regarded as a process only to obtain a low molecular weight polymer which was not useful, but now the direct polycondensation of LLA can also obtain PLLA with a significantly high molecular weight (Khan et al., 2013; Xiao et al., 2012).

Another study from Achmad et al. (2009) has implemented direct polycondensation method in fabricating higher molecular weights of PLA polymers. Lactic acid, used as the reactant, was polymerised using the method without any addition of catalyst, solvent, or initiators. It was done under controlled temperatures and pressures. They have highlighted that under controlled temperature and pressure, molecular weights of the fabricated polymers were affected. The results showed that high molecular weights of 90 kDa could be obtained at 200 °C after ~90 h under vacuum condition.

Apart from that, Dubey et al. (2016) stated that melt polycondensation can be carried out without the usage of any organic solvent. However, this reaction should

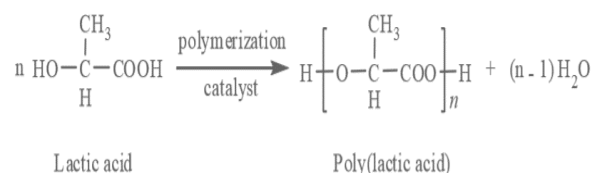


Fig. 2: Direct polycondensation (Mishra et al., 2015)

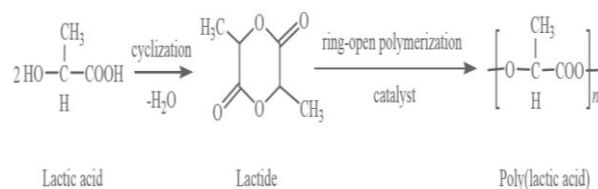


Fig. 3: Ring-opening polymerisation (Mishra et al., 2015)

be done above melting point, T_m of its polymer. This method is simple and remarkably can reduce the costs of synthesis. But sensitivity of its reaction condition is a big problem to be solved (Jérôme & Lecomte, 2018). This melt polycondensation produced water and decompose PLA with high molecular weight at high reaction temperature.

3.1.2 Ring-opening polymerisation (ROP)

Ring-opening Polymerisation (ROP) is the most common method with the presence of catalyst that can produce PLA with high molecular weight (Motta & Duek, 2014; Lee & Hong, 2014; Mezzasalma et al., 2017; Cheng et al., 2009; Luo et al., 2017). Ring-opening polymerisation of lactide commonly known as a reaction process in which cyclic monomers is been propagate by the initiation of different ions. As the reactive centre of propagation, the terminal end of polymer has been classified into three mechanisms which are anionic, cationic and coordination-insertion (Lee & Hong, 2014; Jérôme & Lecomte, 2018; Nuyken & Pask, 2013; Icart et al., 2018). Growth of chain can be hindered by the highly reactive anionic reactants. While anionic polymerisation hindered the chain, cationic polymerisation caused nucleophile reaction to the active centre. Both polymerisations can cause undesirable reactions such as other side reactions, racemisation and decomposition reaction (Lee & Hong, 2014). ROP is generally initiated by the attack of ionic (anionic or cationic) initiator on the cyclic ring monomer. This attack creates an active site for further addition of monomer(s). As the conversion ratio of monomer to initiator increase, polymer molecular weight also increases (Kamber et al., 2017).

The ring opening polymerisation process is a multistep process and in this method many reagents such as catalysts, solvents and initiators are utilised for the synthesis of PLA (Garlotta, 2019). The products obtained by this method require purification, which is a complicated and difficult process, thereby increasing the cost of high molecular weight polylactic acid (Singh & Anthony, 2016).

Many of the researchers have highlighted that this synthesis process requires a catalyst to produce high molecular weight of PLA. Apart of that, the ratio and sequence of D- and L-lactic acid units in the final polymer can be controlled. It can be done by controlling the reactions conditions and type of monomer used. (Lasprilla et al., 2012; Lopes et al., 2014; Cardoso et al., 2013; Gupta et al., 2007). According to Lopes et al. (2014) there are several metallic catalysts that are suitable to use in this reaction due to its ability in producing high molecular weight of PLA, high reaction rates and its solubility in the monomer melt.

Purity of the lactide monomer combined two lactic acids is important to this reaction. This reaction was conducted using a sequence of polycondensation, followed by de-polycondensation which end up with ring-opening polymerisation. Besides, it was carried out in the condition with catalyst by the ring-opening reaction of lactide (Lee & Hong, 2014). Icart et al. (2018) have concluded that by following the procedures, within a short period of time, functionalised polyesters of high molecular weight and low polydispersity can be synthesized.

