Development of Biodegradable Thermoplastic Elastomers Composed of 2-Methyl-1,3-propanediol-based Polyesters and Poly(L-lactide) Blocks

(2-メチル-1,3-プロパンジオール由来ポリエステルとポリ(L-ラクチド)ブロックからなる生分解性熱可塑性エラストマーの開発)

LAMYA ZAHIR

Polymer Chemistry Laboratory
Department of Applied Chemistry
Graduate School of Engineering
Hiroshima University
March 2021

Contents

Chapter I

1.General Introduction

1.1. Climate change and impact on environment

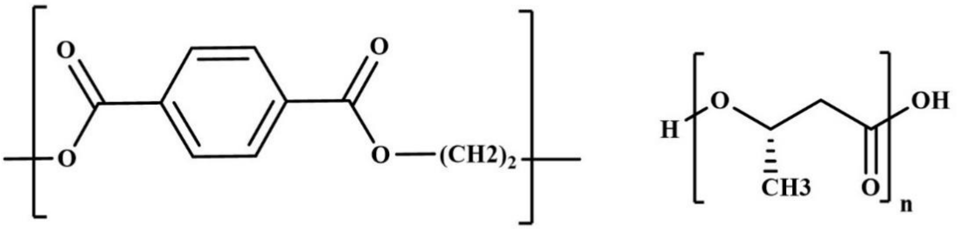
Climate change of the planet has been a vulnerable fact since several years for human existence and other living species. Global warming and the resulting large-scale shifts in weather patterns are the aspects of climate change.[1] According to the report of the World Meteorological Organization (WMO) in "UN Climate Action Summit 2019", the global average temperature has increased by 1.1 °C since the pre-industrial period, and by 0.2 °C compared to 2011-2015. The time span 2015-2019 was set to be the warmest five-year period in the world's history due to the impacts of climate change.[2] Warming of the climate system is unequivocal, and since the 1950s, many of the observed changes are unprecedented over decades to millennia. The atmosphere and ocean have warmed, the amounts of snow and ice have diminished, sea level has risen, and the concentrations of greenhouse gases have increased.[1] The causes of global warming are mainly human activities such as deforestation, farming and burning of fossil fuels. Among these, the most vulnerable and life threatening one is the burning of fossil fuels like coal, oil and gas to generate electricity or power for industrial and household activities and for manufacturing large scale of plastic commodity for end uses.

1.2. Plastic

Plastic is composed of a wide range of high molecular weight organic polymers obtained mostly from the various hydrocarbon and petroleum derivatives. The extensive use of plastics, lack of waste management, and casual community behavior towards their proper disposal pose a significant threat to the environment. As long lasting polymers and having high persistence towards the environment, the production and consumption of plastics due to the excessive industrial and domestic applications is following a continuous upgrowing trend day by day since more than 50 years.[3] In our daily life, plastics are easily found in a form of straw, plastic bottle, plastic bag, detergent and toiletries bottle, credit card, toys, bento boxes, polystyrene, pipes, food tray and many more.[4] Over 250 million tons of commodity plastics are produced worldwide every year until reported in 2015. Polyolefins occupy more than 55% of the global plastic material demand.[5] Chemical structures of some commercially available plastics are mentioned in scheme 1-1.

Polyethylene (PE)

Polycaprolactone (PCL)



Polyethylene Terephthalate (PET)

Polyhydroxy butyrate (PHB)

Scheme 1-1: Chemical structures of some commercially available plastics

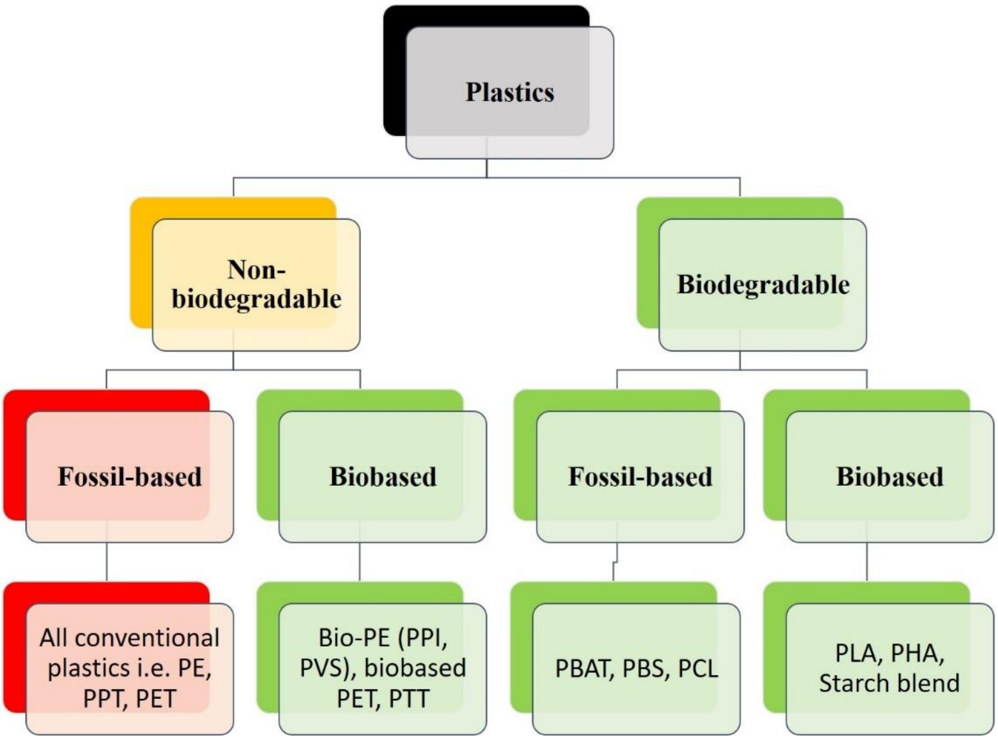
1.3. Classification of Plastics

Plastics can be classified in two group depending on their biodegradability,1) non-biodegradable plastics 2) biodegradable plastics.

Non-biodegradable plastics: can be both petroleum based and biobased. Most of the conventional plastics are synthetic polymers which are made from burning of fossil fuel and are not degradable in environment or degradation rate is too slow to be disintegrated fully.[3] Some features of non-biodegradable polymers are:

- High molecular weight: Extensive repetition monomers makes these difficult to decompose.[6]
- Highly stable and long-lasting: These properties lead these to various application like pipes, sheets, aircrafts etc.

- Heat and water resistant: Suitable for food package, mugs, plates, spoons, tea bags, disposable items, cooking stuffs etc.
- Light weight, cheap and easy to manufacture: These properties ensure availability, convenient to carry, storage at home for years i.e. shopping bag, food storage.
- High persistent in the environment, inert and resistant to microbial attack.

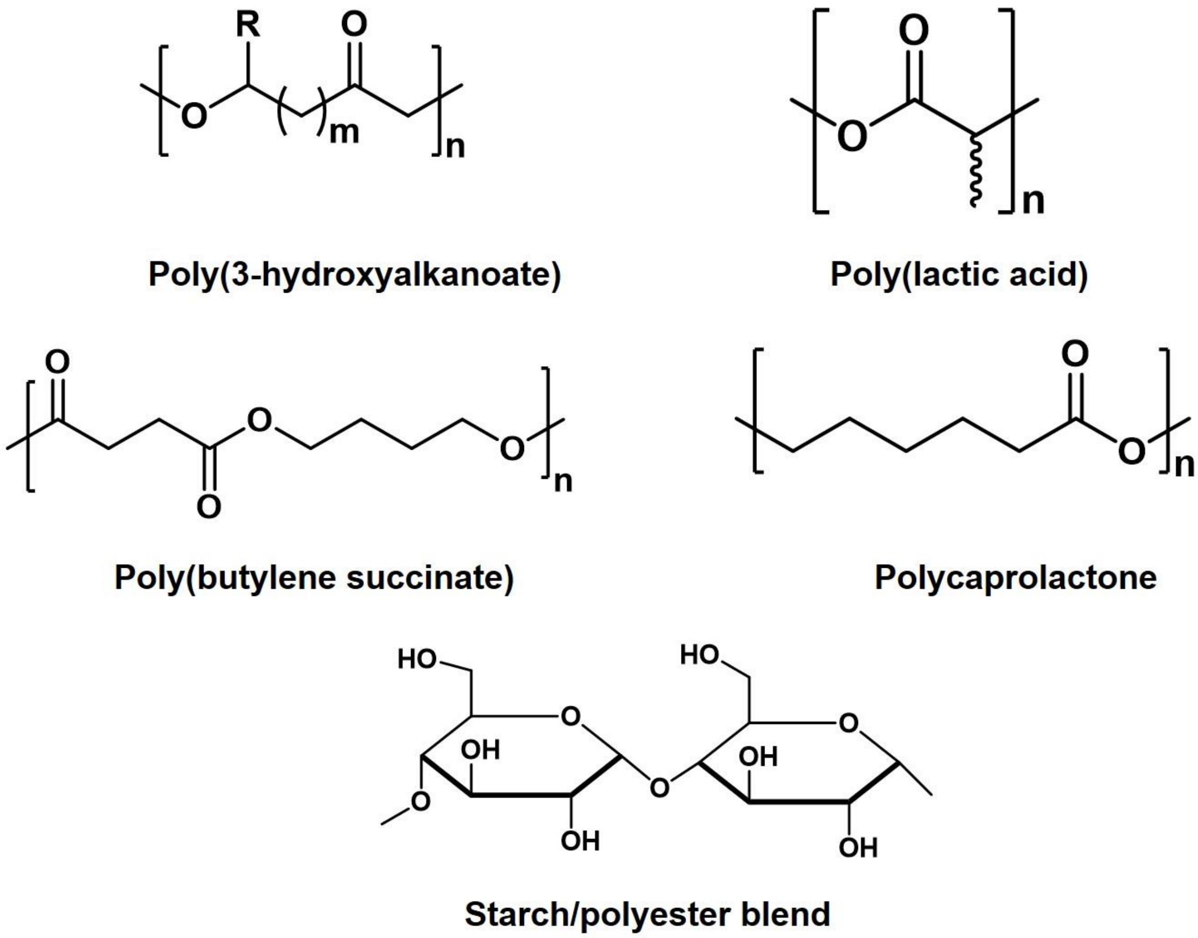


Scheme 1-2: Classification of plastic[7]

An ever-increasing ecological threat : After certain lifetime of all plastic commodities, they accumulate in nature for decades as fragmented parts (called microplastics) due to poor waste management and littering. These microplastics do not readily enter the degradation cycles of the biosphere and create garbage patches which is a major threat for biodiversity. As per global estimation, about 57 million tons of plastics waste is generated annually.[8] In addition, the amount of plastic wastes in the oceans has exceeded six times compared to plankton which is very harmful for sea life and also human health.[9] Crude oil and natural gases are used to manufacture plastic products which go through the synthesis process using energy and water. Huge amount of CO_2 and other greenhouse gases are emitted during the production and incineration of non-biodegradable polymers which is major cause of air pollution and global warming.

1.4. Biodegradable plastics

In contrast to the petroleum based conventional plastics, biodegradable plastics are supposed to be mineralized into water, CO_2 and biomass by organisms after their lifetime. This can be fuel based and biobased depending on the degree of degradability and microbial assimilation. Enzymatic and non-enzymatic hydrolysis cause the degradation of some plastics such as polyesters which depend on the type of organism, nature of pretreatment and polymer characteristics.[10] Molecular weight of the polymer, mobility, crystallinity, tacticity, chemical composition, type of functional group, additive present in polymer are the influential aspects of degradation process and speed.[11] With the increasing awareness of plastic pollution, demand of biodegradable plastics is increasing day by day. Some examples of biodegradable polymers are polycaprolactone (PCL), poly(butylene succinate) (PBS), poly(butylene adipate terephthalate) (PBAT) etc which are fuel based and poly(lactide) and poly(3-hydroxyalkanoates) (PHA) are biobased biodegradable polymers (Figure 1-2). Starch, cellulose and starch-based polymers are mainly used as biodegradable plastics due to its abundance, ready availability, low price and biological, ready and complete degradability.[12,13]



Poly(3-hydroxyalkanoate)

Poly(lactic acid)

Poly(butylene succinate)

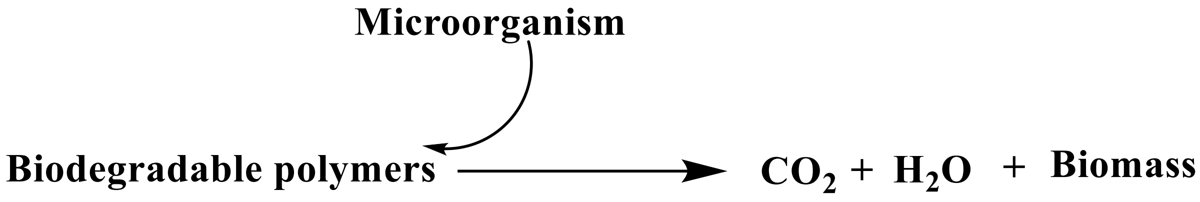
Polycaprolactone

Starch/polyester blend

Scheme 1-3: Examples of biodegradable plastics

Two factors are the most important to define any plastics by biodegradable:

- Biodegradability which is defined by mineralizing or lowering of mass into CO_2, water and biomass in the presence of microorganisms [14].



$$\textbf{Biodegradable polymers} \xrightarrow{\textbf{Microorganism}} \mathbf{CO_2 + H_2O} + \textbf{Biomass}$$

- The time frame of biodegradation which is the time required to degrade the material fully.

Different microorganisms are responsible for degradation of different plastics in different conditions i.e. *Acidovorax faecilis, Aspergillus fumigatus, Comamonas sp., Pseudomonas lemoignei* and *Variovorax paradoxus* are found in soil, while *Alcaligenes faecalis* and *Pseudomonas* have been identified in activated sludge. *Comamonas testosteroni* is one of those traced in seawater*, Ilyobacter delafieldii* is present in the anaerobic sludge.[15]

1.5. Mechanism of degradation

Different factors like particle size and shape of polymer, temperature, moisture, crystallinity, % D-isomer, residual lactic acid concentration, molecular weight, molecular weight distribution, water diffusion, and metal impurities from the catalyst will affect the polymer degradation rate. Polymer degradation, in nature, is the decomposition of organic matters influenced by both abiotic and biotic factors.[16]

1.5.1. Abiotic implication of material degradation

Polymeric materials can undergo various transformations when they are exposed to outdoor conditions like weather, ageing and burying. Abiotic factors contribute to weaken the polymeric structure facilitating the later degradation process either as a synergistic or initiating factor.[17]

Mechanical degradation:

Action: Compression, tension, shear forces.

Causes: A range of constraints during material installation, ageing due to load, air and water turbulences, snow pressure and bird damages.[18–20]

Result: Mechanical damages can activate or accelerate biodegradation process.[21]

- **Light degradation:**

Action: Energy transfer to create unstable states in various molecules.

Causes: Photoionization, radical generation, luminescence, fluorescence, thermal radiation.[22]

Result: Photodegradation can conduce to Norrish reactions, and/or crosslinking reactions, or oxidative processes (autoxidation).[23]

- **Thermal degradation:**

Action: At the melting temperature e.g. 159–178 °C for L-PLA, 137–169 °C for P(HB/HV) (poly[hydroxybutyrate-co-hydroxyvalerate]).[24]

Causes: The morphology of the macromolecular is influenced by temperature.

Result: The mobility and the volume of the polymeric chains are modified at their glass transition temperature (T_g) because the desorganisation of chains facilitate the accessibility to chemical and biological degradations e.g. 50 °C for L-PLA, 25 °C for PBT (poly[butylene terephtalate]), 45 °C for PBS (poly[butylene succinate]).[25]

- **Chemical degradation:**

Action: Oxidative degradation (sometimes in association with light degradation) and hydrolysis.[26]

Causes: Atmospheric pollutants and agrochemicals, atmospheric form of oxygen (i.e. O_2 or O_3).[21]

Result: The polymer containing hydrolysable covalent bonds as in groups ester, ether, anhydride, amide, carbamide (urea), ester amide (urethane), are split by H_2O. Disorganised molecular regions (amorphous domains) are more prone to degrade by H_2O or O_2/ O_3.[27]

1.5.2. Biotic exposure characteristics

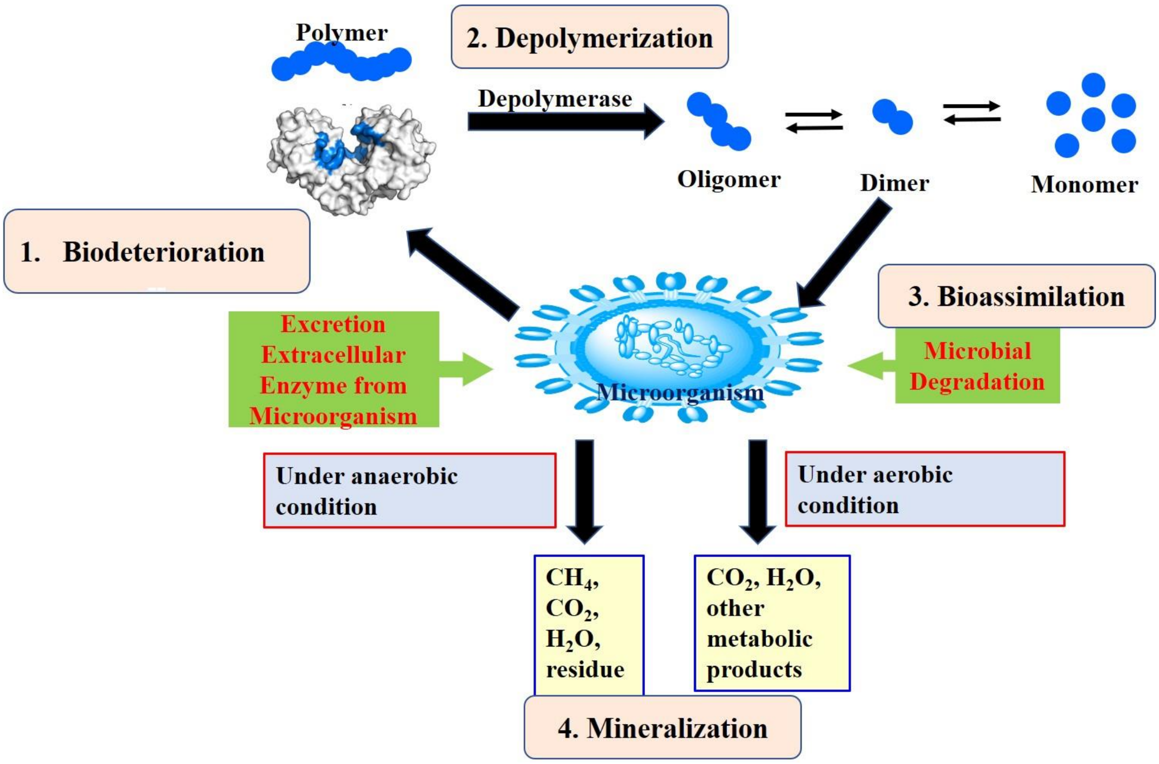
When the polymeric material is influenced by abiotic factors, it becomes weak or some bonds break or ready to break. As biological aspect, biodeterioration is mainly the result of the activity of microorganisms growing on the surface or/and inside a given material.[28,29]

- The specific environmental conditions (e.g. humidity, weather and atmospheric pollutants) and properties of polymers are important parameters for microbial development.[30]
- Enzymes can degrade specific bonds: protease degrades α-ester and amide bonds, poly(hydroxybutyrate)(PHB)-depolymerase β-ester bonds and lipase γ-ω bonds.[12b].
- Microorganisms belong to bacteria, protozoa, algae, fungi groups.[31]
- They can form consortia with a structured organisation called biofilms.[14]
- Recent studies show that atmospheric pollutants and organic dyes are potential sources of nutrients for some microorganisms.[32–35]

The whole process of enzyme-based biodegradation can be divided into four steps:

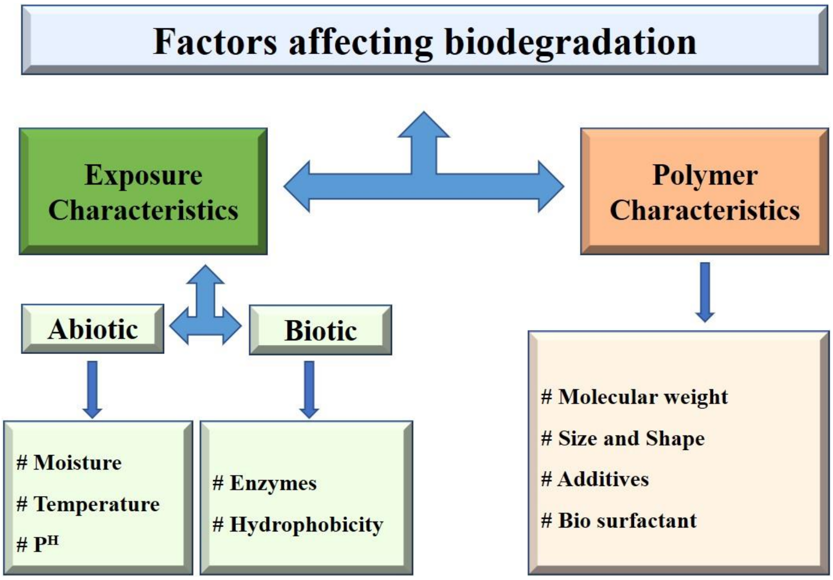
- **Biodeterioration:** It is the superficial degradation where microbes stick of with polymers, causes surface colonization and forms a microbial biofilm, where the polymeric material is fragmented into smaller particles.
- **Depolymerization:** The extracellular enzymes secreted by microorganisms of the biofilm, depolymerize the polymer chain into oligomers, dimers, or monomers. Under aerobic conditions, oxygen is used as an electron acceptor by the bacteria. Under anaerobic conditions, sulfate, nitrate, iron, carbon dioxide, and manganese are used as electron acceptors by anaerobic bacteria. Polymers are crushed down in the absence of oxygen by microorganisms.[36]

- **Assimilation:** It includes the uptake of these produced small molecules by the microbial cell to produce primary and secondary metabolites.
- **Mineralization**: The metabolites from the previous steps are mineralized and CO_2, CH_4, H_2O and N_2 are formed and released into the environment. Validate 3rd and 4th steps are very important to assure the real biodegradability of the products.[37]



Scheme 1-4. Schematic representation of the different steps involved in biodegradation

1.6. Factors affecting biodegradation:



Scheme 1-5. Factors affecting biodegradation

1.6.1. Exposure characteristics

Moisture:

- Microbes need certain demand of water for growth and multiplication. Hence, microbial action become swift in the presence of enough moisture and degradation becomes faster.[38]
- Moisture initiates more chain scission reactions which contributes the hydrolysis.

pH and temperature

- Changing in pH changes the acidic or basic conditions which modify the rate of hydrolysis reactions.

- Polymer with the higher melting point gives rise to less degradable product.
- Potential enzymatic degradability decreases with the increase in deviation from appropriate temperature.

Significance of enzymes:

- The nature and catalytic activity of enzymes vary depending upon the microbial species and even within the strains.
- Due to this specificity, different enzymes are known to degrade various polymer types.
- For example, *Bacillus spp.* and *Brevibacillus spp.* produce proteases.[39]
- Fungi degrades the lignin biologically. It contains Laccases acts as catalyst in an oxidation process to degrade aromatic and non-aromatic compounds.[40]

1.6.2. Polymer characteristics

Molecular weight :

- Degradability is lowered with the increase in molecular weight.
- It becomes convenient for microbial enzymes to attack a substrate low in molecular weight.[41]
- Higher molecular weight PCL (> 4000) was slowly degraded by lipase of a strain R. delemar as compared to low molecular weight polymer.[42]

Shape and size:

- The polymers having large surface area can be degraded quickly as compared to those with a small surface area.[12,43]

Additives and biosurfactants:

- Non-polymeric contaminants such as dyes (waste or debris of catalysts used for the polymerization and additives conversion products) or filler affect the degradation ability.
- Biosurfactants are amphiphilic compounds produced mostly on the living surfaces.Biosurfactants have specific functional groups which facilitate the biodegradation process allowing the activity under extreme temperature, pH, and salinity conditions.[44,45]

1.7. Polylactide- a sustainable polymer

Polylactide (PLA) is one of the most promising biodegradable polymers owing to its mechanical property profile, thermoplastic processibility and biological properties, such as biocompatibility and biodegradability. The demand for PLA is increasing day by day. PLA, alone accounts for 24% of the global production capacity for biodegradable polymers. The highest one is the starch blends (44%) and others including PBS and PBAT (23%) and PHAs (6%) are produced an industrial scale.[46] Due to expanding demand, the price of PLA commodities has dropped from ≈1,000 US$ per kg to a few US$ per kg during the last 20 years and are now at a price level similar to polystyrene.[47]

1.7.1. History

American chemist, Wallace Carothers discovered PLA In 1932, as a low molecular weight product by heating lactic acid in vacuum.[48] Later high molecular weight was developed and DuPont was awarded a patent for it.[49] The commercialization of the polymer for the bioabsorbable high strength suture VICRYL was taken up by Ethicon in 1972.[50] Commercial production of PLA by the new company, as a joint venture of Cargill and Dow chemical company started in 2002.