In addition, many researchers have proven that stannous octoate ($\text{Sn}(\text{Oct})_2$) is the most suitable catalyst used in producing high molecular weight of PLA through this reaction (Duda et al., 2014; Srithep et al., 2019). However, there are study that have stated that ROP of lactides with $\text{Sn}(\text{Oct})_2$ is fairly slow. Therefore, in order to increase the rate of polymerisation, it is desirable to add hydroxyl-functionalised compounds as co-initiator (Xiao et al., 2012). Thus, there are also studies that have conduct experiment on the effect of initiator on synthesizing PLA through ROP.

4.0 Initiator

Initiator can be understood as any chemical species that reacts with a monomer to form an intermediate compound. This compound is successively capable of linking with a large number of other monomers into a

polymeric compound. In previous studies, catalyst is sometimes called as initiator meanwhile solvent of nucleophilic compound is called co-initiator but mostly researcher called the solvent that used together with catalyst in the ring-opening polymerisation as an initiator (Sin & Tueen, 2019). In ring-opening polymerisation, catalyst must be used together with a nucleophilic compound (generally an alcohol as initiator) to initiate the reaction if a controlled synthesis of the polymer is to be obtained.

The polymerisation rate of L,L-lactide in the presence of $\text{Sn}(\text{Oct})_2$ as catalyst and an amount of water traces was found to be significantly low. It is low than that measured in the presence of an alcohol. Therefore, it is well-known that polymerisation rate can be increased in the addition of a specified amount of an alcohol (Korhonen et al., 2001; Báez et al., 2011). Most of the researchers also have agreed that most of the initiator will enhanced the polymerisation reaction by increasing the polymerisation rate of polymer which high molecular weight of polymer is produced.

4.1.1 Various type of initiator

The discussion on the initiators used will be based on hydroxyl group, carboxyl group, aldehyde group, aliphatic polyester and organophosphorus. The same catalyst and method have been chosen in order to discuss the effect of the initiator on synthesizing of lactide through ring-opening polymerisation which catalysed by stannous octoate.

4.1.2 Hydroxyl Group–aliphatic alcohol, polyalcohol

Korhonen et al. (2001) have investigated polymerisation with different co-initiators (butanediol (BD), pentaerythritol (PERYT), polyglycerine (PGL-06 and PGL-10)). They proposed that the application of hydroxyl groups as co-initiators led to higher molecular weight ($>400,000$ g/mol) and faster polymerisation (<5 hours), without affecting the polymer thermal properties.

They have conducted a study to investigate the relationship between the number of hydroxyl groups in the co-initiator and the polymerisation rate to produce high molecular weight of polylactide through ROP with different monomer/initiator ratio used such as 100:1, 100:3 and 100:5. Polymerisations were carried out for one hour. Other cases carried out shorter times of polymerisation and were shown to be sufficient to

obtain the highest molecular weight. The longer times is significant to determine whether higher hydroxyl content in the polymer influences degradation of the polymer.

The results have shown that PGL-10 have the fastest polymerisation rate compared to other co-initiators used in the experiment. It is supported by the largest number of growing chains from PGL-10. In addition to faster polymerisation, increasing hydroxyl group content in the co-initiator yielded polymer with higher molecular weight. Proton nuclear magnetic resonance (H-NMR) results showed that to obtain an average length of the chains closer to the theoretical value, only small amounts of co-initiator should be used. However, the addition of more hydroxyl groups seemed to initiate the polymerisation. Thus, the researchers have highlighted that monomer/initiator ratio have influenced the molecular weight and concluded that more hydroxyl group may lead to produce high molecular weight of PLA.

Since PGL-10 have the highest hydroxyl group and has the highest potential to produce high molecular weight of PLA, the researchers have conducted another study on how concentration of co-initiator can affect the molecular weight of PLA. As expected, GPC results shows that the highest molecular weight was achieved with the lowest concentrations of co-initiator.

Lower concentration of co-initiator caused a decrease in molecular weight. It is noted that its concentration affects the degradation rate of the polymers. In addition, low co-initiator concentration yielded broader molecular weight distribution.

Aliphatic alcohols such as 1-dodecanol, 1-octanol and methanol as initiator

According to Kaihara et al. (2007), the purity of monomers and the amount of water and alcohol in the reaction system are significant factors for increasing molecular weight and conversion of polyesters. The researchers stated that the ratio of monomer to initiator can affects the molecular weight of the resulting polymer based on their previous studies. In fact, water could be an initiator for the ROP. Therefore, the amount of water supplied as reactant to the system must be reduced. This reduction is extremely important in controlling the molecular weight of the resulting polymer. Key to obtain high- molecular-weight polyesters is reduction of water in the reaction system. Besides, high purity of monomer and initiator also contributed to the success.

Therefore, Kaihara et al. (2007) decided on conducting studies on synthesizing PLA which catalysed by Sn(Oct)₂ with 1-dodecanol as initiator at 140 °C for 10 hours. The results obtained have proven the previous studies that 1-dodecanol act as initiator have potential to produce high molecular weight of PLA as it initiated the monomer during the polymerisation. The molecular obtained by Gel Permeation Chromatography (GPC) is 10,000–11,000 g/mol with 95% yield.

Pholharn et al. (2017) have conducted another study on the effect of several aliphatic alcohols such as 1-dodecanol, 1-octanol and methanol as initiators on synthesized of polylactide by ring-opening polymerisation which catalysed by stannous octoate. All the experiment was conducted under same condition which was at 165 °C for 4 hours incubation with the same monomer/initiator molar ratio. Based on the GPC data obtained in the study, methanol showed the highest molecular weight of polymer compared to 1-dodecanol and 1-octanol.

They have concluded that it was affected by the initiation step in which methanol has high initiation rate because all the three sample were conducted under same operating condition except for type of initiator. Based on the insertion-coordination mechanisms, the propagation continues by repeatedly adding additional lactide molecules into tin-oxygen bond. Since all factors governing this propagation step is similar, it is expected that the propagation rates are also similar. Therefore, the higher initiation rate is the only variable affecting the molecular weight. They have concluded that methanol was the most efficient initiator for ROP for their study.

The researchers have concluded that methanol was more effective in coordination-insertion mechanism due to the strongest effect of methanol. It is the smallest alcohol and has lower steric hindrance when attacking the octoate ligand. Hence, it can attack the substrate more easily compared to other longer alcohols such as 1-octanol and 1-dodecanol. This attack results in a more complete polymerisation. Other than that, longer alcohols have more steric hindrance.

Aliphatic alcohols such as 1-butanol, 1-tetradecanol and 1-docosanol as initiator

The same studies were conducted by Báez et al. (2011) on the effect of alkyl end group on lactide which synthesized PLA by ROP catalysed by Sn(Oct)₂ but using different types of aliphatic alcohols as initiators.

In this study, they used different alkyl end group for initiator starting from ($n = 1-10$). All the samples have been polymerised under same conditions at 170 °C for 2 hours. They have concluded that the highest molecular weight obtained was the sample initiated by 1-docasanol (3,600 g/mol) compared to 1-butanol with lowest molecular weight (3520 g/mol) and 1-tetradecanol with 3,550 g/mol. Since 1-docasanol have the highest end group number ($n = 10$), thus, the result expected that it is producing high molecular weight of PLA. Thus, they have concluded that those with highest alkyl end group will producing high molecular weight of polymer due to the high number of alkyl group that can promote into longer chain of polymer linkage during polymerisation.

Aliphatic alcohols such as dipentaerythritol as initiator

Other than that, Wang et al. (2008) have reported on the synthesized of star-shaped PLA with six arms by ROP which catalysed by $\text{Sn}(\text{Oct})_2$ and using dipentaerythritol as initiator at 125 °C for 24 hours. The results showed that high molecular weight produced with the presence of initiator compared to the polymerisation with absence of initiator. Moreover, the results also showed that the high monomer/initiator molar ratio may lead to high molecular weight of polymer due to as this ratio increases, there will be fewer initiating sites for the monomer molecules and thus lead to longer polymer chains.

In this study, they have concluded that molar ratio of monomer to initiator can be used to predict the polymer molecular weight. However, no apparent influence can be related from the molar ratio of monomer to catalyst on the polymer molecular weight.

Aliphatic alcohols such as choline as initiator

Sobczak (2012) has reported the effect of temperature, reaction time, and choline (CHOL) dosage on the ROP in the presence of choline as co-initiator which catalysed by tin octoate. The study shows that lactide in which polymerisation were conducted at 140 °C with (100:0.5:1) monomer (M)/catalyst (C)/co-initiator (I) molar ratio for 24, 48, and 72 hours, respectively showed different molecular weight determined by GPC after polymerisation.

It shows that the lactide have achieve high crystallinity yield at 48 hours as it produced highest molecular weight (7,200 Da) and then drop from 7,200 Da to 5,700 Da which shows the degradation of

lactide at 72 hours. This can be attributed that lactide cannot be polymerised for too long as it will be degraded after achieving its certain maximum crystallinity yield at certain time. Another sample has shown that the highest molecular weight of all the samples conducted at 160 °C for 48 hours in which it has 8,100 Da molecular weight. From this study, it has stated that the temperature, reaction time and even the monomer/catalyst/co-initiator molar ratio have affected the polymerisation reaction. They also found that the reactivity of hydroxyl groups in CHOL increase as the monomer to initiator increase. This is because, the catalyst used, which is $\text{Sn}(\text{Oct})_2$, enhance its efficiency when an alcohol is added as co-initiator and control the polymerisation process.