1.7.2. Source

PLA is commercially manufactured from renewable resources e.g. corn, potato, sugarcane, beetroot etc which are mainly starch and sugar source and from petrochemical feedstock.

PLA involves processing and polymerization of lactic acid (LA) which was first discovered in 1780 from sour milk and later polymerized by Carothers in 1932.[51] Lactic acid (2-hydroxypropionic acid), $HOCH_3CHCOOH$ is an organic acid which is a simple chiral molecule existing as two enantiomers, L- and D-lactic acid (Scheme 1-8), differing in their effect on polarized light. The L isomer rotates the plane of polarized light clockwise, the D isomer rotates it counterclockwise. The optically inactive D, L or meso form is an equimolar (racemic) mixture of D and L isomers.[52,53]

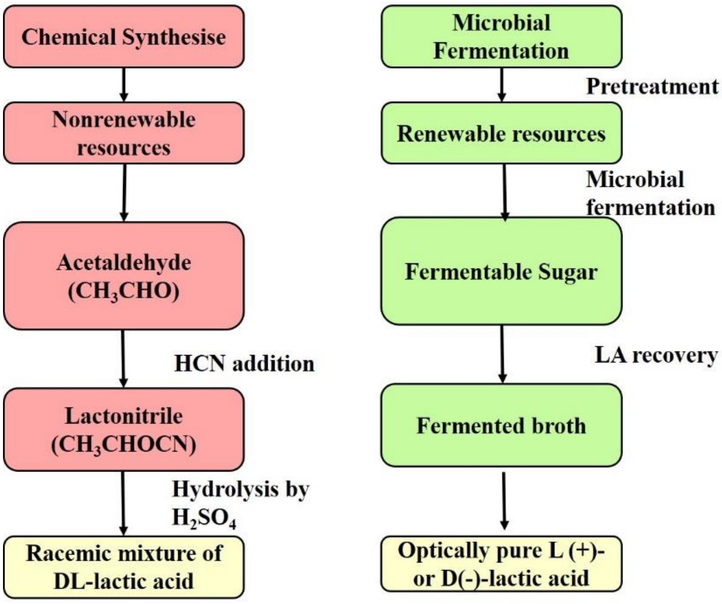
Naturally, lactic acid is produced in mammalian muscles during glycogenolysis and is involved in the Kreb's cycle through pyruvic acid and acetyl- CoA.[54]

Renewable source over petrochemical source:

LA produced by petrochemical route is the optically inactive racemic mixture of L and D enantiomers. [55] But the produced biological lactic acid, is exclusively (499.5%) the L-isomer.[52,53] So, due to

- limited petrochemical resource
- environmental impact and
- optical purity

production from renewable sources are suitable rather than petrochemical sources.[56]



Scheme 1-6. Graphical diagram of synthesis of LA

Recently, bacterial fermentation of glucose has led to a dramatic reduction in manufacturing cost of LA. Corn starch is converted into lactic acid by bacterial fermentation using an optimized strain of *Lactobacillus,* known to be the most popular route of LA production, now-a-days (Figure 1-3)

Stereoregularity:

Since, lactic acid is a chiral molecule, the stereochemistry of PLA may be tailored to fit requirements. It is the stereoregularity that makes poly(L-lactic acid) a highly crystalline polymer.[57] Monomer dyads in the PLA chain may contain identical stereocenters (L:L or D:D) or enantiomeric stereocenters (L/D). With special catalysts isotactic and syndiotactic content with different enantiomeric units can be controlled. Fully amorphous materials can be made by the inclusion of relatively high D content (42%) whereas highly crystalline material is obtained when the D content is low (0.2%).[56,58,59]

For synthesizing many products, crystallinity of PLA is a desirable attribute There is a strong relationship between the level of crystallinity developed in the polymer and the polymer melting point. Poly(L-lactide) has a practical melting point of 180°C. Introduction of meso lactide depresses the crystalline melting point to as low as 130°C.[52]

1.7.3. Advantages

Some major advantages of PLAs are mentioned below

(1) It can be produced from the lactide monomer by fermentation of a renewable agricultural source (corn);

(2) It can contribute to the fixation of significant quantities of greenhouse gas, carbon dioxide

(3) Significant energy saving

(4) Recyclability: PLA can be recycled back to lactic acid (a naturally occurring metabolite) by hydrolysis or alcoholysis.

(5) Compostable hybrid paper-plastic consumer packaging can be made

(6) Reduction of landfill volumes

(7) Improvement of America's farm economy and

(8) The most significant one is its ability to tailor physical properties through material modifications

1.7.4. Application

Now-a-days, PLA is being used not solely because of its degradability, nor because it is made from renewable resources; but also because can be made from used resources and it is being used because it functions very well and provides excellent properties. PLA has potential for use in a wide range of applications.

The commercial application fields can be divided into two types:

1) Plastic application[a]

a. Rigid thermoform	▪ Clear fresh fruit and vegetable clamshells ▪ Deli meat trays ▪ Opaque dairy (yogurt) containers ▪ Bakery, fresh herb, and candy containers ▪ Consumer displays and electronics packaging ▪ Disposable articles and cold drink cups
b. Biaxially oriented	▪ Candy twist and flow wrap films ▪ Envelope and display carton windows ▪ Lamination film ▪ Product (gift basket) overwrap ▪ Lidding stock ▪ Die cut labels ▪ Floral wrap, tapes ▪ Shrink sleeves, stand-up pouches ▪ Cake mix, cereal, and bread bags
c. Bottles	▪ Short shelf-life milk ▪ Edible oils ▪ Bottled water

[a] Ingeo TM plastic and IngeoTM fibers PLA (NatureWorks®) adapted from Vink and others (2004)

2) Fiber application[a]

a. Apparel	- Casual (sports-), active, and underwear fashion item
b. Nonwovens	- Wipes, hygiene products, diapers, shoe liners - automotive head and door liners - paper reinforcement
c. Furnishings	- Blankets and panel, upholstery, and decorative fabrics
d. Industrial carpets	- Agricultural and geotextiles - Residential/institutional broadloom and carpet tiles
c. Fiberfill	- Pillows, comforters, mattresses, duvets, and furniture.

[a] Ingeo^{TM} plastic and Ingeo^{TM} fibers PLA (NatureWorks®) adapted from Vink and others (2004)

Biomedical application

The bioresorbability and biocompatible properties of PLA in the human body has created a vast opportunity in the biomedical application. The most common synthetic biodegradable polymers in medical applications are the poly(a-hydroxyacid)s, including PGA, PLA and polydioxanone (PDS).[60] PLA has been used to manufacture tissue-engineering scaffolds, delivery system materials, covering membranes, bio-absorbable medical implants and sutures in dermatology and cosmetics.[61]

1.7.5. Properties

PLA has unique properties like good appearance, high mechanical strength, and low toxicity, good barrier properties, thermal properties and biodegradability, which have broadened its applications (Table 1).

Thermal properties:

Thermal properties of polymer is very important for different application which includes **:**

Glass transition temperature (T_g)

Physical characteristics such as density, heat capacity, and mechanical and rheological properties of PLA are dependent on its T_g. For amorphous PLA, the T_g is one of the most important parameters since dramatic changes in polymer chain mobility take place at T_g. For semicrystalline PLA, both T_g and T_m are important physical parameters for predicting PLA behavior.[41,62,63] The T_g value of PLA homopolymer is 50-65 °C.

Melting temperature (T_m)

The T_m and degree of crystallinity are depended on the molar mass, thermal history and purity of the polymer.[64]

Lower T_m (melting point) and Tg (glass transition temperature) than some conventional plastics, has made PLA better for heat-sealing and thermal processing.

Melting enthalpy (ΔH_m):

The melt enthalpy estimated for an enantiopure PLA of 100% crystallinity is 93 J/g, it is the value most often referred to in the literature although higher values (up to 148 J/g) also have been reported.[41]

Density

The density of amorphous and crystalline PLLA has been reported as 1.248 g/cm^3 and 1.290 g/cm^3, respectively.[41]

Solubility

- Generally, PLA is soluble in dioxane, acetonitrile, chloroform, methylene chloride, 1,1,2-trichloroethane and dichloroacetic acid.
- PLA is partially soluble in ethyl benzene, toluene, acetone and tetrahydrofuran when cold and but readily soluble when heated to boiling temperatures.
- PLA is insoluble in water, alcohols such as methanol, ethanol and propylene glycol and unsubstituted hydrocarbons (e.g. hexane and heptane). Crystalline PLA is not soluble in acetone, ethyl acetate or tetrahydrofuran.[64,65]

Table 1: Physical properties[66]

Physical Properties	**Units**	**PLA**	**PLLA**	**PDLLA**
T_m	°C	150-162	170-200	am
T_g	°C	45-60	55-65	50-60
ΔH_m (100%)	J/g	-	93, 135, 142, 203	-
ΔE_{td}[a)]	kg/mol	-	87-104	-
Density (ρ)	g/cm^3	1.21-1.25	1.24-1.30	1.25-1.27
WVTR[b)]	$g.m^{-2}.d^{-1}$	-	82-172	-
Tensile strength (σ)	MPa	21-60	15.5-150	27.6-50
Young's Modulus (E)	GPa	0.35-3.5	2.7-4.14	1-3.45
Elongation at break (ε)	%	2.5-6	3-10	2.0-10.0

[a)] Activation energy for thermal degradation estimated by thermogravimetry at a constant temperature. [b)] Water vapor transmission rate at 25 °C.

am- amorphous and thus no melting point

Mechanical properties:

PLAs typically exhibit high tensile strength and low elongation and have high modulus. PLA polymers range from amorphous glassy polymers with a glass transition of 60 °C to semicrystalline/highly crystalline products with crystalline melting points ranging from 130 to 180°C. Quiescent nucleated crystalline products are essentially opaque, whereas stress-induced crystalline materials are transparent. For tensile modulus and flexural modulus, PLA has the highest value and the lowest impact strength in comparison to PS, PP, and HDPE. The elongation at break is low and nearly 4% that is just higher than that of PS.[55] That is to say, PLA is a relatively brittle plastic but possesses good strength.

Crystallinity

Crystallinity influences many polymer properties including hardness, modulus, tensile strength, stiffness, crease point, and melting point. PLA crystals can grow in 3 structural positions called α, β and γ forms. They are characterized by different helix conformations and cell symmetries, which develop upon different thermal and/or mechanical treatments. The α form grows upon melt or cold crystallization, the β form develops upon mechanical stretching of the more stable α form, and the γ form, which only recently has been reported to develop on hexamethylbenzene substrate.[67] It is reported that the high rate of radial growth of the spherulites can be ascribed for high crystallization rate of PLA below 120 ◦C. (spherical semicrystalline regions inside nonbranched linear polymers).

Optical properties:

Optical properties of PLA are important where clarity is desirable. It was found that over the light wavelengths from 300 to 1300 nm, the index of refraction for PLA decreased from 1.499 to 1.448.[68]

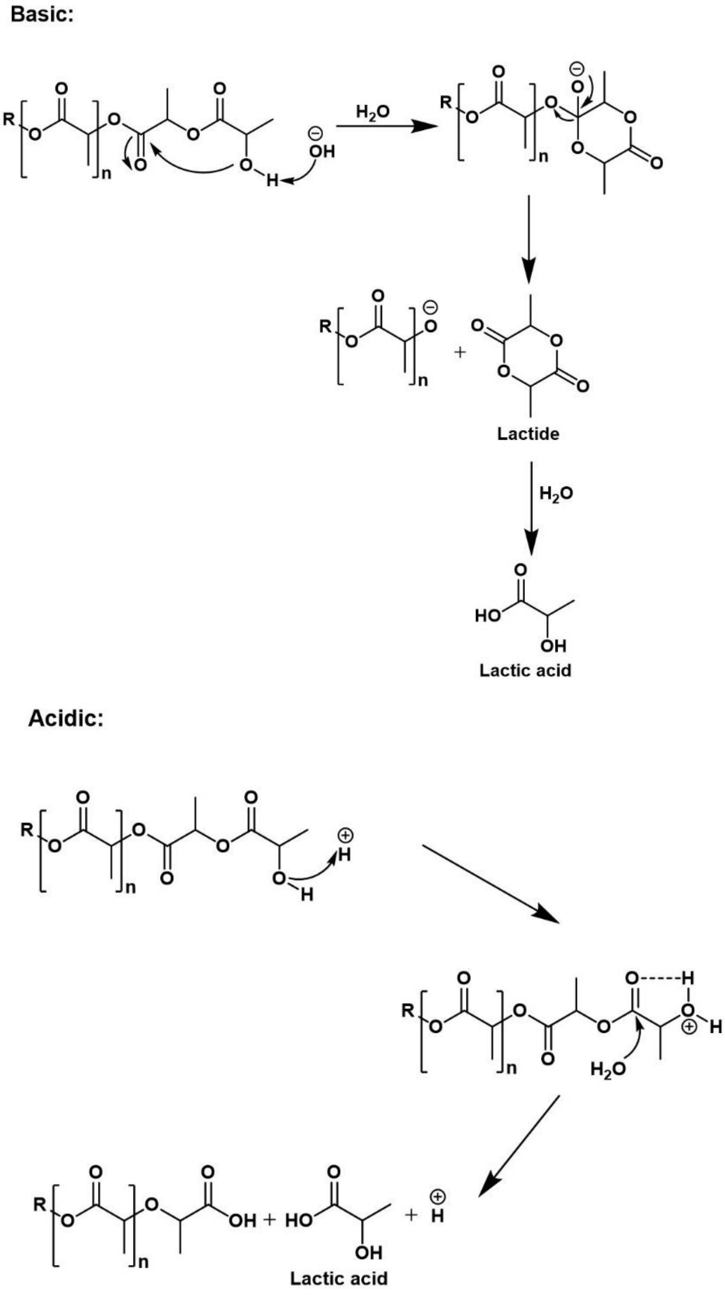
1.7.6. Degradation:

Thermal:

PLA is thermally unstable and exhibits rapid loss of molecular weight as the result of thermal treatment even under melting point. In some cases, the ester linkages of PLA tend to degrade during thermal processing or under hydrolytic conditions. It has been postulated that thermal degradation mainly occurs by random main-chain scissions. Several reactions such as hydrolysis, depolymerization, oxidative degradation, and inter- and intramolecular trans-esterification reactions to mononmer and oligomeric esters, are involved in the degradation process during thermal treatments.[64,69] The most typical product from the thermolysis of PLA is lactide, which can be applied to chemical recycling of PLA.

Biodegradation:

Hydrolysis is another pathway of PLA degradation. PLA polymers are aliphatic polyesters. The susceptibility to moisture observed by Carothers et al. in 1932 provides the primary pathway in the degradation of PLA. Cleavage of the ester linkages by absorbed water produces a successive reduction in molecular weight. PLA degrades by a dezipping mechanism under basic conditions to the intermediate dilactide, while under acidic conditions lactic acid is directly generated (Scheme 1-4). PLA is degraded by both lipase and protease. Protease degrades α-ester bonds while poly(hydroxybutyrate)(PHB)-depolymerase β-ester bonds and lipase γ-ω bonds of the polymer chain. In natural environments, these enzymes work as catalysts to increase the rate of hydrolysis degradation via surface erosion mechanism.



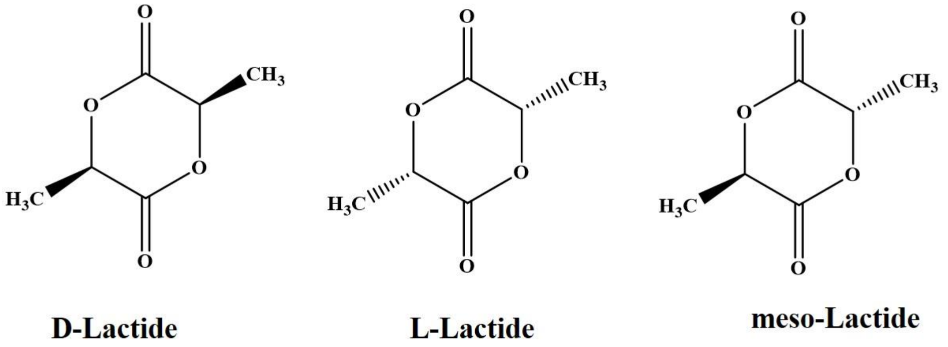
Scheme 1-7: PLA hydrolysis in basic and acid condition

The degradation of PLA can be observed by using different methods, which depict different stages in biodegradation:

- A change in the crystal structure of the polymer monitored by atomic force microscopy (AFM) proves biodeterioration.
- Depolymerization is indicated by a decrease of the molecular weight or a detection of generated lactic acid during the degradation.
- A weight loss of a polymer specimen can determine both complete mineralization, and the formation of water-soluble degradation products.
- In contrast, the detection of CO_2 is a clear indication of the amount of mineralization that has taken place.

1.7.7. Synthesis of PLA:

High molecular weight PLA can be synthesized by polymerization in two ways:



Scheme 1-8: D- lactic acid , L-lactide and meso-lactide

(1) Direct condensation : Solvent is used under high vacuum and temperatures for the removal of by product, water. Longer reaction time requires which produces PLLA with low molecular weight and poor mechanical properties.

(2) Ring-opening polymerization (ROP):

Lactide, a cyclic intermediate dimer is produced by solvent free thermolysis of PLA oligomers and purified by sublimation. PLA, with controlled molecular weight can be synthesized by using catalyst in ROP.[70,71] It is also possible to control the ratio and sequence of D- and L-lactic acid units in the final polymer by controlling the composition of the monomers, residence time and temperatures in combination with catalyst type and concentration. [52–54]

An initiator and a catalyst are important for ring opening polymerization. A polymerization catalyzed by stannous octoate scheme based on the insertion-coordination mechanism as shown in Figure 1.

(a) Stannous octoate as catalyst and a hydroxyl compound (alcohol) is required as an initiator

(b) Alcohol first reacts with stannous octoate to form a tin alkoxide bond by ligand exchange.

(c) Then, an exocyclic carbonyl oxygen of the lactide temporarily coordinates with the catalyst tin atom in the alkoxide form.

(d) Enhance the nucleophilicity of the initiator's alkoxide group and also the lactide carbonyl group's electrophilicity. Then the acyl-oxygen bond (between the carbonyl group and the endocyclic oxygen) of the lactide breaks.

(e) Open the lactide ring allowing insertion into the tin- oxygen bond (alkoxide) of the catalyst.

(f) Repeats addition of additional lactide molecules into the tin-oxygen bond propagates forming the polymer.[72,73]

Catalysts and initiators for synthesizing PLA:

The typical and transition metals such as tin[74], aluminum[75,76], zinc[74] titanium (IV) etc have been reported to catalyze lactide ROP. Lewis pairs such as $[\{NNO\}Zn]^+[B(C_6F_5)_4)]^-$ (Lewis acid) - pentamethylpiperidine (PMP, as Lewis base) can also promote the ROP of lactide efficiently. tin (II) 2-ethylhexanoate or stannous octoate ($Sn(Oct)_2$) has been widely used because of high reaction rates, solubility in the monomer melt and the ability to produce high molecular weight PLAs.[77]

1.7.8. Limitation

PLA has some drawbacks which limit its use in certain applications, mainly:

1) Poor toughness - PLA is a very brittle material with less than 10% elongation at break, the poor toughness limits its use in the applications that need plastic deformation at higher stress levels (e.g., screws and fracture fixation plates).[78]

2) Slow degradation rate - PLA degrades through the hydrolysis of backbone ester groups and the degradation rate depends on several factors. The slow degradation rate leads to a long in vivo lifetime, which could be up to years in some cases (mostly 3-5 years).[78]

3) Hydrophobicity - PLA is relatively hydrophobic, with a static water contact angle of approximately 80 °C. This results in low cell affinity and can elicit, in some cases.[79]

4) Lack of reactive side-chain groups - PLA is chemically inert with no reactive side-chain groups. So, its surface and bulk modification is a challenging task.

How to overcome the limitations of PLA

The major drawback of PLA (with respect to bulk- modification design goals) is its poor ductility and slow degradation rate. Several bulk-modification methods have been employed to improve mechanical properties mainly toughness. Different surface modification is also performed to impart and improve different properties.

Polycondensation copolymerization

Acid and hydroxyl groups present in the lactic acid make it feasible to copolymerize through polycondensation. Fukuzaki et al.[80] copolymerized l-lactic acid and ε-caprolactone without any catalyst to produce low molecular weight (Mw ~6.8–8.8 kDa) copolymers for biomedical applications. A key advantage that condensation copolymerization offers is control over polymer end groups. Lactic acid has been condensation copolymerized with diols or diacids in such a way that the resulting copolymer has either hydroxyl or acid end groups and a particular molecular weight. Although polycondensation produces low molec- ular weight polymers (Mw <10 kDa), this control over the end groups is a valuable tool in addition-type chemistry.[81] These low molecular weight lactic acid-based prepolymers have been further polymerized to produce higher molecular weight (Mw as high as 390kDa) biodegradable polyesters using a chain extender molecule such as diisocyanate to produce poly(ester-urethane)[82] or bis(amino-ether) to produce poly(ester-amide).

Ring-opening copolymerization (ROC):

ROC of L-lactide is a common approach for PLA copolymer synthesis, initiated with hydroxyl groups, such as alcohol or polyol.[83] The ring-opening lactide copolymerization route has been used extensively due to its precise chemistry control and resulting favorable copolymer properties.[64] The polymerization mechanism can be ionic, co-ordination, or free radical depending on the type of catalyst system involved.[64,84]

Grijpma and Pennings copolymerized L-lactide with D-lactide, glycolide, ε-caprolactone, and trimethylene carbonate using an ROC approach involving a stannous octoate ($Sn(Oct)_2$) catalyst. This copolymerization strategy resulted in controlled degradation, thermal, and mechanical properties. The amorphous structure is typically more favored in applications demanding higher (toughness and) degradation rate. In another example, poly(D,L-lactide) - co-poly(ε-caprolactone) elastic properties were modified by chemically crosslinking the copolymer network.

1.8. Thermoplastic elastomer:

Thermoplastic elastomers are biphasic polymeric materials, which exhibit elasticity at ambient temperatures and can be processed as plastics. It possess the combined properties of glassy or semi-crystalline thermoplastics and soft elastomers, and enable rubbery materials to be processed as thermoplastics.[85] They may be single macromolecules in which discrete thermoplastic segments capable of forming rigid nanoscale domains or channels are covalently bonded to rubbery segments that provide a soft matrix in which the rigid domains reside. Due to the covalent linkage between the chemically dissimilar segments, the rigid domains can form a three-dimensional network of physical crosslink sites.[86] The phase separation is the result of limited compatibility of the two phases involved. When the material is heated above the melting point or melting range of the hard phase, its melt becomes homogeneous and can be shaped into desired shapes and/or products. This feature makes TPEs ideally suited for high-throughput thermoplastic processes, such as melt extrusion and injection molding. Two important types of intrinsic TPEs are microphase- separated block (including graft) copolymers and segmented polyurethanes, although additional segmented copolymers are becoming increasingly available.

In order to qualify as a thermoplastic elastomer, a material must have these three essential characteristics:

1. The ability to be stretched to moderate elongations and, upon the removal of stress, return to something close to its original shape.

2. Processable as a melt at elevated temperature.

3. Absence of significant creep.

TPE became a commercial reality when thermoplastic polyurethane polymers became available in the 1950s. During the 1960s styrene block copolymer became available, and in the 1970s a wide range of TPEs came on the scene.

The advantages of TPE materials have the potential to be recyclable since they can be molded, extruded and reused like plastics, but they have typical elastic properties of rubbers which are not recyclable owing to their thermosetting characteristics. TPE also require little or no compounding, with no need to add reinforcing agents, stabilizers, cure systems.