4.1.3 Carboxylic acid group and aldehyde group

Icart et al. (2018) have reported the use of two co-initiators in synthesizing PLA catalysed by $\text{Sn}(\text{Oct})_2$. They are salicylic acid (SAc) and salicyl aldehyde (SAI). There were two experimental designs used in this study which are to identify the best ROP condition by using aldehyde and carboxylic acid as initiator. Meanwhile, both experiments aimed to determine the influence of lactide/catalyst and co-initiator/catalyst molar ratios on the molecular weight of PLA.

As expected, there will be some behaviour for the lactide/catalyst molar ratios as the higher the lactide/catalyst molar ratio, the higher the molecular weight of PLA were synthesized. The results also show that there are slightly increase in molecular weight of PLA in the presence of initiator compared to the absence of initiator during polymerisation.

In addition, the influence of lactide/catalyst, co-initiator (SAI)/catalyst and co-initiator (SAc)/catalyst on the molecular weight of the functionalised PLA was also investigated. The researchers have highlighted that both co-initiators/catalyst molar ratios had showed no statistically significant effect on molecular weight of PLA synthesized.

It is estimated that increasing the lactide/catalyst molar ratio would increases the probability of coordination between lactide and catalyst agent. The increment of this probability helps in synthesizing polymers with higher molecular weight. However, other impurities such as lactic acid and other hydroxyl are also able to coordinate with the catalyst. With that, they have influence on the final polymer molecular weight. However, there were no impurities were assessed in this study on the ROP with aldehyde and

carboxylic acid, thus, the researchers have concluded that aldehyde and carboxylic acid as initiator for ROP of PLA have no influence on molecular weight of PLA.

4.1.4 Aliphatic Polyester as initiator

Pholharn et al. (2019) have conducted another study regarding on synthesizing PLA via ROP catalysed by Sn(Oct)₂ that is initiated by Polybutylene Succinate (PBS) as a macroinitiator and 1-dodecanol as micro-initiator. They conducted study with 0.001 mol% of PBS and 0.1 mol% of 1-dodecanol as initiator to determine the optimum reactions conditions for each initiator.

The results showed that the synthesized PLLA had a yield of 84% and a molecular weight of 24,000 g/mol. These results were obtained using PBS concentration of 0.001 mol% at optimal temperature of 160 °C and incubation time of 4 hours. However, PLLA initiated by 1-dodecanol showed lower yield (65%) and low molecular weight (6,200 g/mol) at the same condition. This shows that as high temperature was required for this reaction, thus the micro-initiator evaporated easily and led to lower efficiency. Thus, they have concluded that the macroinitiator, PBS, was a better initiator under their conditions.

4.1.5 Organophosphorus Compound (triphenylphosphine) as initiator

Since Kaur et al. (2014) have proved that triphenylphosphine can synthesize high molecular weight of PLA in his previous study, he had conducted another study to investigate the comparison of polymerisation kinetics in the presence of stannous octoate (Kaur, 2018) (initiation rate, k_i ; propagation rate, k_p , and termination rate, k_t) with and without triphenylphosphine under two different environments: nitrogen atmosphere and vacuum at 130 ± 1 °C. At first, he stated that triphenylphosphine used as initiator can increase the polymerisation rate that may lead to produce high molecular weight even in a short time for both cases.

The results show that the initiation rate for both conditions is the same since the monomer to initiator

ratio used is similar. However, the different between these two conditions are that the termination rate under nitrogen flow is higher than vacuum that may lead to lower molecular weight synthesized. Since there are always water presents in the polymerisation that will affect the polymerisation rate, thus, no presence of water and other impurities is assumed because at high temperature in vacuum caused most of water and other impurities will be evaporated.

Therefore, vacuum is the most preferred condition to synthesize high molecular weight for this study. They also have conducted a study with different monomer to initiator ratio in vacuum condition. The researcher also has concluded that the increase in molecular weights with increasing initial monomer to initiator ratio is because as this ratio increases, there will be fewer initiating sites for same number of monomer molecules and thus will lead to longer polymer chains.

5.0 Conclusion

This research reviewed the effect of initiators in producing high molecular weight of PLA which concluded that different types of initiators used will synthesised polymers with significantly different molecular weight properties. The addition of initiator has increasing the polymerisation rate. In addition, some studies have stated that monomer/initiator ratio have significant effect in controlling the molecular weight of polymer. For instance, high monomer/initiator ratio (M/I:100/1) of polyglycol have produced higher molecular weight of polymer compared to (M/I:100/5). Moreover, low concentration of PGL-10 can produce more than 400,000 g/mol of PLA. Based on previous studies, most of the researchers have concluded that hydroxyl group are having the highest potential in producing high molecular weight of PLA.

Acknowledgement

The authors would like to acknowledge the School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA for technical support.

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