The disadvantages of TPEs relative to conventional rubber or thermoset are relatively high cost of raw materials, general inability to load TPEs with low cost fillers such as carbon black therefore prevents TPEs from being used in automobiles tires due to their poor chemical and temperature resistance.

1.8.1. Block copolymers:

Since a copolymer consists of at least two types of constituent units (also structural units), copolymers can be classified based on how these units are arranged along the chain.[87] **Linear copolymers** consist of a single main chain, and include alternating copolymers, statistical copolymers and block copolymers. **Branched copolymers** consist of a single main chain with one or more polymeric side chains, and can be grafted, star shaped or have other architectures.

Block copolymers comprise two or more homopolymer subunits linked by covalent bonds. The union of the homopolymer subunits may require an intermediate non-repeating subunit, known as a **junction block**. **Diblock copolymers** have two distinct blocks; **triblock copolymers** have three. Technically, a block is a portion of a macromolecule, comprising many units, that has at least one feature which is not present in the adjacent portions. A possible sequence of repeat units A and B in a triblock copolymer might be ~A-A-A-A-A-A-A-B-B-B-B-B-B-B-A-A-A-A-A~.

Block polymers are an intriguing and useful class of materials due to the ability to precisely tune morphology and properties by changing parameters including composition, molecular weight, and block sequencing.

Great interest in block copolymer synthesis has been stimulated by their fascinating phase separation behavior. The bond between the two blocks prevents macroscopic phase separation, and so the dimensions of the polymer chains result instead in formation of nanoscale domains. These domains can be in the form of a range of morphologies including lamellar, bicontinuous, cylindrical, and spherical. By exploiting this self-assembly, block copolymers have found application in areas as diverse as lithography,[88] photonics,[89] electronics,[90] membranes,[91] and nanoreactors,[92] alongside more traditional applications such as surfactants[93] and thermoplastic elastomers[94] and thus are an important class of advanced material.

So far, diblock and triblock copolymers have been studied extensively in the literature and reported to improve different properties compared to homopolymers.

1.8.2. ABA type triblock copolymers with PLLA

ABA triblock copolymers comprising of the hard end block A and soft midblock B usually show the characteristics of thermoplastic elastomers (TPEs). Such TPEs have been extensively used in the industrial fields and consumer products such as footwear and pressure sensitive adhesives. In the ABA- type TPEs, the end block A is usually a semicrystalline thermoplastic or the thermoplastic with a high glass transition temperature (T_g), whereas the midblock B is a soft, rubbery and flexible polymer. To synthesize biodegradable ABA type TPE, hard segments PLLA can be the best option as biobased polymer because of its availability, biodegradability and mechanical properties.[95] When PLLA was applied to the hard segment of TPE, the material would possess at least partial biodegradability. The triblock copolymers with an aliphatic polyester as a soft segment and PLLA as a hard segment should be completely biodegradable.[96]

1.8.3. Reported works the TPEs with PLLA hard segments

Soft segments:

Some practically non-biodegradable soft midblocks such as polyisobutylene,[97] poly(dimethylsiloxane),[98] polybutadiene (PB),[99] polyisoprene (PI)[100] and poly(ethylene-*co*-butylene) (PEB),[101] can be introduced as soft segment of TPE with PLLA hard segment. Some variety of biodegradable or biobased midblocks such as poly(1,5-dioxepan-2-one),[72] poly(1,3-trimethylene carbonate),[102] poly(ε-caprolactone) (PCL),[103] have been conjugated with PLLAs in different works before. The use of cyclic difunctional soft block poly(1,5-dioxepan-2-one) gave rise to crystal structured TPE with high molecular weight and very low T_g value (< -30 °C).[72] TPEs using poly(1,3-trimethylene carbonate),[102] showed low creep rate. Using a dinuclear indium complex bearing N–N–O tridentate ancillary ligand, Mehrkhodavandi and co-workers synthesized PLLA-*b*-P(*rac*-*β*-BL)-*b*-PLLA (P(*rac*-*β*-BL) = poly(*rac*-*β*-butyrolactone)) and PLLA-*b*-P(*rac*-*β*-BL)-*b*-PDLA (PDLA = poly(D-lactide)).[104] In another work, pentablock copolymers, PLLA-*b*-PεDL-*b*-PEG-*b*-PεDL-*b*-PLLAs (PEG = poly(ethylene glycol)) was synthesized adopting PεDL which is derived from castor oil. [105] Diisocyanate caused the chain-extension of the pentablock copolyester to produce poly(ester-urethane), showing high elongation at break (~723%). Ring-opening polymerization was conducted by successively adding ε-caprolactone and DL-lactide using zinc metal as catalyst to synthesize PLLA-

b-PCL-*b*-PLLA block copolymer showing faster degradation than PCL homopolymer.[103]

With the aim of functional modifications, unsaturated aliphatic polyesters such as poly(2-butene-1,4-diyl malonate) (PBM).[106] and 2-butene-1,4-diol oligomers [107] had been conjugated with PLLA-containing ABA-type triblock copolymers, which provided unsaturated carbon-carbon double bonds.

1,3-Propanediol (1,3-PDO) based polyesters such as poly(1,3-propylene terephthalate) (PPT)[108] has been studied for several years from both academic and industrial perspectives, due to having excellent properties. Although PPT fibers present better resilience and higher stress recovery than poly(ethylene terephthalate) (PET) or poly(1,4-butylene terephthalate) (PBT).[109] PPT is not susceptible to biodegradation in natural environment similarly as PET and PBT. Poly(1,3-propylene adipate) showed very low T_g compared to poly(1,3-propylene succinate) and poly(1,3-propylene gluterate).[110] As a route to prepare tailor-made aliphatic copolyesters, poly(1,3-propylene succinate-*co*-1,4-butylene succinate) copolyesters have been extensively studied.[111–113] Poly(1,2-ethylene succinate-*co*-1,3-propylene succinate),[114] poly(caprolactone)-*block*-poly(1,3-propylene adipate)[115] and poly(1,3-propylene succinate-*co*-1,3-propylene adipate) (PPSA)[116,117] were also synthesized in some other works with improved properties compared to homopolymers. Debuissy and co-workers worked on fully biobased poly(propylene succinate-*ran*-propylene adipate) and revealed excellent thermal stability of the copolymers.[118]

In the previous study of our lab, poly(ε-CL-*r*-D,L-lactide) (poly(CL-*r*-DLLA)) was synthesized and used as soft segment of ABA type triblock copolymer which showed elongation at break up to approximately 2800%. But CL is not biobased material although PLLA-*b*-PCL-*b*-PLLA showed good biodegradability property.[103] Again, the T_g of poly(CL-*r*-DLLA) is mostly limited to higher than –40 °C. In this work the soft segment is replaced by largely biobased aliphatic polyesters made from diol and dicarboxylic acid from better biodegradability standpoint. Moreover, various polyesters having lower T_g than that of poly(CL-*r*-DLLA), desirable for soft segment, can be synthesized from the large variety of diol and different dicarboxylic acids to tune various properties of the copolymers.

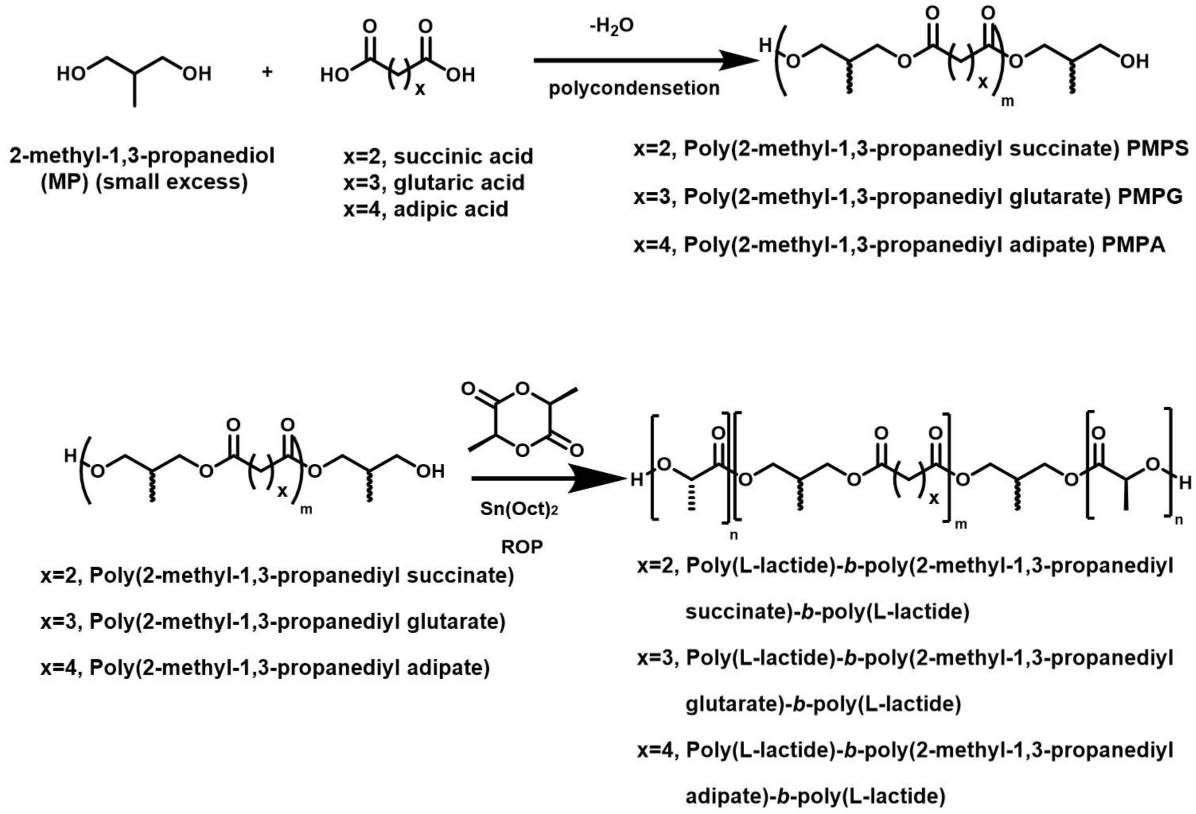
2.Aim of this work

Poly(L-lactide) (PLLA) is a biodegradable and bio renewable material which can be an appropriate alternative of petrochemical plastics due to its good thermo-mechanical properties. Among different strategies to improve the brittleness of PLLA, copolymerization with soft blocks has been extensively investigated as an effective method to overcome the brittleness of PLLA and to improve other properties of the resultant copolymers for further application.

Copolymerization of PLLA with a soft segment to improve the ductility of PLLA is one of the major objectives of this work.

To obtain the properties of thermoplastic elastomers (TPEs), ABA type triblock copolymer consisting of hard end blocks and a soft midblock can be synthesized where PLLA can act as hard block to render biodegradability to TPE. Soft biobased aliphatic polyesters are suitable for midblock of PLLA-containing TPE to play vital role to synthesize a fully biodegradable TPE because biobased PLLA works for partial biodegradability. As soft midblock, polyesters from diol and dicarboxylic acid with -OH groups at both ends can be used as macroinitiator for the lactide polymerization process to synthesize ABA type triblock copolymers. So, the development of novel fully biodegradable thermoplastic elastomers is another purpose of this work.

The methyl group from commercially available diol, 2-methyl-1,3-propanediol (MP), which has introduced into the polymer side chain, helps to inhibit the crystallization of polyester resins. In this work, 2-methyl-1,3-propanediol (MP) as diol have been chosen to synthesize soft aliphatic polyester midblocks by polycondensation reaction with some dicarboxylic acids using stannous octoate as catalyst. These polyesters with -OH end groups were used as macroinitiator for ring opening polymerization of L-lactide catalyzed by stannous octoate (Scheme 1-9).



Scheme 1-9. Aim of this work

In Chapter II, 2-methyl-1,3-propanediol (MP) and succinic acid were used to synthesize poly(2-methyl-1,3-propanediyl succinate) (PMPS) by two stage of polycondensation reaction. PMPS was used as macroinitiator for ROP of LLA in the presence of $Sn(Oct)_2$ as catalyst to synthesize poly(L-lactide)-poly(2-methyl-1,3-propanediyl succinate)-poly(L-lactide). The investigation focused the thermal and mechanical properties and biodegradability of the synthesized homopolymers and the triblock copolymers.

In Chapter III, poly(L-lactide)-*b*-poly(2-methyl-1,3-propanediyl glutarate)-*b*-poly(L-lactide) was synthesized as triblock thermoplastic elastomer. Poly(2-methyl-1,3-propanediyl glutarate) (PMPG) was used as soft segment of TPE. The molecular structure and thermal properties were determined. Tensile tests were also performed in case of copolymers. Biodegradability of the synthesized homo and copolymers were investigated.

In Chapter IV, ABA type triblock thermoplastic elastomer where A block is PLLA and B-soft block is poly(2-methyl-1,3-propanediyl adipate) (PMPA) were synthesized. The physical and mechanical properties and biodegradability in enzyme and seawater of the obtained polymers were measured.

In Chapter V, the results obtained in the previous chapters were summarized to compare the effect of the diacid on the physical properties and biodegradability of the triblock copolymers.

3.References

1 Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, *Cambridge Univ. Press. Cambridge, United Kingdom New York, NY, USA.*, , DOI:10.1260/095830507781076194.

2 I. World Meteorological Organization, UN Environment, in *UN Climate Action Summit 2019*, 2019.

3 T. Ahmed, M. Shahid, F. Azeem, I. Rasul, A. A. Shah, M. Noman, A. Hameed, N. Manzoor, I. Manzoor and S. Muhammad, *Environ. Sci. Pollut. Res.*, 2018, **25**, 7287–7298.

4 W. N. A. W. Muhamad, R. Othman, R. I. Shaharuddin and M. S. I. Hasni, *Adv. Environ. Biol.*, 2015, **9**, 8–13.

5 PlasticsEurope, in *PlasticsEurope Market Research Group (PEMRG) / Consultic Marketing & Industrieberatung GmbH*, 2015, p. 8.

6 S. K. Ghosh, S. Pal and S. Ray, *Environ. Sci. Pollut. Res. Int.*, 2013, **20**, 4339–4355.

7 T. Ahmed, M. Shahid, F. Azeem, I. Rasul, A. A. Shah, M. Noman, A.

Hameed, N. Manzoor, I. Manzoor and S. Muhammad, *Environ. Sci. Pollut. Res.*, 2018, 25, 7287–7298.

8 C. Vijaya and R. Mallikarjuna Reddy, *Indian J. Biotechnol.*, 2008, **7**, 235–239.

9 E. D. Comăniţă, R. M. Hlihor, C. Ghinea and M. Gavrilescu, *Environ. Eng. Manag. J.*, 2016, **15**, 675–685.

10 L. P. Wackett and C. D. Hershberger, *Biocatalysis and biodegradation : microbial transformation of organic compounds, ASM press in Washington (D.C)*, 2001.

11 T. Artham and M. Doble, *Macromol. Biosci.*, 2008, **8**, 14–24.

12 G. Kale, T. Kijchavengkul, R. Auras, M. Rubino, S. E. Selke and S. P. Singh, *Macromol. Biosci.*, 2007, **7**, 255–277.

13 S. K. Chattopadhyay, S. Singh, N. Pramanik, U. K. Niyogi, R. K. Khandal, R. Uppaluri and A. K. Ghoshal, *J. Appl. Polym. Sci.*, 2011, **121**, 2226–2232.

14 J. D. Gu, *Int. Biodeterior. Biodegrad.*, 2003, **52**, 69–91.

15 W. D. Luzier, *Proc. Natl. Acad. Sci. U. S. A.*, 1992, **89**, 839–842.

16 I. Kyrikou and D. Briassoulis, *J. Polym. Environ.*, 2007, **15**, 125–150.

17 I. Jakubowicz, N. Yarahmadi and H. Petersen, *Polym. Degrad. Stab.*, 2006, **91**, 1556–1562.

18 D. Briassoulis, *Biosyst. Eng.*, 2004, **87**, 209–223.

19 D. Briassoulis, *Polym. Degrad. Stab.*, 2006, **91**, 1256–1272.

20 D. Briassoulis, *Polym. Degrad. Stab.*, 2007, **92**, 1115–1132.

21 D. Briassoulis, *Polym. Degrad. Stab.*, 2005, **88**, 489–503.

22 M. Koutny, J. Lemaire and A.-M. Delort, *Chemosphere*, 2006, **64**, 1243–1252.

23 H. Nakamura, T. Nakamura, T. Noguchi and K. Imagawa, *Polym. Degrad. Stab.*, 2006, **91**, 740–746.

24 T. V. Ojumu, J. Yu and B. O. Solomon, *African J. Biotechnol.*, 2004, **3**, 18–24.

25 R. Iovino, R. Zullo, M. A. Rao, L. Cassar and L. Gianfreda, *Polym. Degrad. Stab.*, , DOI:10.1016/j.polymdegradstab.2007.10.011.

26 S. Bonhomme, A. Cuer, A. M. Delort, J. Lemaire, M. Sancelme and G. Scott, *Polym. Degrad. Stab.*, , DOI:10.1016/S0141-3910(03)00129-0.

27 F. Le Digabel and L. Avérous, *Carbohydr. Polym.*, 2006, **66**, 537–545.

28 H. J. Hueck, *Int. Biodeterior. Biodegradation*, 2001, **48**, 5–11.

29 J. H. Walsh, *Int. Biodeterior. Biodegradation*, 2001, **48**, 16–25.

30 A. Lugauskas, L. Levinskait≐ and D. Pečiulyt≐, *Int. Biodeterior. Biodegradation*, 2003, **52**, 233–242.

31 S. Wallström, E. Strömberg and S. Karlsson, *Polym. Test.*, 2005, **24**, 557–563.

32 E. Zanardini, P. Abbruscato, N. Ghedini, M. Realini and C. Sorlini, *Int. Biodeterior. Biodegradation*, 2000, **45**, 35–42.

33 Y. Nuhoglu, E. Oguz, H. Uslu, A. Ozbek, B. Ipekoglu, I. Ocak and İ. Hasenekoglu, *Sci. Total Environ.*, 2006, **364**, 272–283.

34 R. . Tharanathan, *Trends Food Sci. Technol.*, 2003, **14**, 71–78.

35 F. Faÿ, I. Linossier, J. J. Peron, V. Langlois and K. Vallée-Rehel, *Prog. Org. Coatings*, 2007, **60**, 194–206.

36 N. Priyanka and T. Archana, *J. Environ. Anal. Toxicol.*, , DOI:10.4172/2161-0525.1000111.

37 N. Lucas, C. Bienaime, C. Belloy, M. Queneudec, F. Silvestre and J. E. Nava-Saucedo, *Chemosphere*, 2008, **73**, 429–442.

38 K. L. G. Ho, A. L. Pometto and P. N. Hinz, *J. Environ. Polym. Degrad.*, 1999, **7**, 83–92.

39 A. Sivan, *Curr. Opin. Biotechnol.*, 2011, **22**, 422–426.

40 A. Mayer, *Phytochemistry*, 2002, **60**, 551–565.

41 R. Auras, B. Harte and S. Selke, *Macromol. Biosci.*, 2004, **4**, 835–864.

42 Y. Tokiwa, B. Calabia, C. Ugwu and S. Aiba, *Int. J. Mol. Sci.*, 2009, **10**, 3722–3742.

43 E. S. Stevens, *Biocycle*, 2003, **44**, 24–27.

44 F. Kawai, M. Watanabe, M. Shibata, S. Yokoyama and Y. Sudate, *Polym. Degrad. Stab.*, 2002, **76**, 129–135.

45 F. Kawai, M. Watanabe, M. Shibata, S. Yokoyama, Y. Sudate and S.

Hayashi, *Polym. Degrad. Stab.*, 2004, **86**, 105–114.

46 European Bioplastics, *Eur. Bioplastics*, 2017, 1–7.

47 D. K. Schneiderman and M. A. Hillmyer, *Macromolecules*, 2017, **50**, 3733–3749.

48 W. H. Carothers and J. A. Arvin, *J. Am. Chem. Soc.*, 1929, **51**, 2560–2570.

49 C. E. Lowe, *United states Pat. Off.*, 1954, 2–4.

50 G. PITT, M. GRATZL, G. KIMMEL, J. SURLES and A. SOHINDLER, *Biomaterials*, 1981, **2**, 215–220.

51 R. P. John, K. M. Nampoothiri and A. Pandey, *Appl. Microbiol. Biotechnol.*, 2007, **74**, 524–534.

52 J. Lunt, *Polym. Degrad. Stab.*, 1998, **59**, 145–152.

53 J. Lunt and A. L. Shafer, *J. Ind. Text.*, 2000, **29**, 191–205.

54 L. Fambri, A. Pegoretti, R. Fenner, S. D. Incardona and C. Migliaresi, *Polymer (Guildf).*, 1997, **38**, 79–85.

55 J. R. Dorgan, H. Lehermeier and M. Mang, *J. Polym. Environ.*, 2000, **8**, 1–9.

56 J. A. Cicero, J. R. Dorgan, J. Janzen, J. Garrett, J. Runt and J. S. Lin, *J. Appl. Polym. Sci.*, 2002, **86**, 2828–2838.

57 J. Huang, M. S. Lisowski, J. Runt, E. S. Hall, R. T. Kean, N. Buehler and J. S. Lin, *Macromolecules*, 1998, **31**, 2593–2599.

58 J. A. Cicero and J. R. Dorgan, *J. Polym. Environ.*, 2001, **9**, 1–10.

59 J. A. Cicero, J. R. Dorgan, J. Garrett, J. Runt and J. S. Lin, *J. Appl. Polym. Sci.*, 2002, **86**, 2839–2846.

60 J. C. Middleton and A. J. Tipton, *Biomaterials*, 2000, **21**, 2335–2346.

61 B. Gupta, N. Revagade and J. Hilborn, *Prog. Polym. Sci.*, 2007, **32**, 455–482.

62 H. Tsuji and K. Suzuyoshi, *Polym. Degrad. Stab.*, 2002, **75**, 347–355.

63 H. Tsuji and Y. Ikada, *Polym. Degrad. Stab.*, 2000, **67**, 179–189.

64 A. Södergård and M. Stolt, *Prog. Polym. Sci.*, 2002, **27**, 1123–1163.

65 A. J. R. Lasprilla, G. A. R. Martinez, B. H. Lunelli, A. L. Jardini and R. M. Filho, *Biotechnol. Adv.*, 2012, **30**, 321–328.

66 K. Van de Velde and P. Kiekens, *Polym. Test.*, 2002, **21**, 433–442.

67 M. L. Di Lorenzo, *Eur. Polym. J.*, 2005, **41**, 569–575.

68 M. H. Hutchinson, J. R. Dorgan, D. M. Knauss and S. B. Hait, *J. Polym. Environ.*, 2006, **14**, 119–124.

69 V. Taubner and R. Shishoo, *J. Appl. Polym. Sci.*, 2001, **79**, 2128–2135.

70 C. P. Radano, G. L. Baker and M. R. Smith, *J. Am. Chem. Soc.*, 2000, **122**, 1552–1553.

71 Hans R. Kricheldorf, I. Kreiser-Saunders, Cristian Jurgens and Dieter Wolter, *Macromolcular Symp.*, 1996, 85–102.

72 M. Ryner, K. Stridsberg, A. C. Albertsson, H. Von Schenck and M. Svensson, *Macromolecules*, 2001, **34**, 3877–3881.

73 K. Masutani and Y. Kimura, *RSC Polym. Chem. Ser.*, 2015, **12**, 3–36.

74 M. Fuchs, S. Schmitz, P. M. Schäfer, T. Secker, A. Metz, A. N. Ksiazkiewicz, A. Pich, P. Kögerler, K. Y. Monakhov and S. Herres-Pawlis, *Eur. Polym. J.*, 2020, **122**, 109302.

75 S. K. Roymuhury, D. Chakraborty and V. Ramkumar, *Eur. Polym. J.*, 2015, **70**, 203–214.

76 Y. Nakayama, S. Kosaka, K. Yamaguchi, G. Yamazaki, R. Tanaka and T. Shiono, *J. Polym. Sci. Part A Polym. Chem.*, 2017, **55**, 297–303.

77 G. Swift, *Acc. Chem. Res.*, 1993, **26**, 105–110.

78 R. M. Rasal, A. V. Janorkar and D. E. Hirt, *Prog. Polym. Sci.*, 2010, **35**, 338–356.

79 K. J. L. Burg, W. D. Holder, C. R. Culberson, R. J. Beiler, K. G. Greene, A. B. Loebsack, W. D. Roland, D. J. Mooney and C. R. Halberstadt, *J. Biomater. Sci. Polym. Ed.*, 1999, **10**, 147–161.

80 H. Fukuzaki, M. Yoshida, M. Asano, M. Kumakura, T. Mashimo, H. Yuasa, K. Imai and Y. Hidetoshi, *Polymer (Guildf).*, 1990, **31**, 2006–2014.

81 K. Hiltunen, M. Härkönen, J. V. Seppälä and T. Väänänen, *Macromolecules*, 1996, **29**, 8677–8682.

82 K. Hiltunen, J. V. Seppala and M. Harkonen, *J. Appl. Polym. Sci.*, 1997, **63**, 1091–1100.

83 F. Tasaka, Y. Ohya and T. Ouchi, *Macromol. Rapid Commun.*, 2001, **22**, 820–824.

84 S. Penczek, A. Duda, R. Szymanski and T. Biela, *Macromol. Symp.*, 2000, **153**, 1–15.

85 A. W. Birley, *Br. Polym. J.*, 1989, 21, 181.

86 D. Whelan, in *Brydson's Plastics Materials*, Elsevier, 2017, pp. 653–703.

87 A. D. Jenkins, R. F. T. Stepto, P. Kratochvíl and U. W. Suter, *Pure Appl. Chem.*, 1996, **68**, 2287–2311.

88 R. Ruiz, H. Kang, F. A. Detcheverry, E. Dobisz, D. S. Kercher, T. R. Albrecht, J. J. de Pablo and P. F. Nealey, *Science (80-.).*, 2008, **321**, 936–939.

89 C. Paquet and E. Kumacheva, *Mater. Today*, 2008, **11**, 48–56.

90 H.-C. Kim, S.-M. Park and W. D. Hinsberg, *Chem. Rev.*, 2010, **110**, 146–177.

91 M. T. Martello and M. A. Hillmyer, *Macromolecules*, 2011, **44**, 8537–8545.

92 A. Lu and R. K. O'Reilly, *Curr. Opin. Biotechnol.*, 2013, **24**, 639–645.

93 A. Muñoz-Bonilla, S. I. Ali, A. del Campo, M. Fernández-García, A. M. van Herk and J. P. A. Heuts, *Macromolecules*, 2011, **44**, 4282–4290.

94 Y. Luo, X. Wang, Y. Zhu, B.-G. Li and S. Zhu, *Macromolecules*, 2010, **43**, 7472–7481.

95 Y. Huang, R. Chang, L. Han, G. Shan, Y. Bao and P. Pan, *ACS Sustain. Chem. Eng.*, 2016, **4**, 121–128.

96 Y. Nakayama, K. Aihara, H. Yamanishi, H. Fukuoka, R. Tanaka, Z. Cai and T. Shiono, *J. Polym. Sci. Part A Polym. Chem.*, 2015, **53**, 489–495.

97 L. Sipos, M. Zsuga and G. Deák, *Macromol. Rapid Commun.*, 1995, **16**, 935–940.

98 S. Zhang, Z. Hou and K. E. Gonsalves, *J. Polym. Sci. Part A Polym. Chem.*, 1996, **34**, 2737–2742.

99 N.-Y. Kim, Y. S. Yun, J.-Y. Lee, C. Choochottiros, H. Pyo, I.-J. Chin and

H.-J. Jin, *Macromol. Res.*, 2011, **19**, 943–947.

100 E. M. Frick, A. S. Zalusky and M. A. Hillmyer, *Biomacromolecules*, 2003, **4**, 216–223.

101 Y. Huang, P. Pan, G. Shan and Y. Bao, *RSC Adv.*, 2014, **4**, 47965–47976.

102 Z. Zhang, D. W. Grijpma and J. Feijen, *Macromol. Chem. Phys.*, 2004, **205**, 867–875.

103 M. H. Huang, S. Li and M. Vert, *Polymer (Guildf).*, 2004, **45**, 8675–8681.

104 D. C. Aluthge, C. Xu, N. Othman, N. Noroozi, S. G. Hatzikiriakos and P. Mehrkhodavandi, *Macromolecules*, 2013, **46**, 3965–3974.

105 J. O. Lin, W. Chen, Z. Shen and J. Ling, *Macromolecules*, 2013, **46**, 7769–7776.

106 A. Höglund, S. Målberg and A. C. Albertsson, *Macromol. Biosci.*, 2012, **12**, 260–268.

107 M. K. Kiesewetter, J. A. Edward, H. Kim and R. M. Waymouth, *J. Am. Chem. Soc.*, 2011, **133**, 16390–16393.

108 R. M. Ho, K. Z. Ke and M. Chen, *Macromolecules*, 2000, **33**, 7529–7537.

109 I. M. Ward, M. A. Wilding and H. Brody, *J. Polym. Sci. Polym. Phys. Ed.*, 1976, **14**, 263–274.

110 D. N. Bikiaris, G. Z. Papageorgiou, D. J. Giliopoulos and C. A. Stergiou, *Macromol. Biosci.*, 2008, **8**, 728–740.

111 G. Z. Papageorgiou and D. N. Bikiaris, *Biomacromolecules*, , DOI:10.1021/bm0703113.

112 Y. Xu, J. Xu, B. Guo and X. Xie, *J. Polym. Sci. Part B Polym. Phys.*, 2007, **45**, 420–428.

113 Y. Xu, J. Xu, D. Liu, B. Guo and X. Xie, *J. Appl. Polym. Sci.*, 2008, **109**, 1881–1889.

114 G. Z. Papageorgiou and D. N. Bikiaris, *Macromol. Chem. Phys.*, 2009, **210**, 1408–1421.

115 S. G. Nanaki, K. Pantopoulos and D. N. Bikiaris, *Int. J. Nanomedicine*, 2011, **6**, 2981–2995.

116 S. S. Umare, A. S. Chandure and R. A. Pandey, *Polym. Degrad. Stab.*, 2007, **92**, 464–479.

117 M. Soccio, N. Lotti, L. Finelli, M. Gazzano and A. Munari, *Eur. Polym. J.*, 2009, **45**, 3236–3248.

118 T. Debuissy, E. Pollet and L. Avérous, *J. Polym. Sci. Part A Polym. Chem.*, 2017, **55**, 2738–2748.

Chapter II

Synthesis of Biodegradable Thermoplastic Elastomer from 2-methyl-1,3-propanediol, Succinic Acid and L-lactide

1. Introduction

Recently, one of the cardinal challenges in polymer research and technology is the replacement of petroleum-based monomers by renewable biobased ones as well as stepping towards sustainability.[1] Poly(L-lactide) (PLLA) is one of the auspicious biomass-based polymers, and its good biocompatibility, biodegradability, and mechanical strength have brought PLLA under the limelight of research interests. The tensile strength and elastic modulus of PLLA are comparable to poly(ethylene terephthalate) (PET).[2] As a rigid polymer PLLA possesses melting temperature (T_m) up to 180 °C and glass-transition temperature (T_g) at approximately 60 °C. However, its relatively brittle nature confines the use of PLLA to limited applications. Incorporation of soft segment in block copolymer with PLLA can be a worthier solution to improve the toughness of PLLA.[3] PLLA can be the ideal candidate to use as the hard end blocks of ABA type TPEs.[4]

Some variety of biodegradable or biobased midblocks such as poly(ε-decalactone) (PεDL)[5], poly(butylene succinate)[6] and poly(recenoleic acid)[7] have been conjugated with PLLAs in different works before. Hillmyer and co-workers reported PLLA-*b*-PM-*b*-PLLA (PM = polymenthide) and PLLA-*b*-PMCL-*b*-PLLA (PMCL = poly(6-methyl-ε-caprolactone)), which showed high elongation at break of 960% and ~1880%, respectively.[8,9] Among different aliphatic polyesters from diols and dicarboxylic acids, poly(ethylene succinate-*co*-butylene succinate),[10] poly(butylene succinate-*co*-butylene adipate)[11,12] and poly (butylene succinate-*co*-hexylene succinate)[13,14] have been used in TPEs as biodegradable polymers. In some work, incorporation of poly(butylene succinate) (PBS) soft block with PLLA hard segment could remarkably enhance the segmental flexibility of hard PLLA blocks and the assembled PLLA and PBS crystal structure coexisted also in TPE.[15] In our previous study, poly(*ε*-caprolactone-*stat*-D,L-lactide) (P(CL-*stat*-DLLA)) was adopted as a soft mid segment for PLLA-containing triblock copolymer which showed very high elongation at break up to 2800% with elastic properties.[16]

To widen the field of practical application, in this work, we used the amorphous hydroxy-telechelic polyester, poly(2-methyl-1,3-propanediyl succinate) (PMPS), made from the polycondensation of MP and SA, as the soft midblock, and synthesized a new kind of potentially biodegradable ABA type triblock copolymers consisting of PLLA hard end blocks via the ring-opening polymerization (ROP). MP is an inherently biodegradable diol and SA is derived from biomass which can be used as precursor in polyester synthesis. PMPS was reported to be amorphous, however, its detailed properties were not described.[17] The chemical structure, thermal and mechanical properties of the synthesized triblock copolymers as well as those of the PMPS and PLLA homopolymers were investigated and discussed. Their biodegradation behaviors were also investigated.

2. Experimental

2.1 General considerations

All the polymerization reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Varian system 500 spectrometer (500 and 125 MHz for ^{1}H and ^{13}C nuclei, respectively). Chemical shifts of ^{1}H and ^{13}C NMR in chloroform-d were calibrated by using the signals for the residual chloroform (δ = 7.26 ppm) and for chloroform-d (δ = 77.16 ppm), respectively. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) measurements on a Tosoh GPC system (HLC-8320) equipped with RI detector. GPC curves were calibrated using standard polystyrenes. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1.0 mL/min at 40 °C. The melting point (T_m), heat of fusion (ΔH_m) and glass transition temperature (T_g) of the polymers were measured on a differential scanning calorimetry (DSC) using a Seiko DSC 6220 apparatus. The heating rate was 10 °C/min in a nitrogen stream. Thermal history difference in the polymers was eliminated by first heating the specimen to 200 °C, cooling at

10°C/min to -100 °C, and then recording the second DSC scan at a heating rate of 10 °C/min. In this study, T_g was defined as the midpoint temperature between the extrapolated onset and ending of the DSC curve (Figure 1).

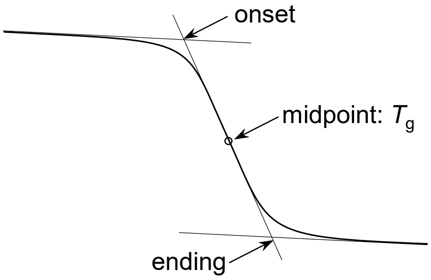
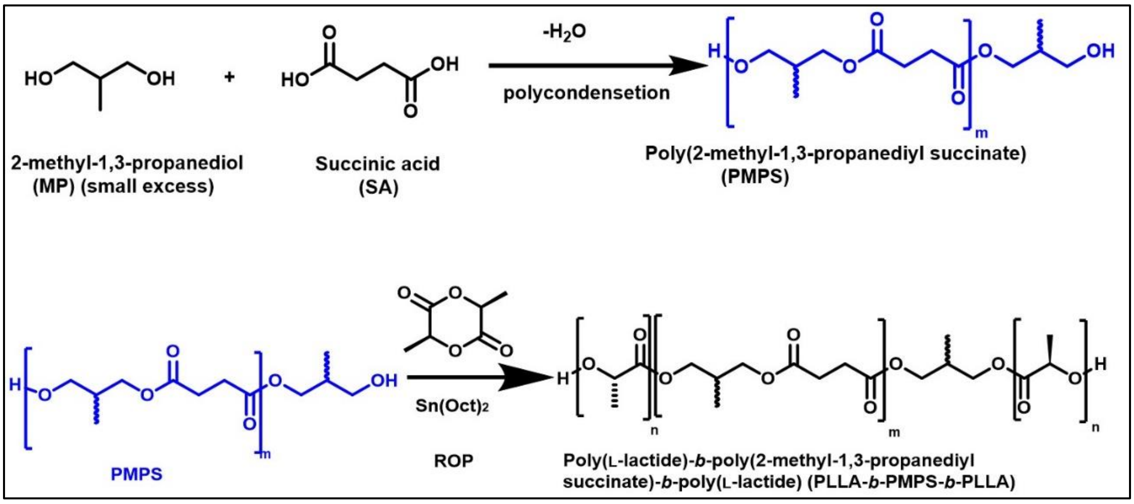


Figure 1. Schematic presentation of T_g on a DSC curve.

The measurement of decomposition temperature losing 5% of sample weight (T_{d5}) was carried out using SII Seiko EXSTAR 6000 TG/DTA 6300 instrument. The tensile tests of the obtained copolymer films were performed by using Shimadzu EZ-LX HS tensile testing machine at an elongation rate of 5 mm/min. Dumbbell-shaped specimens (width, 4 mm; gauge length, 10 mm; thickness, approximately 0.1 mm) were cut from the copolymer sample sheets for the tensile tests. Young's modulus values were determined as the slope of the straight line in the first 2 to 5% of elastic region of the stress-strain curve and the strength and strain at break were determined from the break point of the sample. Enzymatic biodegradation test of polymers was carried out using lipase PS and proteinase K enzymes where the total organic carbon concentration (TOC) was measured by TOC analyzer (Shimadzu TOC-VCSH). Biodegradation lab test in seawater was evaluated from determination of oxygen consumption using BOD tester (TAITEC, BOD200F) and was carried out at 27 °C with stirring for 28 days.



Scheme 1. Synthesis of PMPS macroinitiator and PLLA -*block*-PMPS-*block*-PLLA triblock copolymer

2.2 Materials

L-Lactide (LLA), succinic acid (SA) and 2-methyl-1,3-propanediol (MP) were purchased from Tokyo Chemical Industry. L-Lactide was sublimated under nitrogen before use. MP and SA were used without further purification. THF and toluene were purchased from Kanto Chemical and purified by distillation from sodium benzophenone under nitrogen prior to use. Both solvents were stored over sodium. Tin(II) 2-ethylhexanate ($Sn(Oct)_2$) was purchased from Sigma Aldrich and stored over activated molecular sieves (3A).

2.3 Synthesis of poly(2-methyl-1,3-propanediyl succinate) (PMPS)

A typical procedure: Hydroxy-telechelic PMPS was synthesized from MP (small excess) and SA using two-stage reaction of esterification and simple polycondensation processes using $Sn(Oct)_2$ as the catalyst (scheme 1). MP (20.3 g, 0.225 mol), SA (24.18 g, 0.205 mol) and catalyst $Sn(Oct)_2$ (0.04g, 0.1 mmol) were placed into a reactor. The mixture was heated slowly to 180 °C under N_2 gas atmosphere (1 atm). H_2O was collected using a trap device and esterification was continued for 1 hr. The 2nd stage of polycondensation process was done to remove the excess glycol and promote the chain extension. The temperature was gradually raised to prescribed temperature at pressure below 1.0 mmHg and kept for predetermined time. The synthesized polyester was dissolved in chloroform and then precipitated into 10 times larger amount of methanol. The precipitates were washed with methanol and finally dried in vacuo at room temperature for 2-3 days.

2.4 Polymerization of L-lactide using PMPS as a Macroinitiator

A typical procedure ($[L\text{-}LA]_0 : [PMPS]_0 = 100:1$): At first, 3 ml toluene and PMPS-2 (0.19 g, 1.7×10^{-2} mmol) were placed into a 10 ml Schlenk tube and the mixture was stirred at room temperature to dissolve it properly. Then LLA (0.25 g, 1.73mmol) was added to the solution of PMPS in toluene and dissolved at 100 °C. After dissolving properly, catalyst $Sn(Oct)_2$ (0.18 mg, 0.004 mmol) was injected into the Schlenk Tube. The polymerization was allowed to proceed at 100 °C for 24 hrs. After the polymerization, the reaction was quenched with acidic methanol and the mixture was poured into methanol. The precipitated triblock copolymer was collected by centrifugation and dried in vacuo at room temperature for 24 hrs (93 wt% yield).

2.5 Preparation of Films of the Triblock Copolymers

To prepare the film sample for measurements, PLLA-*b*-PMPS-*b*-PLLA (0.30 g) was dissolved in chloroform (4.0 mL). The solution was cast on a PTFE plate followed by evaporation of solvent under atmospheric pressure at room temperature for 3 days which was further dried in vacuo at room temperature for 1 day.

2.6 Biodegradability test of the polymers

Enzymatic biodegradation: Proteinase K was chosen as the hydrolytic catalyst because of its outstanding efficiency in enzymatic biodegradation of PLLA. Enzyme lipase PS was also used for this test due to its activity for the degradation of other aliphatic polyesters. 0.02 M Phosphate buffer (pH = 8.0) was used to prepare enzyme solution (1 mg/0.02 M buffer). A polymer sample (10 mg) was moved to a vial filled with 1 ml phosphate buffer and 1 ml H_2O that contained 0.5 ml of proteinase K or lipase PS solution. The reactions were carried out by shaking the vial at 45 °C for 6 hrs and 24 hrs separately. Finally, the solution was filtered and stored in the refrigerator (-30 °C) until TOC measurement.

Seawater biodegradation: Biodegradation lab test of polymers in seawater was evaluated from determination of oxygen consumption using BOD tester (TAITEC, BOD200F). Seawater was taken at the shoreline from the sea surface of Osaka South Port area with bucket. The seawater was used within one or two days. Typically, 30 mg of polymer specimens was added into 250 mL BOD testing bottle each and then 200mL supernatant of seawater was added. Evolved carbon dioxide (CO_2) was removed by calcium hydroxide from the BOD closed system. The biodegradation test was carried out at 27 °C with stirring for 1 month. The observed O_2 consumption volume was corrected by subtraction to O_2 consumption volume of the control. The theoretical O_2 consumption volume was calculated according to the structure formula of polymers that degraded products are completely mineralized to CO_2. Biodegradation (%) of copolymers was calculated according to following equation:

% Biodegradation = (Absorbed O_2 consumption volume/ theoretical O_2 consumption volume) x 100

3. Result and Discussion

3.1 Preparation of PMPS-diols:

A polyester PMPS was synthesized by a two stage of polycondensation process from MP and SA in bulk. MP and SA were first dehydrolyzed using excess diol at a MP to SA feed ratio of 1.1:1 at 180 °C under N_2 (1atm) to obtain a mixture of PMPS oligomers having MP units at both ends. Then the mixture of the oligomers was subjected to the second step of the polycondensation at 180 °C under reduced pressure for different time using $Sn(Oct)_2$ as a catalyst to obtain PMPS-diol samples, for the purpose of judging the appropriate polymerization time to use it as a soft segment in TPE (Table1).

The PMPSs were obtained in >90% yields as viscous liquids. Successful synthesis of PMPS was verified by ^{1}NMR and GPC analysis. A typical 500 MHz ^{1}H-NMR spectrum of a PMPS-diol is shown in figure 2. The signals for PMPS repeating units appeared at 0.99, 2.17, 2.63 and 4.02 ppm.[18,19] In addition, the resonance peak of the methylene proton linked to the terminal hydroxyl group was observed at 3.52 ppm in 2 (peak E of PMPS). So, PMPS has the -OH terminated structure similar to that of the hydroxyl-terminated structure of PPS-diols reported previously.

Table 1. Synthesis of PMPS-diol by two stage polycondensation of MP and SA[a]

Sample	Time[min] (2nd stage)	M_n [b]($\times 10^3$) [g mol^{-1}]	M_w/M_n [b]	T_g [c] [°C]	T_{d5} [d] [°C]
PMPS-1	120	19	1.7	-24.1	360
PMPS-2	100	11	1.6	-27.7	353
PMPS-3	50	6	1.7	-44.2	320

[a] Bulk polycondensation, cat.= $Sn(Oct)_2$ (0.1mmol), feed ratio $[MP]_0 : [SA]_0 : [Cat.]$ = 1.1 : 1 : 0.0005, temp (1st stage)= 180 °C, temp (2nd stage) = 180 °C, time (1st stage) = 1 hr, pressure = 1 atm (1st stage), reduced pressure = below 1.0 mmHg (2nd stage), mechanical stirrer = 300 rpm. [b] Determined by GPC in THF calibrated with standard polystyrene. [c] Determined with DSC 2nd heating scan. [d] Decomposition temperature losing 5% of sample weight.

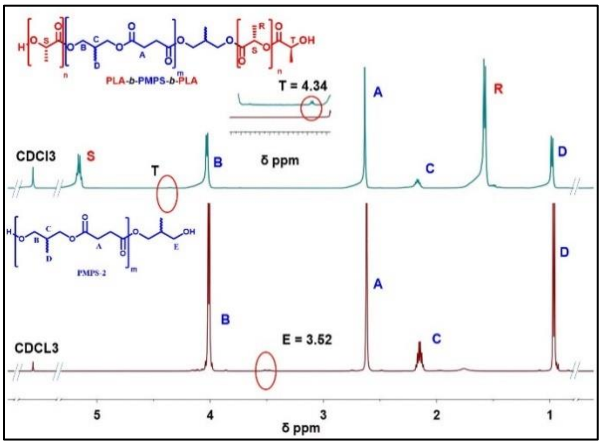


Figure 2. ^{1}H-NMR spectrum of PMPS-2 and PLLA-*b*-PMPS-*b*-PLLA (TPE1) ($CDCl_3$, r.t., 500 MHz).

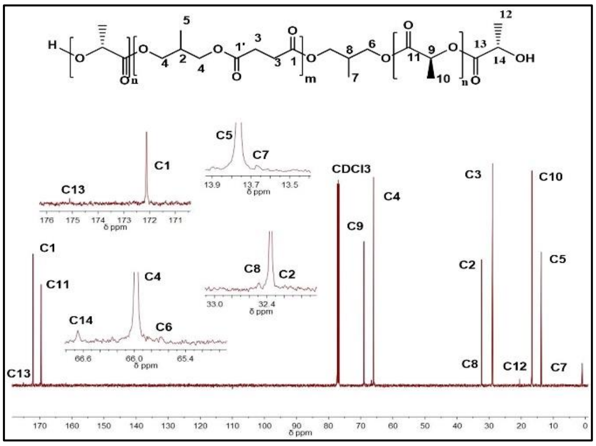


Figure 3. ^{13}C-NMR spectrum of PLLA-*b*-PMPS-*b*-PLLA (TPE1) ($CDCl_3$, r.t., 500 MHz).

In a 125 MHz ^{13}C-NMR spectrum of the macroinitiator PMPS (Figure 4), three resonances at 65.96 (C4), 32.34 (C2) and 13.74 (C5) ppm are associated with carbons derived from the MP monomer. The chemical shifts of the ethylene carbons and the carbonyl carbons of the succinic moiety are 28.91 (C3) and 172.1 (C1) ppm, respectively.

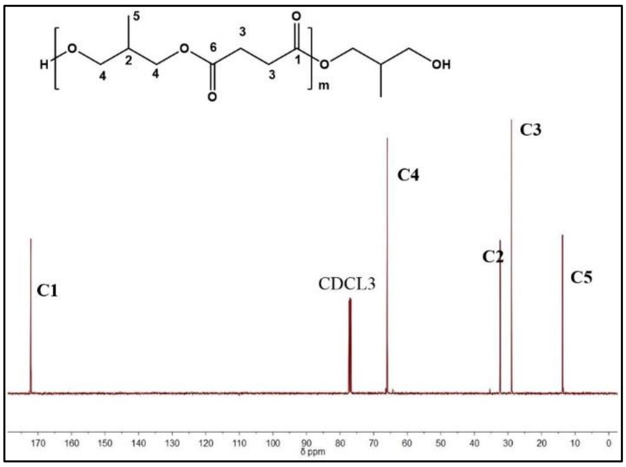


Figure 4. ^{13}C-NMR spectrum of PMPS-2.

The PMPS-diol samples obtained from polycondensation under vaccum condition for 120, 100 and 50 mins are named as PMPS-1, PMPS-2 and PMPS-3, respectively. The M_n of these PMPS-diols was controlled by the polycondensation time. The prepared each PMPS-diol exhibits a single elution peak in the GPC curves (Figure 5) showing increasing number average molecular weight (M_n) with time. All their polydispersities (M_w/M_n) were nearly constant (1.7). Figure 6 shows the DSC profiles of the obtained PMPSs where none of them exhibited melting transition indicating their amorphous nature. The glass transition temperatures of the obtained PMPSs were below -24.1 °C and tended to rise with increasing their molecular weight. The thermal decomposition temperature of the PMPS ranges from 320 to 360 °C. The amorphous nature and low T_g of PMPS is desirable as a soft segment of TPE, while the higher molecular weight of the macroinitiator can contribute to higher molecular weight of the resulting TPE. Thus, it is decided to use PMPS-2 as soft block of the following PLLA-*b*-PMPS-*b*-PLLA triblock copolymers having relatively low T_g and high M_n.

3.2 Synthesis of ABA triblock copolymers

LLA was polymerized to synthesize PLLA-*b*-PMPS-*b*-PLLA triblock copolymers using the PMPS-2 as the macroinitiator at different feed ratio of LLA and PMPS (Table 2) in the presence of $Sn(Oct)_2$ as a catalyst. Copolymer composition and molecular weight were controlled by changing the lactide-to-macroinitiator feed ratio with keeping relatively narrow molecular weight distribution. As shown in Table 2, the ROP of lactide showed relatively high yields. The characteristic resonances of PLLA block are observed at 1.58 (peak R) and 5.16 (peak S) ppm in the ^{1}H NMR spectra of the products (Figure 2), assigned to the methyl and methine protons of PLLA blocks, respectively, in addition to those of PMPS block.[20]

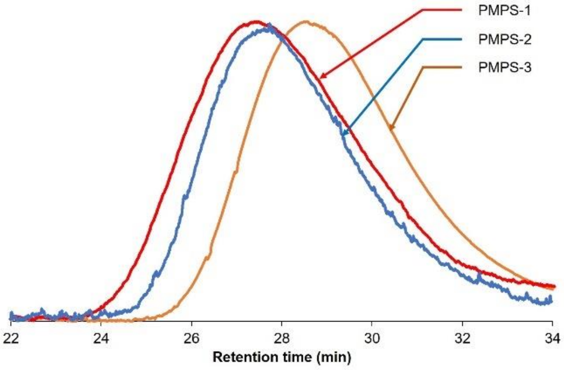


Figure 5. GPC curve of PMPS-1, PMPS-2 and PMPS-3.

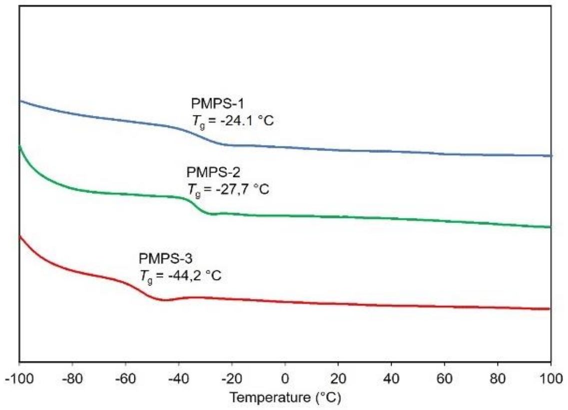


Figure 6. DSC curves of PMPS collected upon cooling and heating. The cooling and heating rate at 10 °C/min.

The signal due to the hydroxyl terminal of the original PMPS-diol shown at 3.52 (peak E) has completely been replaced by the signal of the hydroxyl terminal of PLLA detected at 4.34 ppm (peak T) (Figure 2) in the ^{1}H NMR spectra of the products. These results are consistent with the expected triblock structure of PLLA-*b*-PMPS-*b*-PLLA in which the PLLA chains have grown from the hydroxyl tails of the PMPS-diol. Figure 3 represents a 125 MHz ^{13}C-NMR spectrum of the PLLA-*b*-PMPS-*b*-PLLA. Here, the expanded carbonyl spectra showed signal C1 (δ = 172.0 ppm) derived from the PMPS repeating units and signal C11 (δ = 169.6 ppm) derived from the PLLA repeating units, and no other signals due to the scrambled sequences (e.g., lactyl-succinate) that could be formed by the transesterification reaction. It should be noted that signal C13 (δ = 175.1 ppm) is assigned to carboxyl carbon of the terminal lactate units. Here, signal C13 is correlated with the α-CH signal C14 (δ = 66.66 ppm) and β-CH_3 signal C12 (δ = 20.50 ppm).[21]

Table 2. The ROP of L-LA catalyzed by $Sn(Oct)_2$ using PMPS-2 as macroinitiator [a]

Sample	Feed Ratio $[LA]_0$:[PMPS-2]	Yield [%]	M_n[b] (×10^3) [g mol^{-1}]	M_{NMR}[c] (×10^3) [g mol^{-1}]	M_w/M_n[b]	F_{PLLA}[c] [mol%]
TPE1	100:1	93	23	24	1.3	55
TPE2	75:1	92	21	21	1.3	47
TPE3	50:1	93	17	18	1.3	39
TPE4	25:1	91	15	15	1.4	27
PLLA-1	50:1	97	5	5.7	1.4	100
PLLA-2	25:1	97	3	3.1	1.4	100

[a] PMPS-2 (M_n = 10.8×10^3 $gmol^{-1}$, M_w/M_n = 1.61, T_g = -27.7 °C), Cat = $Sn(Oct)_2$ (4×10^{-3} mmol) , temp = 100 °C, time = 24 hrs. [b] Determined by GPC in THF calibrated with standard polystyrene. [c] Determined by ^{1}H-NMR analysis.

Figure 7 shows the typical GPC curves of the PLLA-*b*-PMPS-*b*-PLLA and the PMPS-diol used as the macroinitiator. The shift of the curves to the higher molecular weight region is evident in the copolymers in comparison with that of the macroinitiator, suggesting that the block copolymers have efficiently been formed without involving residual PMPS-diol. As shown in the GPC curves (Figure 7), the elution time of the copolymers decreased with increasing the lactide/PMPS feed ratio in ROP, indicating the increase of molecular weight.

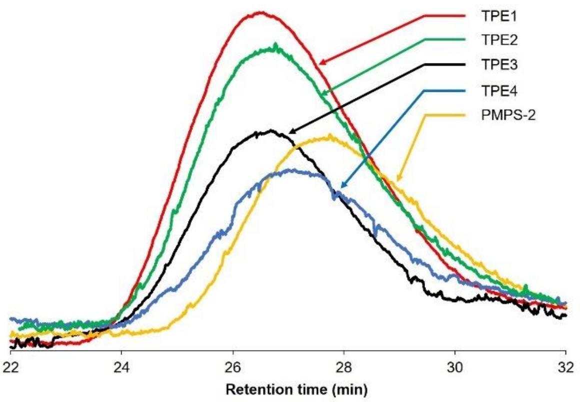


Figure 7. GPC curves of PLLA-*b*-PMPS-*b*-PLLA samples (TPE 1,2,3 and 4) and PMPS-2.

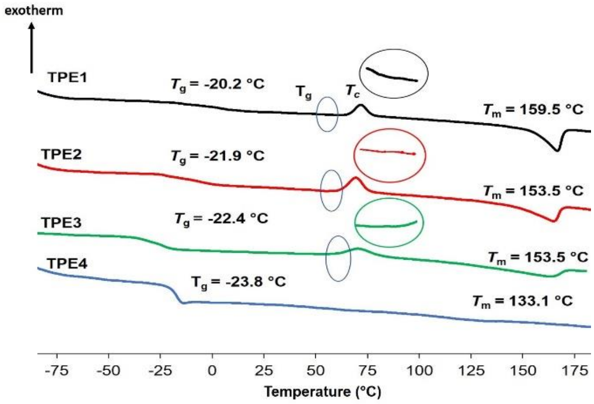


Figure 8. DSC curves of PLLA-*b*-PMPS-*b*-PLLA samples (TPE 1,2,3 and 4) collected in the 2nd heating scan. Both the cooling and heating rates are 10 °C/min.

The dispersity of the copolymer's ranges from 1.3 to 1.4. Molecular weights of the PLLA-*b*-PMPS-*b*-PLLAs were also estimated from their NMR spectra by comparing NMR peak intensities of PLLA and PMPS main chains with that of the end group. The molecular weights derived from GPC ($M_{n,GPC}$) and NMR ($M_{n,NMR}$) were consistent and both increase with increasing the lactide/PMPS feed ratio (Table 2). All these NMR and GPC results demonstrate the successful synthesis of PLLA-*b*-PMPS-*b*-PLLA triblock copolymers with controlled PLLA block length. Homopolymers of LLA, PLLA-1 and PLLA-2, with similar chain length to those of the PLLA segments in TPE-1 and TPE-3, respectively, were also prepared using benzyl alcohol as an initiator instead of PMPS-2 for comparison.

3.3 Thermal Properties of PLLA-*b*-PMPS-*b*-PLLA

Thermal properties (Table 3) and crystallization behavior of PLLA-*b*-PMPS-*b*-PLLA triblock copolymers were examined by DSC analysis (Figure 8). The T_g values of the triblock copolymers were somewhat higher than that of the PMPS-2 (-27.7 °C) while still remained below -20 °C. Also, high content of PLLA resulted in another glass transition at around 60 °C from PLLA segment due to phase separation.

Table 3. Thermal properties of the copolymers (PLLA-*b*-PMPS-*b*-PLLA)

Sample	F_{PLLA} [mole%]	T_g[a] [°C]	T_c[a] [°C]	ΔH_c[a] [J/g]	T_m[a] [°C]	ΔH_m[a] [J/g]	T_{d5}[b] [°C]
TPE1	55	-20.2, 59.7	65.8	-3.00	159.5	6.52	220
TPE2	47	-21.9, 60.7	64.5	-3.03	153.5	6.56	221
TPE3	39	-22.4, 62.4	63.9	-2.87	146.8	3.34	224
TPE4	27	-23.8	-	-	133.1	0.60	252

[a] Determined by DSC at 2nd heating scan. [b] Decomposition temperature losing 5% of sample weight.

Figure 9 shows the plot of T_g of the block copolymers as a function of the PLLA content, exhibiting a clear linear relationship. The copolymers consisting of longer PLLA blocks (TPE1,2,3) showed both crystallization and melting temperatures, while the copolymer with short PLLA blocks (TPE4) did not show clear T_c. T_c values of TPE1-3 are relatively low due to the presence of soft segment[19] and gradually raised with the increase of PLLA content. The T_m and ΔH_m of the copolymers are also plotted as a function of the PLLA contents in Figure 10.

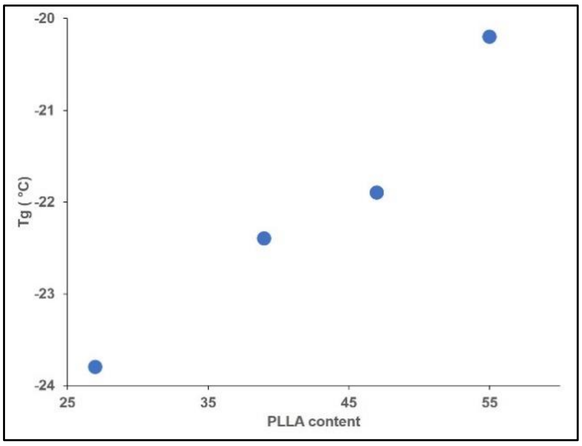


Figure 9. T_g vs PLLA content of copolymers.

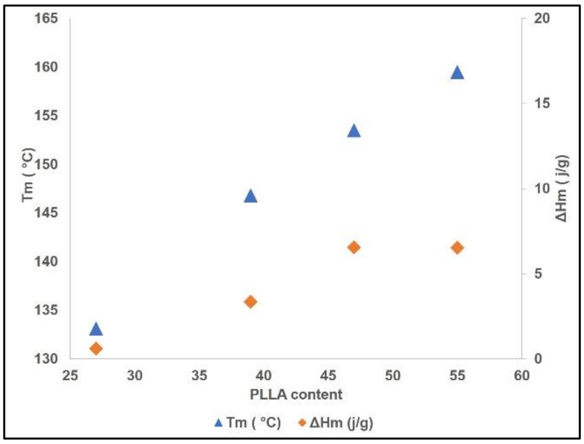


Figure 10. T_m, ΔH_m vs PLLA content of copolymers.

It is indicated that T_m changes from 133.1 to 159.5 °C, while ΔH_m changes from 0.6 to 6.5 J/g and that both T_m and ΔH_m have also linear relationship with the PLLA content, indicating that the crystallization of PLLA was not hindered much by the presence of PMPS block. Thermal degradation of these polymers was monitored by TG/DTA analysis (Figure 11). The T_{d5} values for all the copolymers were rising with decreasing PLLA-contents and lower than that of PMPS macroinitiator. The two different zones in the curve is very prominent which represents the presence of two different blocks in the copolymers. The first degradation stage started at around 220 °C can be attributed to the degradation of PLLA block and the weight loss at the first stage increased with increasing PLLA contents in the triblock copolymers. Relatively low thermal stabilities of the triblock copolymers could come from residual Sn catalyst and could be improved by end group modification. The second degradation stage started at over 300 °C should come from the degradation of the PMPS block.

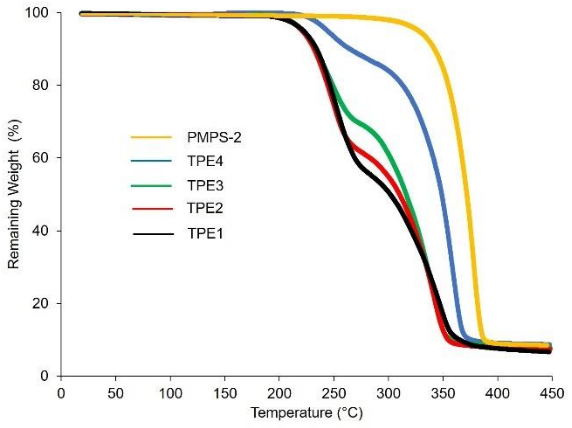


Figure 11. TG/DTA curves of PLLA-*b*-PMPS-*b*-PLLAs (TPE1,2,3 and 4) and PMPS-2

3.4 Mechanical properties of the copolymer films

The copolymer samples were casted into thin films (thickness: approximately 0.1 mm) from $CHCl_3$ solution and cut into a nonstandard dumbbell shape for the measurement of mechanical properties by tensile test (Table 4).

Because the pure soft segment PMPS was a viscous oily material and could not be shaped into self-standing film, its mechanical properties could not be measured by tensile test.

Figure 12 shows typical stress–strain curves of the copolymer films. The copolymer films showed a yielding point as the ordinary plastic materials. They also behaved as flexible polymers and exhibited much lower Young Modulus and significantly higher elongation at breaks than those of PLLA.[20]

Table 4. Mechanical properties of copolymers

Sample	F_{PLLA}[a] [mol%]	**Young modulus [MPa]**	**Strength[*] [MPa]**	**Elongation at break (%)**
TPE1	55	114.0 ± 3.4	6.16	16.2
TPE2	47	84.6 ± 3.1	3.58	62.4
TPE3	39	71.05 ± 10.9	2.19	16.7
TPE4	27	2.8 ± 0.8	0.37	23.1

[a] Calculated from ^{1}H NMR. *strength is defined as the stress at the strain at break. Determined by tensile tester with elongation rate 3.5 mm/min. Number of measurement times 3.

In particular, the elongation of the film reached around 62.4%. Therefore, the brittleness of PLLA can be effectively improved by introducing PMPS as soft segment. The tensile strength and modulus of the copolymers increased with increasing the chain length of the PLLA block. The dependences of Young modulus and strength on the PLLA contents of the copolymer films are compared in Figure 13. Each series showed almost linear relationship with the

PLLA content. Physical crosslinking should contribute to increase the tensile modulus and strength values with length of the hard segment.

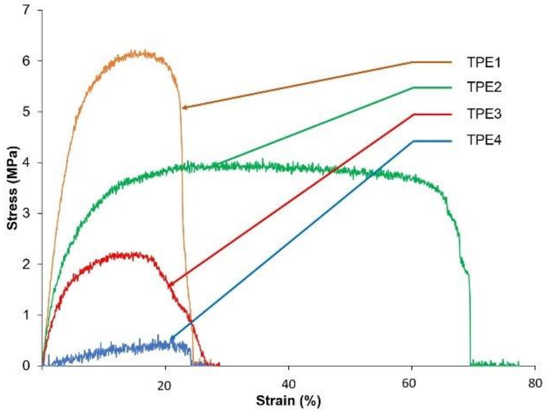


Figure 12. Comparison of stress-strain curves of the copolymer films of TPE1, 2, 3 and 4.

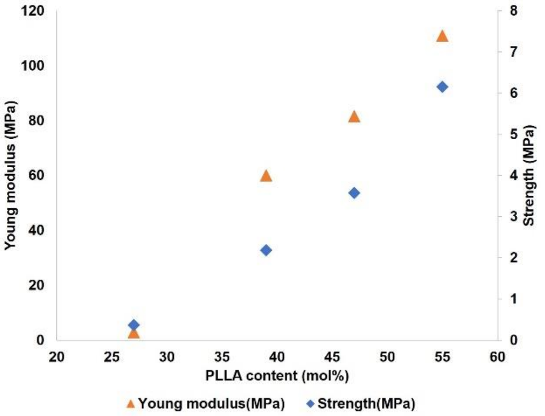
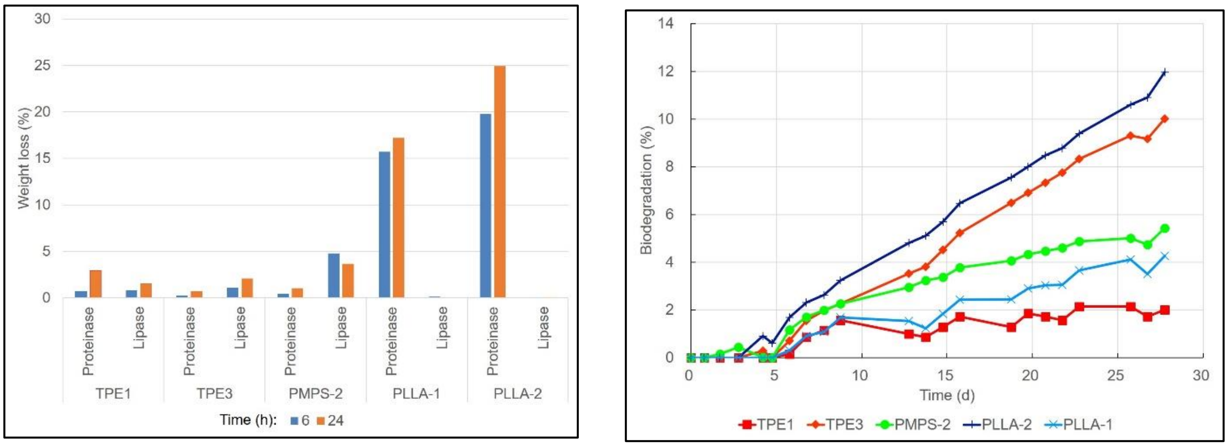


Figure 13. Changes in strength (MPa) (z-axis) and Young Modulus (MPa) (y-axis) of the copolymer films as the function of the PLLA content (x-axis).

3.5 Biodegradability of the synthesized copolymers

To the best of our knowledge, the biodegradability of PMPS has not been reported, while PLLA is well known as a biodegradable polymer. In order to evaluate the biodegradability of the obtained polymers, their biodegradation tests were performed using enzymes and seawater. The enzymatic degradation behaviors of the copolymers were monitored in view of weight loss (%). Proteinase K was chosen as the hydrolytic catalyst because of its outstanding efficiency in enzymatic biodegradation of PLLA.[22] Lipase PS was also used to study the biodegradability of PLLA-*b*-PMPS-*b*-PLLA due to its activity for degradation of general aliphatic polyesters.[23,24]



(a) (b)

Figure 14. Comparison of (a) weight loss % due to enzymatic degradation (b) seawater biodegradation % of the copolymers, PMPS-2 and PLLA homopolymers using proteinase K and lipase PS in different time.

Figure 14a shows the loss of weight of the PMPS soft polymer, PLLA homopolymers (PLLA-1: M_n = 5000 g/mol; PLLA-2: M_n = 3100 g/mol) and PLLA-*b*-PMPS-*b*-PLLA triblock copolymers during proteinase K and lipase PS catalyzed enzymatic hydrolysis. For 6 and 24 hours the percentage weight loss of the polymer samples as a result of enzymatic hydrolysis increased with time in the presence of enzymes while lipase PS might be deactivated within 6 hours for PMPS-2. There was no significant weight loss even after 24 hours for the homopolymer PLLA-1 and PLLA-2 immersed in the buffer solution with lipase PS. (Figure 14a). These results suggest that the degradation of the PLLA segment occurred only in the presence of proteinase K enzyme under these conditions. In contrast, the degradation of PMPS by lipase PS was faster than that by proteinase K. The weight loss for the triblock copolymers TPE1 and TPE3 suggests that the trend of weight loss also depends on the composition of the copolymer. In the presence of proteinase K, the sample of TPE1 was more degraded than that of TPE3. However, PLLA-1 and PLLA-2 exhibit significantly higher degradation rate than the copolymers taking into accounts the copolymer composition. This result may suggest that PMPS segments could suppress the degradation of PLLA segment in TPE1 and TPE3. In the degradation test by lipase PS, the weight loss of the TPEs was more proportional to their PMPS contents.

In recent years, marine biodegradable polymers are attracting attentions because of marine pollution by microplastics.[25] Figure 14b shows the result of the biodegradation tests of those polymers in seawater. Biodegradation BOD test was carried out at 29 °C with the seawater collected at Osaka port area and conducted for 28 days for each sample. A few days after the experiment started, O_2 consumption started and gradually increased. From figure 10b, it is observed that, PLLA-2 showed rapid and good degradation (%) among the five sample polymers. While PLLA was reported to be hardly degradable in sea water,[26] relatively low molecular weight of the PLLA-2 might enhance its biodegradability. PLLA-1 with higher molecular weight than that of PLLA-2 showed slower biodegradation than that of PLLA-2. Copolymer TPE3 also degraded fast which has the PLLA segments with similar length to that of

PLLA-2. PMPS-2 showed biodegradation of 5% after 4 weeks, while its structural isomer poly(butylene succinate) (PBS) was reported to be biodegraded by ~1.3% under the similar conditions.[27] Higher biodegradability of PMPS than that of PBS could be attributed to the amorphous nature of PMPS. Slower degradation of TPE1 was observed than that of TPE-3. Low biodegradation of PLLA-1 might be a reason behind this lower biodegradation (%) of the TPE1. Biodegradation (%) of triblock copolymer TPE1 and TPE3 suggests that the biodegradability of each segment is an important factor for biodegradation, especially the segment length in this case. These results demonstrated that these polymers can slowly be biodegraded in seawater.

4. Conclusion

A series of triblock copolymers, PLLA-*b*-PMPS-*b*-PLLA, composed of the soft PMPS midblock and hard PLLA end blocks with different molecular weight, was synthesized for the first time in a controlled manner by the ROP of LLA using PMPS-diol as a macroinitiator using $Sn(Oct)_2$ as a catalyst. The soft block PMPS was synthesized from two stage polycondensation reaction of MP with SA. Thus, the triblock copolymers can be produced from common and relatively cheap monomers, MP, SA and LLA. The triblock copolymers exhibited T_g at below -20 °C for the soft segment and T_m at 133-159.5 °C for the PLLA segment. The triblock copolymer synthesized with LLA to PMPS feed ratio 75 to 1 containing 53% PMPS showed the highest elongation at break up to 62.4% with good elastic properties. The presence of PMPS soft block with different content in the PLLA-*b*-PMPS-*b*-PLLA triblock copolymers demonstrated significant influence on the biodegradation behavior of the synthesized TPE. These copolymers were slowly but surely biodegraded in seawater and in enzyme solution.

5. References

1 T. Keijer, V. Bakker and J. C. Slootweg, *Nat. Chem.*, 2019, **11**, 190–195.

2 R. Auras, B. Harte and S. Selke, *Macromol. Biosci.*, 2004.

3 M. Sheth, R. A. Kumar and V. Dave, 2008, 1495–1505.

4 W. Wang, W. Lu, A. Goodwin, H. Wang, P. Yin, N. G. Kang, K. Hong and J. W. Mays, *Prog. Polym. Sci.*, 2019, **95**, 1–31.

5 J. O. Lin, W. Chen, Z. Shen and J. Ling, *Macromolecules*, 2013, **46**, 7769–7776.

6 C. Ba, J. Yang, Q. Hao, X. Liu and A. Cao, *Biomacromolecules*, 2003, **4**, 1827–1834.

7 T. Lebarbé, E. Ibarboure, B. Gadenne, C. Alfos and H. Cramail, *Polym. Chem.*, 2013, **4**, 3357–3369.

8 C. L. Wanamaker, L. E. O’Leary, N. A. Lynd, M. A. Hillmeyer and W. B. Tolman, *Biomacromolecules*, 2007, **8**, 3634–3640.

9 M. T. Martello and M. A. Hillmyer, *Macromolecules*, 2011, **44**, 8537–8545.

10 Y. Cao and H. Tan, *Carbohydr. Res.*, 2002, **337**, 1291–1296.

11 B. D. Ahn, S. H. Kim, Y. H. Kim and J. S. Yang, *J. Appl. Polym. Sci.*, 2001, **82**, 2808–2826.

12 A. Almontassir, S. Gestí, L. Franco and J. Puiggalí, *Macromolecules*, 2004, **37**, 5300–5309.

13 E. Ranucci, Y. Liu, M. S. Lindblad and A. C. Albertsson, *Macromol. Rapid Commun.*, 2000, **21**, 680–684.

14 Y. Yoo, M. S. Ko, S. Il Han, T. Y. Kim, S. Im and D. K. Kim, *Polym. J.*, 1998, **30**, 538–545.

15 Y. Xu, J. Xu, D. Liu, B. Guo and X. Xie, *J. Appl. Polym. Sci.*, 2008, **109**, 1881–1889.

16 Y. Nakayama, K. Aihara, H. Yamanishi, H. Fukuoka, R. Tanaka, Z. Cai and T. Shiono, *J. Polym. Sci. Part A Polym. Chem.*, 2015, **53**, 489–495.

17 K. W. Doak and H. N. Campbell, *J. Polym. Sci.*, 1955, **18**, 215–226.

18 Y. Nishiwaki, Y. Kimura, K. Masutani and C. W. Lee, *J. Polym. Sci. Part A Polym. Chem.*, 2018, **56**, 1795–1805.

19 O. Martin and L. Avérous, *Polymer (Guildf).*, 2001, **42**, 6209–6219.

20 N. Ding, B. Shentu, P. Pan, G. Shan, Y. Bao and Z. Weng, *Ind. Eng. Chem. Res.*, 2013, **52**, 12897–12905.

21 Y. Nishiwaki, K. Masutani, Y. Kimura and C. Lee, *J. Polym. Sci.*, 2020, **58**, 860–871.

22 N. Hegyesi, Y. Zhang, A. Kohári, P. Polyák, X. Sui and B. Pukánszky, *Ind. Crops Prod.*, 2019, **141**, 111799.

23 C. Tsutsumi, N. Hayase, K. Nakagawa, S. Tanaka and Y. Miyahara, *Macromol. Symp.*, 2003, **197**, 431–442.

24 Y. Tokiwa and B. P. Calabia, *J. Polym. Environ.*, 2007, **15**, 259–267.

25 Y. Picó and D. Barceló, *ACS Omega*, 2019, **4**, 6709–6719.

26 A. R. Bagheri, C. Laforsch, A. Greiner and S. Agarwal, *Glob. Challenges*, 2017, **1**, 1700048.

27 A. Nakayama, N. Yamano and N. Kawasaki, *Polym. Degrad. Stab.*, 2019, **166**, 290–299.

Chapter-III

Synthesis and Properties of Biodegradable Thermoplastic Elastomers using 2-Methyl-1,3-propanediol, Glutaric Acid and Lactide

1.Introduction

Glutaric acid is a linear organic dicarboxylic acid which is natutally produced in human body. It can also be synthesized by ring-opening of butyrolactone and potassium cyanide and can be used as plasticizer and precursor for polyesters and polyamides. Actually, most even-even aliphatic polyesters have the disadvantage of weak toughness and slow biodegradation rate owing to their high crystallinity. By contrast, odd-odd polyesters derived from odd diacids and odd diols have weak crystallizability and tend to be amorphous. They show low T_g value and can balance low crystallinity and large elongation.[1] If glutaric acid is picked up as dicarboxylic acid to synthesize soft block, it is expected to have lower T_g and to improve biodegradability property than previously reported PMPS and related ABA type triblock copolymers. PMPG has been reported in the study for the solubility of polyesters in CO_2, however its detailed properties were not described.[2]

In this study, we adopted poly(2-methyl-1,3-propanediyl glutarate) (PMPG) as a soft segment for PLLA-containing triblock copolymers, which were prepared from common and easily available monomers, glutaric acid, MP and

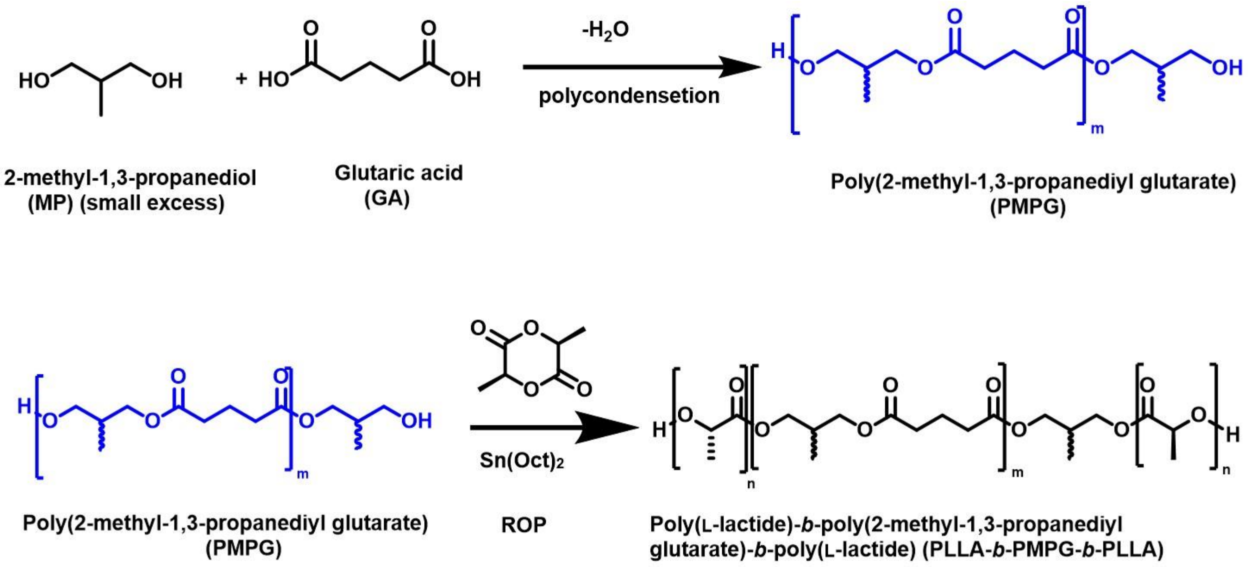
L-lactide. The molecular structures, thermal properties and degradability behavior of PMPG and synthesized triblock copolymer were investigated. The contribution of this work was to demonstrate the influence of newly synthesized PMPG as soft midblock on the thermal and mechanical properties and degradability of the PLLA-containing triblock copolymers along with the comparison with the previously synthesized PMPS-contained ABA type triblock copolyesters.

2. Experimental

2.1 General considerations

All the experiments of the polymerizations were carried out in a nitrogen stream using Schlenk techniques. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) measurements were performed on a Varian system 500 spectrometer at room temperature. The signals for the residual chloroform ($\delta = 7.26$ ppm) and for chloroform-d ($\delta = 77.16$ ppm) were used for the calibration of the chemical shifts in ^{1}H and ^{13}C NMR spectra in chloro-form-d, respectively. Molecular weight distributions of the obtained polymers were evaluated by gel permeation chromatography (GPC) on a Tosoh GPC system (HLC-8320) equipped with a RI detector at 40 °C using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min. GPC traces were calibrated by polystyrene standards. The thermal properties such as melting point (Tm), melting enthalpy (ΔH_m) and glass transition temperature (T_g) of the products were evaluated by a differential scanning calorimetry (DSC) on a Seiko DSC 6220 instrument, where the DSC data of the polymers were collected in the second heating scan at a heating rate of 10 °C/min after elimination of thermal history by first heating of the sample to 200 °C and cooling to −100 °C at 10 °C/min. T_g of the polymers were determined from the middle point of the phase transition of the second heating scan. The decomposition temperature losing 5% of sample weight (T_{d5}) was measured by thermogravimetry (TG) on SII Seiko EXSTAR 6000 TG/DTA 6300 in the temperature range of 25−500 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The tensile tests of the obtained copolymer films were performed by using Shimadzu EZ-LX HS tensile testing machine at an elongation rate of 5 mm/min. Dumbbell-shaped specimens (width, 4 mm; gauge length, 10 mm; thickness, approximately 0.1 mm) were cut from the copolymer sample sheets for the tensile tests. Each tensile test was repeated three times and averaged. Young's modulus values were determined as the slope of the straight line in the first 2 to 5% of elastic region of the stress-strain curve and the strength and strain at break were determined from the strain at break point of the sample.

\



Scheme 1. Synthesis of PMPG macroinitiator and PLLA-*block*-PMPG-*block*-PLLA triblock copolymer

2.2 Materials

L-Lactide (LLA), glutaric acid (GA) and 2-methyl-1,3-propanediol (MP) were purchased from Tokyo Chemical Industry. LLA was sublimated under nitrogen before use. MP and GA were used without further purification. THF and toluene were purchased from Kanto Chemical and purified by distillation from sodium benzophenone under nitrogen prior to use. Both solvents were stored over sodium. Tin(II) 2-ethylhexanoate [$Sn(Oct)_2$] was purchased from Sigma Aldrich and stored over activated molecular sieves (3A).

2.3 Synthesis of poly(2-methyl-1,3-propanediyl glutarate) (PMPG)

A typical procedure: Hydroxy-telechelic PMPG was synthesized from MP (small excess) and GA using two-stage reaction of esterification and simple polycondensation processes using $Sn(Oct)_2$ as the catalyst (scheme 1). After adding MP (20.3 g, 0.225 mol), GA (27.06g, 0.205 mol) and catalyst $Sn(Oct)_2$

(0.04 g, 0.1 mmol) into a reactor, the mixture was heated slowly to 180 °C under N_2 gas atmosphere (1 atm). H_2O was collected using a trap device. After continuation of esterification for 90 mins, polycondensation process was conducted to remove the excess glycol and promote the chain extension. The temperature was kept at 180 °C, at pressure below 1.0 mmHg and the reaction continued for predetermined time. The synthesized polyester was dissolved in chloroform. Excess amount of methanol was added to precipitate the polymer, which was washed with the methanol. Finally, the residue was dried in vacuo at room temperature for 2-3 days to yield PMPG as a colorless viscous oil in 93% yield.

2.4 Polymerization of L-lactide using PMPG as a Macroinitiator

A typical procedure $[LLA]_0 : [PMPG\text{-}1]_0 = 100:1$): At first, PMPG-1 (0.16 g, 1.7×10^{-2} mmol) was dissolved with 3ml toluene in a 10 ml Schlenk tube. It took about 1hr continuous stirring at room temperature to dissolve properly. Then LLA (0.25g, 1.73mmol) was added to the PMPG-toluene solution and the tube was dipped in the oil bath at 100 °C to dissolve LLA in the solution. After dissolving, $Sn(Oct)_2$ (1.6 mg, 0.004 mmol) was injected into the mixture and the polymerization was continued for 24 hrs at 100 °C. The polymerization was quenched with acidic methanol and the synthesized polymer was washed with excess methanol. The copolymer was separated from methanol by centrifugation and dried in vacuo at room temperature for 24 hrs as a colorless solid in 94 wt% yield.

2.5 Formation of Films of the obtained polymers

The solution of PLLA-*b*-PMPG-*b*-PLLA (0.30 g) in THF (4.0 mL) was poured in a PTFE plate. The slow evaporation of the solvent at room temperature under ambient pressure for 3 days followed by further evaporation in vacuo at room temperature for 1 day yielded the self-standing films of the samples.

2.6. Enzymatic biodegradation test of the polymers

The enzyme solutions (1 mg/0.02 M buffer) of lipase PS and proteinase K were prepared using 0.02 M phosphate buffer (pH = 8.0). The phosphate buffer (1 ml), 1 ml of H_2O containing 0.5 ml of enzyme solution and a sample polymer (10 mg) were placed in a vial. The enzymatic degradations were carried out at 45 °C with shaking the vial for 6 hrs and 24 hrs separately. The filtrate of the solution was analyzed by total organic carbon concentration (TOC) measurement by using TOC analyzer (Shimadzu TOC-VCSH) to evaluate the weight loss of the samples. The degradation test was repeated four times for each sample and the results were averaged.

2.7. Biodegradation test of the polymers in seawater

The biodegradation of the obtained polymers in seawater was monitored by biological oxygen demand (BOD) measurements. The seawater was collected at the shoreline of Osaka South Port area using bucket and used within two days. The seawater used for TPE100 and TPE50 was taken on 10th October 2020, and that for PMPG was taken on 13th November 2020. In a typical procedure, 250 mL BOD testing bottle was charged with polymer sample (30 mg) and 200 mL of the supernatant of seawater, which was equipped to BOD tester (TAITEC, BOD200F). Calcium hydroxide was used to remove carbon dioxide (CO_2) evolved from metabolism of the sample by microorganisms from the closed BOD system. The BOD testing bottle was stirred at 27 °C for 28 days with monitoring O_2 consumption. The control O_2 consumption volume was subtracted from the observed O_2 consumption volume of the sample for correction. The theoretical volume of O_2 consumption for each sample was calculated based on the composition of the polymer samples determined by ^{1}HNMR analysis assuming the complete mineralization of the samples to CO_2. The % biodegradation values of the samples were simply calculated by the following equation:

% Biodegradation = (consumed O_2 volume/ theoretical volume of O_2 consumption) x 100

Each biodegradation test was repeated twice and averaged.

3. Result:

3.1 Preparation of PMPG-diols

In this work, dihydroxyl terminated PMPG with different molecular weights were synthesized following a two-stage reaction of polycondensation from MP and GA in bulk. In the 1st step, esterification between MP and GA using excess diol was conducted. The MP to GA feed ratio was 1 : 1 at 180 °C under N_2 (1atm) resulted in a mixture of PMPG oligomers having MP units at the both ends. Then, the transesterification of the PMPG oligomers was performed under reduced pressure at 180 °C for different time using $Sn(Oct)_2$ as a catalyst with removing excess MP to bring out a significant increase in molar masses of the PMPGs (Table 1). PMPGs were obtained as colorless viscous liquid with >90% yields.

Table 1. Synthesis of PMPG-diol by two stage polycondensation of MP and GA[a]

Sample[a]	**Time [min] (2nd stage)**	**Yield (%)**	**M_n [b] (×10^3) [g mol^{-1}]**	**M_w/M_n [b]**	**T_g [c] [°C]**	**T_{d5} [d] [°C]**
PMPG-1	120	94	9.06	1.56	-46	377.1
PMPG-2	100	91	8.27	1.63	-48	365.7
PMPG-3	50	90	5.43	1.66	-51	208.9

[b]Determined by GPC in THF calibrated with standard polystyrene. [c] Determined with DSC 2nd heating scan. [d] Decomposition temperature losing 5% of sample weight.

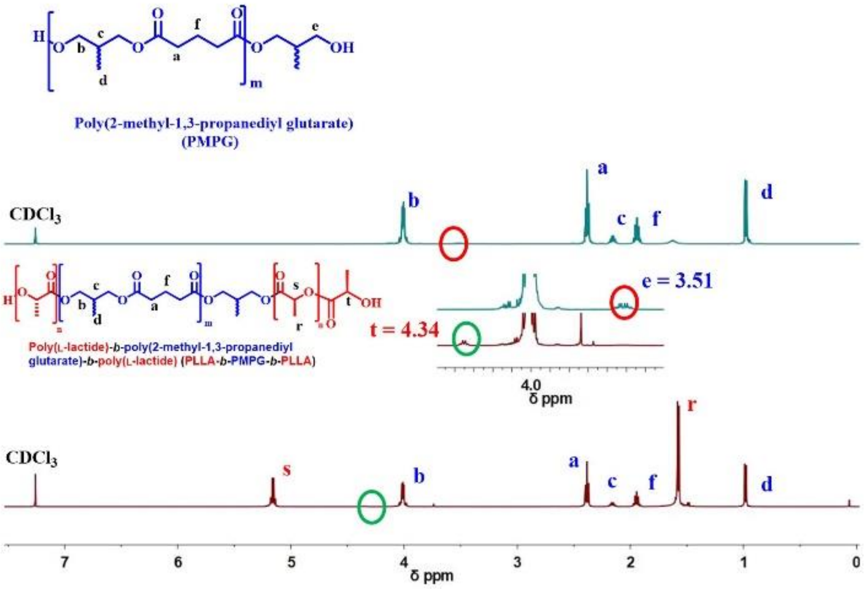


Figure 1. ^{1}H-NMR spectrum of PMPG-1 (upper) and PLLA-*b*-PMPG-*b*-PLLA (TPE100, lower) ($CDCl_3$, r.t., 500 MHz).

The 500MHz 1H-NMR spectrum of PMPG-1 is shown in Figure 1 (upper). The signals at δ = 0.99 (d), 1.94 (f), 2.16 (c) 2.38 (a) and 4.00 (b) ppm can be assigned to the protons of the repeating units in PMPG.[143] In addition, the resonance peak at 3.52 ppm (peak e of PMPG) can be assigned to the α-methylene protons linked to the terminal hydroxyl group, indicating the hydroxy-telechelic structure of PMPG similarly to PMPS.[3]

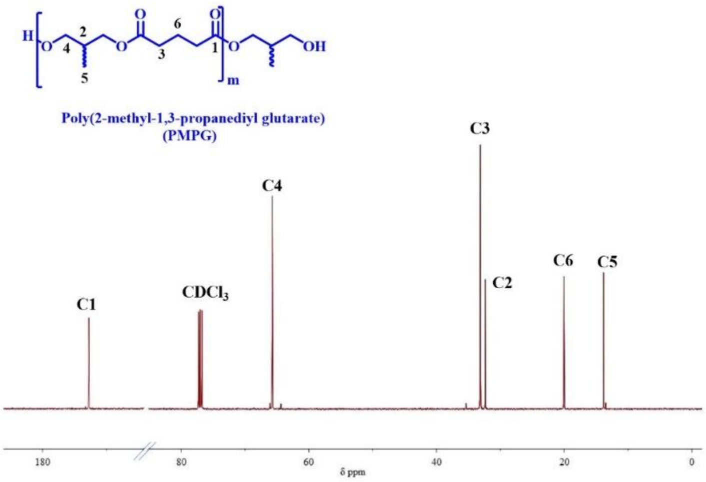


Figure 2: ^{13}C NMR spectrum of PMPG-1 ($CDCl_3$, r.t., 125 MHz).

In a 125 MHz ^{13}C-NMR spectrum of the macroinitiator PMPG, three resonances at $\delta = 65.66$ (C4), 32.38 (C2) and 13.89 (C5) ppm are associated with carbons derived from the MP monomer. The signals of the α-(CO-CH_2-), β-(CO-CH_2-CH_2) and the carbonyl carbons (*C*O-) of the glutarate moiety appeared at $\delta = 33.75$ (C3), 24.31(C6) and 173.15 (C1) ppm, respectively (Figure 2). Six sharp resonances assignable to the carbons of the repeating units in PMPG was exhibited in ^{13}C-NMR spectrum.

Figure 3 represents the GPC curves of the synthesized PMPGs. A monomodal peak in each GPC curve shifted to smaller retention time with increasing the reaction time on the 2nd stage, indicating the increasing number average molecular weight (M_n) of these PMPGs with increasing the reaction time on the 2nd stage. The polydispersities (M_w/M_n) were 1.56, 1.63 and 1.66 for PMPG-1, 2 and 3, respectively.

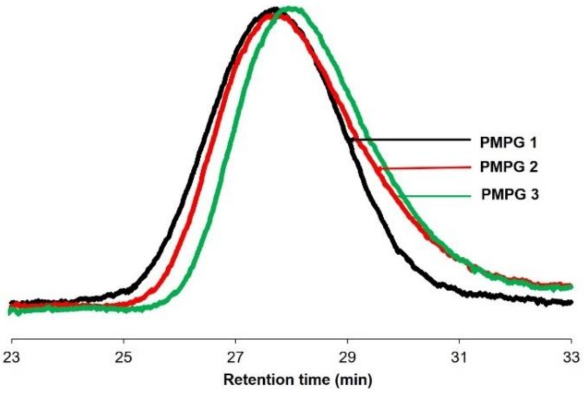


Figure 3. GPC curve of PMPG-1, PMPG-2 and PMPG-3.

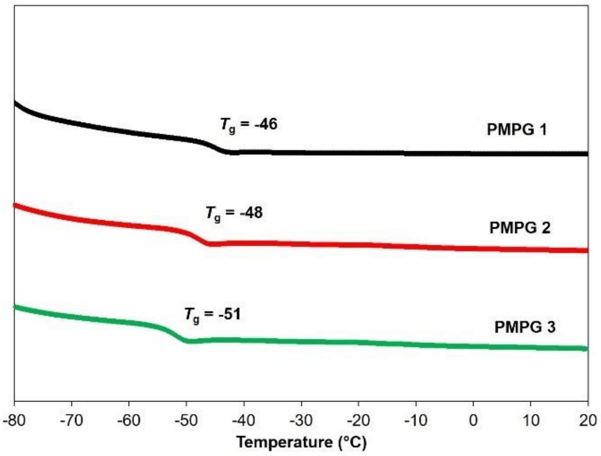


Figure 4. DSC curves of PMPG-1 collected upon cooling and heating. The cooling and heating rate at 10 °C/min.

The DSC curves of the obtained PMPGs are shown in Figure 3. All the PMPGs exhibited no visible melting peak on their DSC curves. The glass transition of the obtained PMPGs were observed at from −46 to −50 °C. Although the T_g values of the PMPGs tended to increase with the molecular weight, the T_g of PMPG-1 was as low as −46 °C, resulting in a very sticky transparent polymer at ambient temperature. The thermal decomposition temperatures of the PMPGs were raised with increasing their molecular weights, and the highest T_{d5} was observed for PMPG-1 at 377 °C.

3.2 Synthesis of PLLA-*b*-PMPG-*b*-PLLA as TPE

The PMPG-1 was applied as a macroinitiator in the LA polymerization at different feed of $[LLA]_0$: [PMPG-1] ratio (Table 2) catalyzed by $Sn(Oct)_2$ to synthesize triblock co-polymers PLLA-*b*-PMPG-*b*-PLLA as novel biodegradable TPEs. In the sample names, the numbers following 'TPE' denote the feed $[LLA]_0/[PMPG]$ molar ratio. The products were characterized by NMR and GPC analysis.

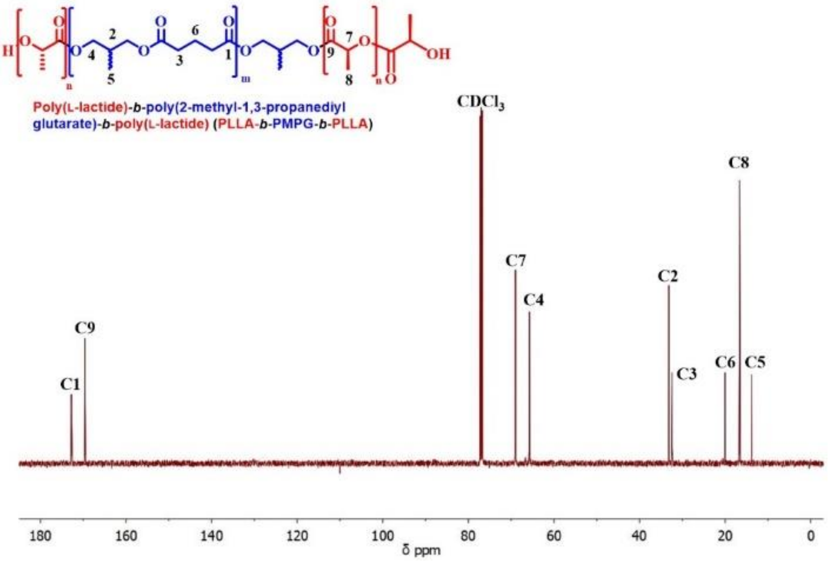


Figure 5. ^{13}C-NMR spectrum of PLLA-*b*-PMPG-*b*-PLLA (TPE100) ($CDCl_3$, r.t., 125 MHz).

Figure 1 (lower) shows the ^1H NMR spectrum of the TPE100. The signal at 3.52 (peak e, Figure 1 (upper)) for the terminal hydroxyl group of the PMPG-1 disappeared and the new resonance at 4.34 ppm (peak t) for the hydroxyl terminal of PLLA appeared in the spectrum of TPE100, indicating that the hydroxyl end of the PMPG-1 initiated the LLA polymerization. Apart from the PMPG-peaks, the characteristics peaks of PLLA segment appeared at 5.2 ppm and 1.6 ppm in the spectrum of TPE100, which are the quartet peak (s) of the methine proton in the -OCH(CH_3)CO- unit and the doublet peak of the methyl proton (r), respectively.[4] In figure 4, the 125 MHz ^{13}C NMR spectrum of TPE100 showed the signals C7 ($\delta = 69.0$ ppm), C8 ($\delta = 16.6$ ppm) and C9 ($\delta = 169.6$ ppm) for the methine, methyl and carbonyl carbons of the PLLA segment, respectively. Apart from the signal for the carbonyl carbon of PMPG, no other signals appeared in the carbonyl region of $\delta = 169\text{-}174$ ppm which could be assigned to the mixed comonomer junctions.[5] These results are supported by the observations in the previous reports on the block copolymerization of LLA from other aliphatic polyesters.[6-9]

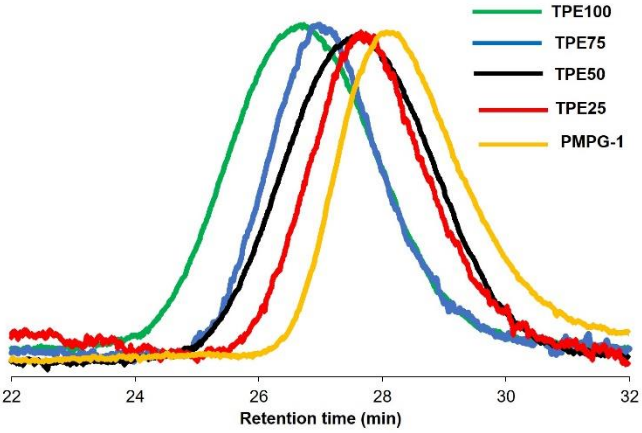


Figure 6. GPC curves of PLLA-*b*-PMPG-*b*-PLLA samples (TPE100,75,50 and 25) and PMPG-1

Figure 5 represents the GPC traces of PMPG-1 and PLLA-*b*-PMPG-*b*-PLLAs (TPEs). The peak in the GPC curve shifted from longer retention time to shorter one with in-creasing feed $[LLA]_0$: [PMPG-1] ratio. The distributions were kept unimodal and relatively narrow in a range of the feed $[\mathrm{LLA}]_0$: [PMPG-1] ratio from 25 : 1 to 100 : 1.

Table 2 summarizes the molecular weights and compositions of the obtained TPEs determined by GPC and NMR characterization. The $M_\mathrm{w}/M_\mathrm{n}$ of the synthesized copolymers (1.2-1.3) were narrower than that of the macroinitiator (PMPG-1, $M_\mathrm{w}/M_\mathrm{n}$ = 1.56) and M_n of the copolymer increased when the $[\mathrm{LLA}]_0$/[PMPG-1] feed ratio was increased from 25 to 100 suggesting that the molecular weights of the PLLA segment can be con-trooled by the $[\mathrm{LLA}]_0$/[PMPG-1] feed ratio. The molecular weights of the TPEs can also be evaluated from the intensity ratio of the signals for repeating units and the end group in their ^{1}H NMR spectra as in Table 2. The PLLA-1 and PLLA-2 are the homopoly(L-lactide)s having chain length similar to those of the PLLA blocks in TPE100 and TPE50, respectively, which were prepared in the previous study for comparison.[3]

Table 2. The ROP of L-LA catalyzed by $Sn(Oct)_2$ using PMPG-1 as macroinitiator [a]

Sample	Feed Ratio $[LLA]_0$:[PMPG-1]	Yield [%]	$M_{n(GPC)}$ [b] (×10³) [g mol⁻¹]	$M_{n(NMR)}$ [c] (×10³) [g mol⁻¹]	M_w/M_n [b]	f_{LLA} [c] [mol%]
TPE100	100:1	92	20.2	19.7	1.2	54
TPE75	75:1	92	18.7	17.3	1.2	49
TPE50	50:1	92	16.2	15.2	1.3	45
TPE25	25:1	88	14.9	14.0	1.3	40
PLLA-1[143]	50:1[d]	97	5	5.7	1.4	-
PLLA-2[143]	25:1[d]	97	3	3.1	1.4	-

[a] PMPG-1 (M_n = 10.8×10³ gmol⁻¹, M_w/M_n = 1.61, T_g = -27.7 °C), Cat = $Sn(Oct)_2$ (4 ×10⁻³ mmol), $[LLA]_0$: [Cat] = 400 : 1, temp = 100 °C, time = 24 hrs. [b] Determined by GPC in THF calibrated with standard polystyrene. [c] Determined by ^{1}H-NMR analysis. [d] BnOH was used as macroinitiator instead of PMPG-1.

3.3 Thermal Properties of PLLA-*b*-PMPG-*b*-PLLA

Table 3 summarizes the measured thermal properties of the TPEs. Their DSC curves (2nd heating) are shown in Figure 7. The melting points, Tm, were observed at 152, 145, 142 and 130 °C for the TPE100, 75, 50 and 25, respectively. The Tg values of the copolymers were observed in a range from −48 to −42 °C. Crystallization peaks were not observed in the heating scan of the TPEs.

Table 3. Thermal properties of the synthesized triblock copolymers, PLLA-*b*-PMPG-*b*-PLLA

Sample	Feed Ratio $[\mathrm{LLA}]_0$: [PMPG-1]	F_{LLA} [mol%]	$T_g{}^a$ [°C]	$T_m{}^a$ [°C]	$\Delta H_m{}^a$ [J/g]	T_{d5} [°C]
TPE100	100:1	54	-41.7	151.7	34.8	256.9
TPE75	75:1	49	-42.9	144.8	29.5	270.5
TPE50	50:1	45	-44.8	141.8	27.3	285.4
TPE25	25:1	40	-47.7	129.8	10.7	300.8

[a] Determined by DSC at 2nd heating scan. [b] Decomposition temperature losing 5% of sample weight.

Thermal stability of the PLLA-*b*-PMPG-*b*-PLLAs copolymers was evaluated by thermogravimetry (TG) analysis (Figure 8). This test illustrated that the thermal degradation process of the triblock copolymers proceeded in two steps. The T_{d5} values of the co-polymers were 257, 271, 285 and 301 °C for TPE100, 75, 50 and 25, respectively.

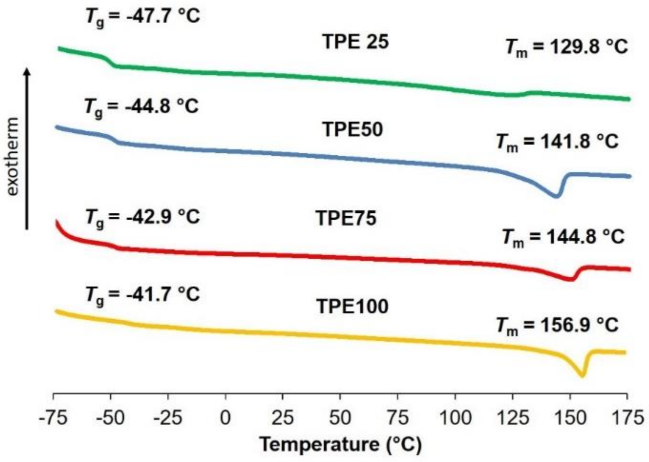


Figure 7. DSC curves of PLLA-*b*-PMPG-*b*-PLLA samples (TPE100, 75, 50 and 25) collected in the 2nd heating scan. Both the cooling and heating rates are 10 °C/min.

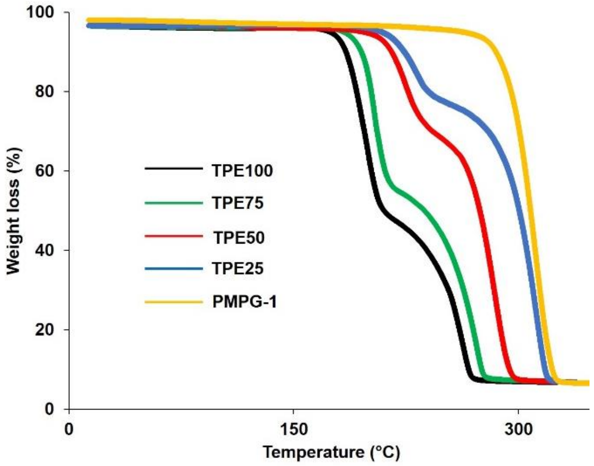


Figure 8. TG curves of PLLA-*b*-PMPG-*b*-PLLAs (TPE100, 75, 50 and 25) and PMPG-1.

3.4 Mechanical properties of the TPEs

The mechanical properties of the TPE100, 75, 50 and 25 were evaluated by tensile tests. The self-standing copolymer films (thickness: approximately 0.1 mm) were prepared by solution casting using THF as a solvent and were cut into a nonstandard dumbbell shape. The film of the pure soft segment PMPG could not be formed due to its oily nature. Figure 9 plots the representative stress-strain curves of the copolymers. Table 4 summarizes their tensile properties. The Young's modulus and tensile strength of the copolymers tended to increase with increasing LLA content of the copolymers. On the other hand, the elongation at break of the TPEs increased with decreasing LA content.

Table 4 . Mechanical properties of the synthesized triblock copolymers.

Sample	F_{LLA} [a] [mol%]	Young Modulus [MPa]	Strength [MPa]	Elongation at Break(%)
TPE100	54	207	6.1	14
TPE75	49	36	2.0	18
TPE50	45	20	1.3	21
TPE25	40	7	0.4	23

[a]Calculated from ^{1}H NMR. *strength is defined as the stress at the strain at break. Determined by tensile tester with elongation rate 5 mm/min. Number of measurement times 3.

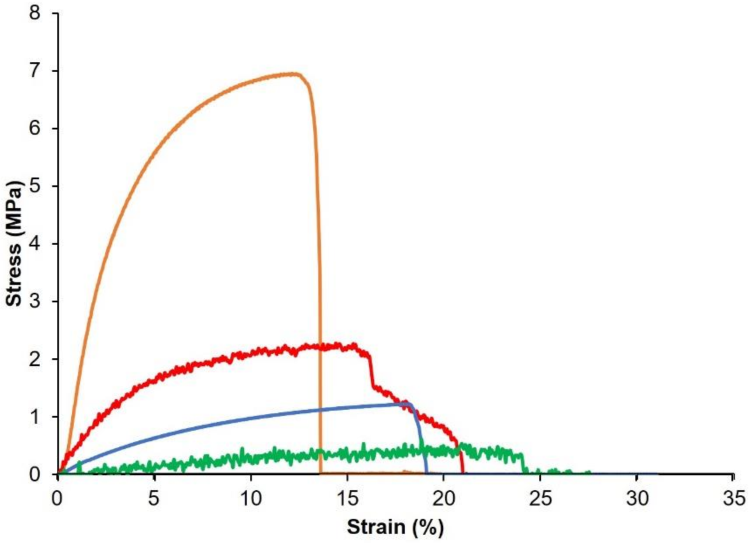


Figure 9. Typical stress-strain curves of the TPE100, TPE75, TPE50 and TPE25.

3.4 Biodegradability of the synthesized copolymers

The biodegradation tests of the polymers were carried out using enzymes proteinase K and lipase PS. Figure 10 shows the weight loss (%) of the TPE100, TPE50, PMPG-1, PLLA-1, and PLLA-2 (PLLA-1: M_n = 5000 g/mol; PLLA-2: M_n = 3100 g/mol) by the enzymes after 6 hrs and 24 hrs. The results of PLLA-1 and PLLA-2 are the data from our previous paper for comparison.[143] The PLLA-1 and PLLA-2 were degraded by 15-25% in a day by proteinase K, while they were hardly degraded in 24 hrs by Lipase PS.[143] For TPE100, the weight loss increased with time from 6 hrs to 24 hrs by both enzymes, while TPE 50 and PMPA did not exhibit significant increase of weight loss from 6 hrs to 24 hrs. The degradation of PMPG-1 was ca. 2% within 24 hrs by both proteinase K and lipase PS. The degradation of TPE100 were ca. 4% by both proteinase K and lipase PS, while TPE 50 showed the degradation of ca. 1% and ca. 4% by proteinase K and lipase PS, respectively.

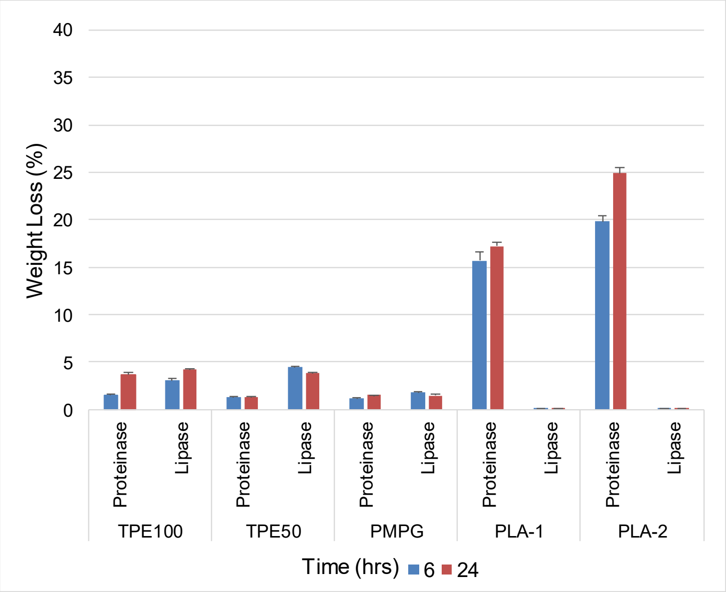


Figure 10. Comparison of weight loss % due to enzymatic degradation of the copolymers, PMPG-1 and PLLA homopolymers using proteinase K and lipase PS in different time.

The exponential increase of global plastic production has arisen the issue of marine pollution by plastic debris, which has led the research works towards the improvement of biodegradability property of the plastic polymeric materials in seawater,[10] so we performed the microbial biodegradation of the obtained polymers in sea-water. Figure 11 represents the biodegradation (%) of TPE100, TPE50, PMPG-1, PLLA-1, and PLLA-2 at 27 °C for total 28 days in the seawater collected at Osaka port area. This biodegradation of the polymers was monitored by the amount of O_2 consumed by metabolization (BOD) of the samples by the microorganisms in the seawater. Although the used seawater for PMPG was taken on different day from that used for TPEs, the results could be roughly compared. The results of PLLA-1 and PLLA-2 in our previous report[3] was also included in Figure 10 for rough comparison. For all samples, O_2 consumption gradually increased with time. The observed biodegradations of TPE100, TPE50, and PMPG after 28 days were around 15%, 12%, and 9%, respectively.

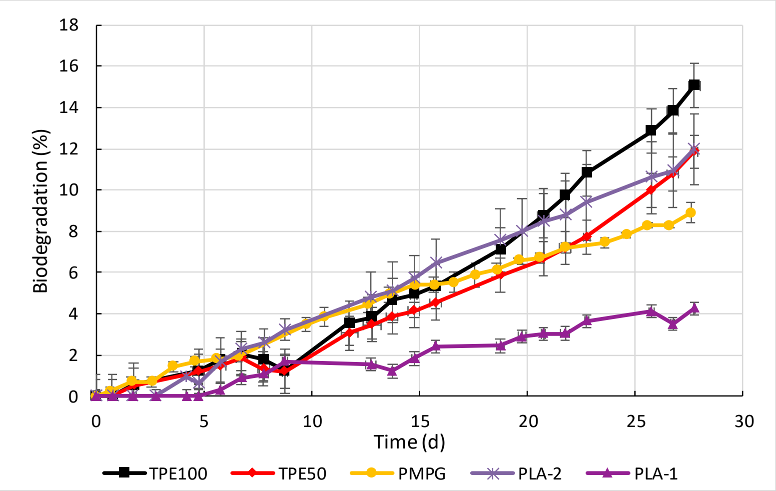


Figure 11. Comparison of seawater biodegradation % of the copolymers, PMPG-1 and PLLA homopolymers using proteinase K and lipase PS in different time.

4. Discussion

The two-stage polycondensation of MP (small excess) and GA in bulk successfully afforded PMPG as a viscous oily material in high yield. The molecular weights of the obtained PMPG could be modulated by the polymerization time on the second stage. The ^{1}H and ^{13}C NMR analysis of the obtained PMPGs confirmed their expected structure. DSC analysis of the PMPG did not exhibit melting transition indicating its amorphous nature. The PMPGs have enough low T_g at around −50 °C to be used as soft segment for PLLA-conjugated triblock copolymers. The T_g of the PMPGs were lower than that of PMPS (around −30 °C),[3] reflecting the higher chain mobility of the PMPG than that of PMPS. In order to obtain higher molecular weight copolymers, PMPG-1 was used as a macroinitiator in the following LLA-polymerization to synthesize the following triblock copolymers having enough low T_g (−46 °C) and relatively high M_n (9.06 kg mol^{-1}). The PMPG-1 showed higher Td5 at 377 °C than that of the previously reported PMPS (around 360 °C).[3]

The PLLA-*b*-PMPG-*b*-PLLA triblock copolymers (TPE100, 75, 50, and25) were synthesized for the first time by the ROP of LLA using PMPG-1 as a macroinitiator. The NMR and GPC data of the products strongly supported the successful formation of the expected triblock copolymers.

The thermal properties of the obtained triblock copolymers were analyzed by DSC and TG analysis of the samples. DSC analysis of the TPE100, 75, 50 and 25 exhibited their T_m at 152, 145, 142 and 130 °C, the respectively. As PMPG did not show any melting peak for being amorphous, so the melting peaks of copolymers must come from the melting transition of the PLLA crystaline phase. The T_m and ΔH_m vs. LLA content plots of the TPEs in Figure 12 demonstrates their linear relationship, indicating the controllable thermal properties of the TPEs by LLA content. The absence of crystallization peak in heating scan of PLLA-b-PMPG-b-PLLA suggested their accelerated crystallization in the cooling process.

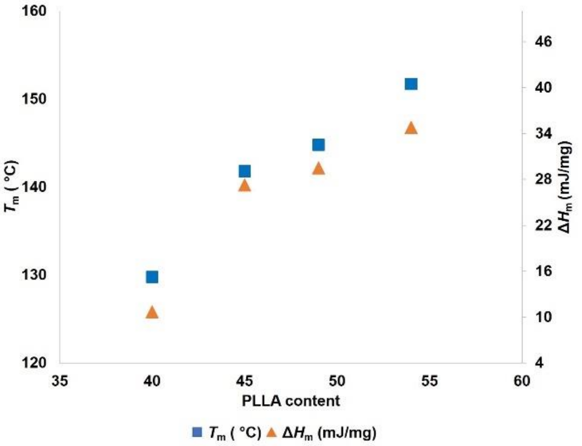


Figure 12. Plots of T_m (°C) and ΔH_m (mJ/mg)vs LLA content of the PLLA-*b*-PMPG-*b*-PLLA triblock copolymers.

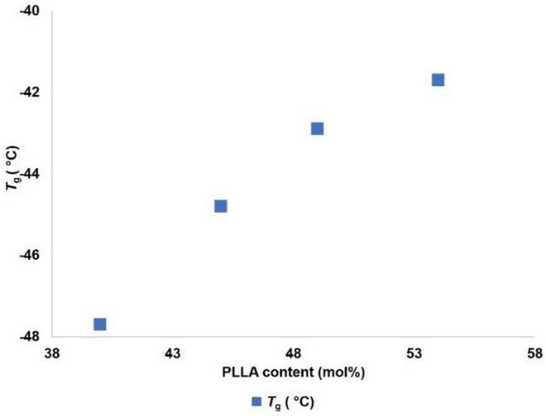


Figure 13. Plots of T_g (°C) vs LLA content of the PLLA-*b*-PMPG-*b*-PLLA triblock copolymers.

The T_g values of the copolymers below −42 °C corresponds to that of the PMPG soft segment although those of TPE50, 75 and 100 are slightly higher than that of PMPG-1 (−46 °C) because of the presence of hard PLLA segment, and are enough low for their use as TPE. Only one T_g for each TPE indicated the partial miscibility of the PLLA and PMPG segments in the amorphous phase of the copolymers. Figure 12 shows the plot of T_g vs. LLA content of the TPEs. The T_g value also increased with increasing LLA content in the copolymers exhibiting a clear linear relationship. The T_g values of the PLLA-b-PMPG-b-PLLAs are substantially lower than those of PLLA-*b*-PMPS-*b*-PLLAs (around −20 °C),[143] demonstrating the better cold-resistance of the former. All these data of the thermal properties of the PLA-b-PMPG-b-PLAs revealed that they have both low Tg of the soft segment and high Tm of the hard segment required for thermoplastic elastomers.

The TG analysis of the PLLA-*b*-PMPG-*b*-PLLAs (Figure 8) showed two step thermal degradation behaviors, where the PLLA block degraded at first, then the PMPG block degraded. The copolymers containing shorter PLLA block showed higher T_{d5} values but lower than that of PMPG macroinitiator due to the lower thermal stability of PLLA segment than that of PMPG. The residual Sn catalyst could promote the thermal de-composition of PLLA. [11-13]

All the copolymers contain both semicrystalline hard PLLA segment and amorphous soft PMPG segment, so they behaved as flexible semicrystalline polymers in their tensile tests, exhibiting elastic deformation. All the copolymers showed significantly higher elongation at break and lower Young modulus than those of the typical PLLA. In other words, these TPEs are much softer than PLLA because of the incorporated soft segment. The triblock copolymers' tensile modulus and strength increased and elongation at break decreased with increasing LLA content, most probably due to the increasing physical cross-linking with increasing LLA content, indicating the controllable physical properties of the TPEs by their compositions. The similar trends are observed in the previously reported PLLA-*b*-PMPS-*b*-PLLA.[3]

The enzymatic degradations of the triblock copolymers and the corresponding homopolymers were performed by two enzymes, proteinase K and Lipase PS, because their specificities to the kinds of polymers are different. The enzymatic degradation rates of polyesters should also greatly depend on their chemical structure, molecular weight, morphology, crystallinity and so on.[14] Hydrolytic catalyst proteinase K is known for its high activity for PLA degradation,[15] and the PLLA homopolymers (PLLA-1 and -2) were actually degraded up to 25% in 24 hrs.[3] Lipase PS shows high efficiency towards the hydrolysis of poly(alkanediyl dicarboxylate).[16,17] The degradation of PMPG by proteinase K (ca 2% after 24 hrs) was similar to that of PMPS.[3] On the other hand, the degradation of PMPG by lipase PS after 24 hrs (ca. 2%) was considerably lower than PMPS (ca. 4%),[3] which could come from the deactivation of lipase PS within 6 hrs in the PMPG degradation indicated by the similar degradation of PMPG after 6 hrs. The degradation of the copolymers TPE100 and TPE50 by proteinase K (ca. 4% and 2% after 24 hrs for TPE100 and 50, respectively) are lower than homopolymers PLLA-1 and -2 considering their compositions, suggesting suppression of degradation by PMPG segment. The degradation of TPE100 and 50 by lipase PS were ca. 4% after 24 hrs, higher than that of PMPG. Although the reason for this observation is not clear yet, we speculate that the deactivation of lipase PS could be suppressed in the TPE100 and 50 systems.

Although there are growing concerns about marine pollution caused by polymer debris, the soft and/or elastic polymer materials that are biodegradable in seawater are still limited compared to hard ones. The biodegradation tests of the triblock copolymers as well as PMPG revealed their relatively high biodegradability in seawater. Although the conditions are not the same due to the difference of the used seawater, the biodegradation of PMPG in seawater (about 9% after 28days) seems faster than that of PMPS (about 5% after 28 days). The microbial biodegradation of polymers in seawater is affected by the kinds and numbers of microorganisms in it, which may have different substance specificities and activities, so, it is difficult to specify the reason for the higher biodegradability of PMPG than PMPS, but we speculate that the higher mobility of the polymer chain of PMPG, suggested by its lower T_g than that of PMPS, could be one of the factors for the faster biodegradation of PMPG. Both TPE100 and TPE50 showed similar biodegradability to that of PMPG. Somewhat higher degradation of TPE100 and TPE50 than that of PMPG could come from the different date when the used sweater was collected. For rough estimation, these materials will be completely degraded within 7-10 months in seawater assuming linear degradation with time. The seawater biodegradation of the PLLA-*b*-PMPG-*b*-PLLA and PMPG seems faster than those of typical biodegradable polymers such as poly(butylene succinate) and commercial PLLA, and slower than poly(3-hydroxybutyrate) and poly(ε-caprolactone).[18] Therefore, the PLLA-*b*-PMPG-*b*-PLLA and PMPG can be regarded as polymers with moderate biodegradability in seawater. The data of PLLA-1 and -2 are from our previous study,[3] where PLLA-2 (about 11% after 28 days) was more degraded than PLLA-1 (about 4% after 28 days). Thus, the PLLA-b-PMPG-b-PLLAs can be regarded as totally biodegradable polymers in seawater. Some marine bacteria such as C. testosterone, Alcaligenes faecalis AE122, Marinobacter sp., Nocardiopsis aegyptia sp., and Shewanella sp. have been reported to degrade PHB and its derivatives.[19-22] They excrete extracellular enzymes to degrade PHB and metabolize the water-soluble decomposed products as nutrients. The present triblock copolymers and PMPG should most probably be biodegraded in a similar way.

5. Conclusion

In this work, triblock copolymers PLLA-*b*-PMPG-*b*-PLLA with different feed ratios were synthesized by ROP of LLA using PMPG as macroinitiator and $Sn(Oct)_2$ catalyst for the first time. PMPG was synthesized by polycondensation of easily available monomers, MP and GA. PMPG showed T_g value at below

−46 °C which was low enough for the use as soft segment of TPE. From DSC analysis, the synthesized triblock copolymers showed Tg at lower than −40 °C from PMPG segment and T_m at 152 to 130 °C from PLLA segment. Finally, from the biodegradation tests, the copolymers and PMPG were found to show relatively high biodegradability in seawater. Thus, the PLLA-b-PMPG-b-PLLA can be a potential candidate of practical TPEs with relatively high biodegradability.

6. References

1 Z. Wei, R. Che, S. Shao, Y. Wang, X. Leng and Y. Li, *Polym. Test.*, 2020, **83**, 106348.

2 C. L. Bray, B. Tan, S. Higgins and A. I. Cooper, *Macromolecules*, 2010, **43**, 9426–9433.

3 L. Zahir, T. Kida, R. Tanaka, Y. Nakayama, T. Shiono, N. Kawasaki, N. Yamano and A. Nakayama, *Polym. Degrad. Stab.*, 2020, **181**, 109353.

4 Y. Nishiwaki, K. Masutani, Y. Kimura and C. Lee, *J. Polym. Sci.*, 2020, **58**, 860–871.

5 Z. Wei, R. Che, S. Shao, Y. Wang, X. Leng and Y. Li, *Polym. Test.*, 2020, **83**, 106348.

6 A. Watts, N. Kurokawa and M. A. Hillmyer, *Biomacromolecules*, 2017, **18**, 1845–1854.

7 C. L. Wanamaker, L. E. O’Leary, N. A. Lynd, M. A. Hillmeyer and W. B. Tolman, *Biomacromolecules*, 2007, **8**, 3634–3640.

8 D. B. Konwar, S. Sethy, B. K. Satapathy and J. Jacob, *Polymer (Guildf).*, 2017, **123**, 87–99.

9 M. Xiong, D. K. Schneiderman, F. S. Bates, M. A. Hillmyer and K. Zhang, *Proc. Natl. Acad. Sci.*, 2014, **111**, 8357–8362.

10 Y. Picó and D. Barceló, *ACS Omega*, 2019, **4**, 6709–6719.

11 Y. Fan, H. Nishida, Y. Shirai and T. Endo, *Polym. Degrad. Stab.*, 2004, **84**, 143–149.

12 H. Nishida, T. Mori, S. Hoshihara, Y. Fan, Y. Shirai and T. Endo, *Polym. Degrad. Stab.*, 2003, **81**, 515–523.

13 Y. Nakayama, S. Kosaka, K. Yamaguchi, G. Yamazaki, R. Tanaka and T. Shiono, *J. Polym. Sci. Part A Polym. Chem.*, 2017, **55**, 297–303.

14 D. N. Bikiaris, G. Z. Papageorgiou, D. J. Giliopoulos and C. A. Stergiou, *Macromol. Biosci.*, 2008, **8**, 728–740.

15 N. Hegyesi, Y. Zhang, A. Kohári, P. Polyák, X. Sui and B. Pukánszky, *Ind. Crops Prod.*, 2019, **141**, 111799.

16 C. Tsutsumi, N. Hayase, K. Nakagawa, S. Tanaka and Y. Miyahara, *Macromol. Symp.*, 2003, **197**, 431–442.

17 Y. Tokiwa and B. P. Calabia, *J. Polym. Environ.*, 2007, **15**, 259–267.

18 A. Nakayama, N. Yamano and N. Kawasaki, *Polym. Degrad. Stab.*, 2019, **166**, 290–299.

19 K. Mukai, K. Yamada and Y. Doi, *Polym. Degrad. Stab.*, , DOI:10.1016/0141-3910(93)90066-R.

20 K. Kita, K. Ishimaru, M. Teraoka, H. Yanase and N. Kato, *Appl. Environ. Microbiol.*, , DOI:10.1128/aem.61.5.1727-1730.1995.

21 K. I. Kasuya, K. I. Takagi, S. I. Ishiwatari, Y. Yoshida and Y. Doi, *Polym. Degrad. Stab.*, 1998, **59**, 327–332.

22 N. B. Ghanem, M. E. S. Mabrouk, S. A. Sabry and D. E. S. El-Badan, *J. Gen. Appl. Microbiol.*, 2005, **51**, 151–158.

Chapter IV

Synthesis of Biodegradable Thermoplastic Elastomer from 2-methyl-1,3-propanediol, Adipic Acid and L-lactide

1. Introduction

Adipic acid (AA) is a very interesting aliphatic six-carbon diacid used as a building block in the synthesis of polyamides, polyurethanes and polyesters.[1] Recently, new biological pathways were discovered for the bioproduction of AA from different biomass such as glucose[2], lignin[3] and fatty acids . Non-toxic poly(2-methyl-1,3-propanediyl adipate) (PMPA) was used to synthesize photo crosslinked, porous electrospun ultra-fine fibers and mats as solvent stable and thermally stable material.[4] Polymer compound consisting L-lysine and PMPA was found to be a good organogelators which could form organogels in many organic solvents and oils.[5] Nanocomposites were synthesized from carbon nanotube and PMPA in different ratios by Mahyari and his team with high tensile strength and electrical conductivity suitable for industry application.[6] However, to the best of our knowledge, the biodegradability of PMPA has not been reported.

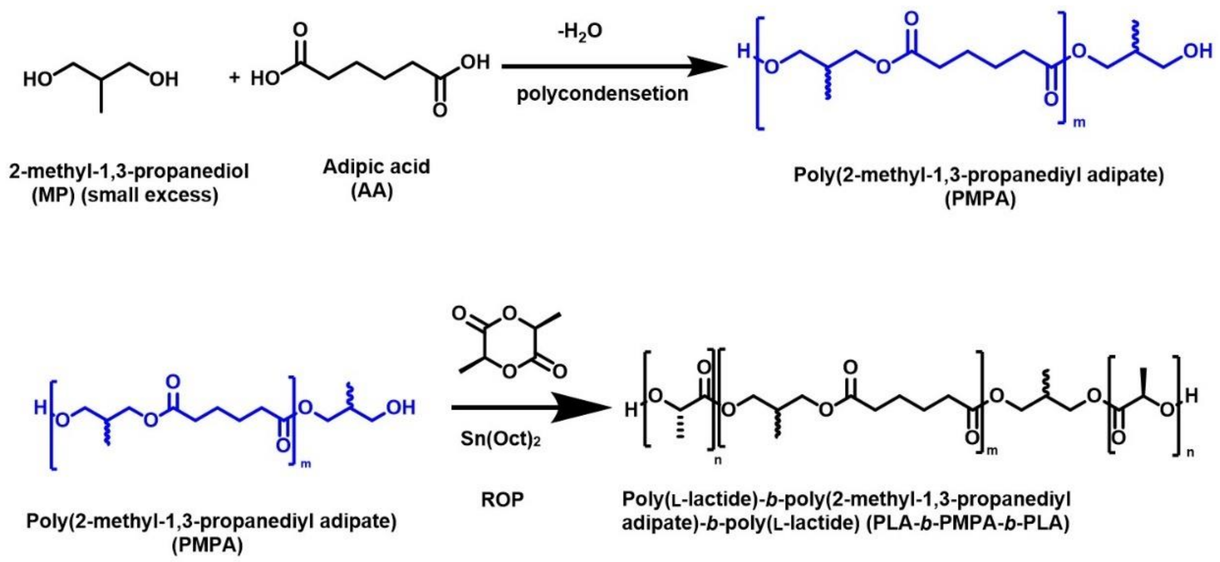
We expected that the replacement of succinate moiety in PLLA-*b*-PMPS-*b*-PLLA with adipate could produce TPE with lower glass transition temperature (T_g) reflecting its higher chain mobility. In this work, aliphatic polyester PMPA was synthesized by melt polycondensation from biobased MP and AA to use as soft midblock of ABA-type thermoplastic elastomer containing PLLA hard segment. Lower T_g value and good biodegradability property of PMPA might have influence on the brittleness, thermal stability and degradability of the PLLA containing TPE to make it suitable for further applications. Overall characterization of synthesized triblock copolymers PLLA-*b*-PMPA-*b*-PLLA as well as PMPA homopolymers were carried out. Their mechanical properties and biodegradable properties were studied to reveal their very high biodegradabilities in seawater.

2. Experimental

2.1 General considerations

All the polymerization reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Varian system 500 spectrometer (500 and 125 MHz for ^{1}H and ^{13}C nuclei, respectively). Chemical shifts of ^{1}H and ^{13}C NMR in chloroform-d were calibrated by using the signals for the residual chloroform ($\delta = 7.26$ ppm) and for chloroform-d ($\delta = 77.16$ ppm), respectively. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) measurements on a Tosoh GPC system (HLC-8320) equipped with RI detector. GPC curves were calibrated using standard polystyrenes. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1.0

mL/min at 40 °C. The melting point (T_m), heat of fusion (ΔH_m) and glass transition temperature (T_g) of the polymers were measured on a differential scanning calorimetry (DSC) using a Seiko DSC 6220 apparatus. The heating rate was 10 °C/min in a nitrogen stream. Thermal history difference in the polymers was eliminated by first heating the specimen to 200 °C, cooling at 10 °C/min to -100 °C, and then recording the second DSC scan at a heating rate of 10 °C/min. T_g of the polymers were determined from the middle point of the phase transition of the second heating scan. The measurement of decomposition temperature losing 5% of sample weight (T_{d5}) was carried out using SII Seiko EXSTAR 6000 TG/DTA 6300 instrument. The tensile tests of the obtained copolymer films were performed by using Shimadzu EZ-LX HS tensile testing machine at an elongation rate of 5 mm/min. Dumbbell-shaped specimens (width, 4 mm; gauge length, 10 mm; thickness, approximately 0.1 mm) were cut from the copolymer sample sheets for the tensile tests. Young's modulus values were determined as the slope of the straight line in the first 2 to 5% of elastic region of the stress-strain curve and the strength and strain at break were determined from the strain at break point of the sample.



Scheme 1. Synthesis of PMPA macroinitiator and PLLA -*block*-PMPA-*block*-PLLA triblock copolymer.

2.2 Materials

L-Lactide (LLA), adipic acid (AA) and 2-methyl-1,3-propanediol (MP) were purchased from Tokyo Chemical Industry. LLA was sublimated under nitrogen before use. MP and AA were used without further purification. THF and toluene were purchased from Kanto Chemical and purified by distillation from sodium benzophenone under nitrogen prior to use. Both solvents were stored over sodium. Tin(II) 2-ethylhexanoate [Sn(Oct)$_2$] was purchased from Sigma Aldrich and stored over activated molecular sieves (3A).

2.3 Synthesis of poly(2-methyl-1,3-propanediyl adipate) (PMPA)

A typical procedure: Hydroxy-telechelic PMPA was synthesized from MP (small excess) and AA using two-stage reaction of esterification and simple polycondensation processes using $Sn(Oct)_2$ as the catalyst (scheme 1). After placing MP (20.3 g, 0.225 mol), AA (29.93 g, 0.205 mol) and catalyst $Sn(Oct)_2$ (0.004 g, 0.1 mmol) into a reactor, the mixture was heated slowly to 180 °C under N_2 gas atmosphere (1 atm). H_2O was collected using a trap device and esterification was continued for 90 mins. To remove the excess glycol and promote the chain extension, polycondensation process was conducted. The temperature was kept at 180 °C at pressure below 1.0 mmHg and the reaction continued for predetermined time. The synthesized polyester was dissolved in chloroform and then precipitated into 10 times larger amount of methanol. The precipitates were washed with methanol and finally dried in vacuo at room temperature for 2-3 days.

2.4 Polymerization of L-lactide using PMPA as a Macroinitiator

A typical procedure ($[LLA]_0 : [PMPA]_0 = 100:1$): At first, 3 ml toluene and PMPA-2 (0.19g, 1.7×10^{-2} mmol) were placed into a 10 ml Schlenk tube and the mixture was stirred at room temperature to dissolve it properly for about 1 hr. Then LLA (0.25g, 1.73mmol) was added to the solution of PMPA in toluene and the tube was dipped in the oil bath to dissolve LLA at 100 °C. After dissolving properly, catalyst $Sn(Oct)_2$ (0.18 mg, 0.004 mmol) was injected into the mixture. The polymerization was proceeded at 100 °C for 24 hrs. After the polymerization, the reaction was quenched with acidic methanol and the mixture was poured into methanol. The precipitated triblock copolymer was collected by centrifugation and dried in vacuo at room temperature for 24 hrs (91 wt% yield).

2.5 Preparation of Films of the Triblock Copolymers

To prepare the film sample for measurements, PLLA-*b*-PMPA-*b*-PLLA (0.30 g) was dissolved in toluene (4.0 mL) at 100 °C. The solution was cast on a PTFE plate followed by evaporation of solvent under atmospheric pressure at room temperature for 3 days which was further dried in vacuo at room temperature for 1 day.

2.6 Biodegradability test of the polymers

Enzymatic biodegradation: Proteinase K and lipase PS were applied for the enzymatic biodegradation tests of the polymers. 0.02 M Phosphate buffer (pH = 8.0) was used to prepare enzyme solution (1 mg/0.02 M buffer). A polymer sample (10 mg) was added to a vial filled with 1 ml phosphate buffer and 1 ml H_2O that contained 0.5 ml of proteinase K or lipase PS solution. The reactions were carried out by shaking the vial at 45 °C for 6 hrs and 24 hrs separately. Finally, the solution was filtered and stored in the refrigerator (-30 °C) until total organic carbon concentration (TOC) measurement. Each degradation test was repeated twice and averaged by using TOC analyzer (Shimadzu TOC-VCSH).

Seawater biodegradation: Biodegradation lab test of the obtained polymers in seawater was evaluated from determination of oxygen consumption using BOD tester (TAITEC, BOD200F). Seawater was taken at the shoreline from the sea surface of Osaka South Port area with bucket and was used within one or two days. Typically, 30 mg of polymer specimen was added into 250 mL BOD testing bottle each and then 200 mL supernatant of seawater was added. Evolved carbon dioxide (CO_2) was removed by calcium hydroxide from the BOD closed system. The biodegradation test was carried out at 27 °C with stirring for 28 days. The observed O_2 consumption volume was corrected by subtraction to O_2 consumption volume of the control. The theoretical O_2 consumption volume was calculated according to the structure formula of polymers that degraded products are completely mineralized to CO_2. Each biodegradation test was repeated twice and averaged. Biodegradation (%) of the polymers was calculated according to the following equation:

% Biodegradation = (Absorbed O_2 consumption volume/ theoretical O_2 consumption volume) x 100

3. Result and discussion

3.1 Preparation of PMPA-diols

PMPAs with different molecular weights were synthesized following a two stage of polycondensation method from MP and AA in bulk. In the 1st step, esterification between MP and AA using excess diol at a MP to AA feed ratio of 1.1:1 at 180 °C under N_2 (1atm) with removing H_2O resulted in a mixture of PMPA oligomers having MP units at the both ends. In the second step of the polycondensation, the transesterification of the previously synthesized PMPA oligomers was performed under reduced pressure at 180 °C for different time using $Sn(Oct)_2$ as a catalyst with removing excess MP to bring out a significant increase in molar masses of the products (Table 1). With high vacuum and suitable temperature, this melt polycondensation process guaranteed relatively high molecular weight of the PMPA.

The PMPAs were obtained in >90% yields as colorless viscous liquids. Successful synthesis of PMPA was verified by ^{1}H-NMR and GPC analysis. A typical 500 MHz ^{1}H-NMR spectrum of a PMPA-diol is shown in figure 1. The signals at $\delta = 0.98$ (D), 1.62 (F), 2.16 (C) and 2.33 (A) ppm were ascribed to CH_3- protons from MP repeating units, -CO-CH_2-CH_2- protons from adipate repeating units, -O-CH_2-CH-(-CH_3)-CH_2-O- protons from MP repeating units and -CO-CH_2- protons from adipate repeating units. The presence of ester function was verified by the signal at 3.97- 4.03 (B) ppm assigned to -COO-CH_2- protons from

MP repeating units. In addition, the resonance peak of the methylene proton linked to the terminal hydroxyl group was observed at 3.52 ppm with low intensity in figure 2 (peak E of PMPA), indicating -OH terminated structure of PMPA similar to that of PMPS-diols.[7]

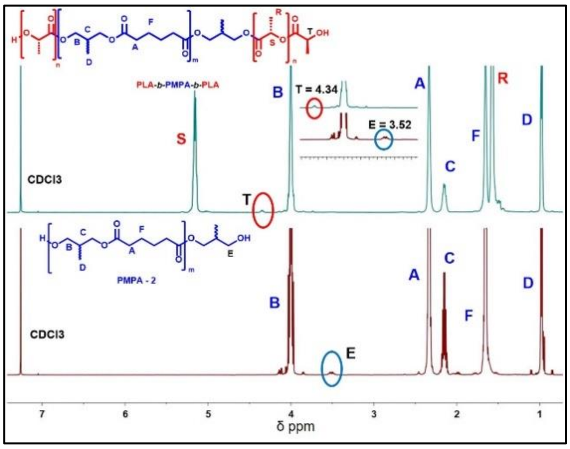


Figure 1. ^{1}H-NMR spectrum of PMPA-2 and PLLA-*b*-PMPA-*b*-PLLA (TPE100) (CDCl$_3$, r.t., 500 MHz).

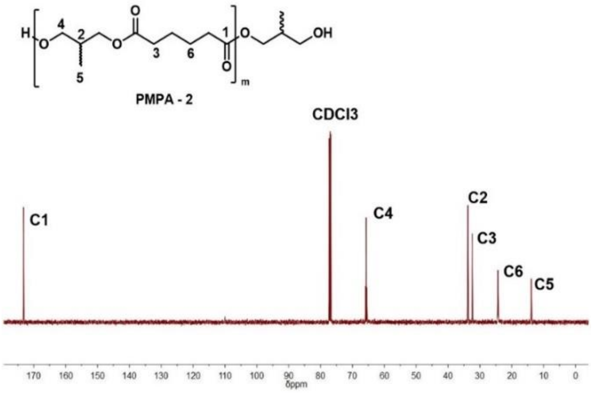


Figure 2. ^{13}C-NMR spectrum of PMPA-2.

In a 125 Hz ^{13}C-NMR spectrum of the macroinitiator PMPA (Figure-2), three resonances at δ = 65.67 (C4), 33.75 (C2) and 13.89 (C5) ppm are associated with carbons derived from the MP monomer. The signals of the α-carbon (CO-*C*H$_2$-), β-carbons (CO-CH$_2$-*C*H$_2$) and the carbonyl carbons (*C*O-) of the adipate moiety appeared at δ = 32.39 (C3), 24.32(C6) and 173.17 (C1) ppm, respectively.

Table 1. Synthesis of PMPG-diol by two stage polycondensation of MP and AA[a]

Sample	**Time [min] (2^{nd} stage)**	**Yield (%)**	**M_n [b] ($\times 10^3$) [g mol^{-1}]**	**M_w/M_n [b]**	**T_g [c] [°C]**	**T_{d5} [d] [°C]**
PMPA-1	70	91	13.9	1.59	-45.8	351
PMPA-2	35	93	10.8	1.77	-51.3	326
PMPA-3	25	94	9.1	1.84	-52.7	345

[b] Determined by GPC in THF calibrated with standard polystyrene. [c] Determined with DSC 2nd heating scan. [d] Decomposition temperature losing 5% of sample weight.

The PMPA-diol samples obtained from the polycondensation under vacuum conditions for 70, 35 and 25 mins are named as PMPA-1, PMPA-2 and PMPA-3 respectively. The M_n of these PMPA-diols was controlled by the polycondensation time. The prepared each PMPA-diol exhibits a single elution peak in the GPC curves (Figure 4) showing increasing number average molecular weight (M_n) with time. The polydispersities (M_w/M_n) were 1.59, 1.77 and 1.84 for PMPA-1, 2 and 3, respectively.

Figure 5 shows the DSC curves of the obtained PMPAs. The T_m peak could not be identified for any of the PMPAs which represented their amorphous nature. The glass transition temperatures of the obtained PMPAs were observed at around -50 °C upon heating at 10 °C/min and inclined to rise with increasing their molecular weight, that resulted in a very sticky transparent polymer to be used in the next step. These T_g values of the the PMPAs were satisfactorily low to be considered as soft segment for PLLA-conjugated triblock copolymers and lower than that of PMPS[7], which should make the resulting triblock copolymers applicable to the use at lower temperature. Moreover, it is expected that the higher molecular weight of the resulting TPE could be achieved if comparatively higher molecular weight soft segment can be used as macroinitiator in the LLA polymerization step. Thus, PMPA-2 got selected as soft block of the following PLLA-based triblock copolymers having relatively low T_g and high M_n. The thermal decomposition temperature of the PMPA ranged from 345 to 351 °C is similar to those of PMPS.[7]

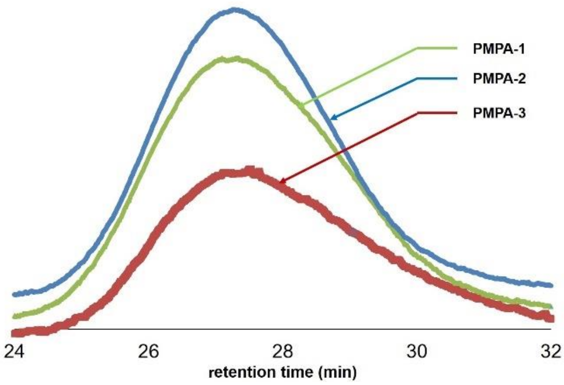


Figure 3. GPC curve of PMPA-1, PMPA-2 and PMPA-3.

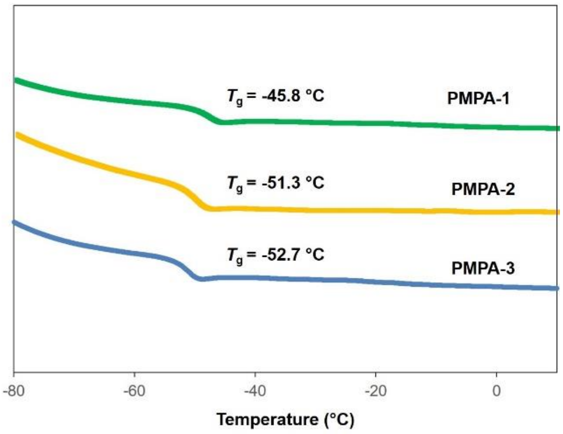


Figure 4. DSC curves of PMPA collected upon cooling and heating. The cooling and heating rate at 10 °C/min.

3.2 Synthesis of ABA triblock copolymers

PLLA-*b*-PMPA-*b*-PLLA triblock copolymers were prepared by the ring-opening polymerization (ROP) of LLA using the PMPA-2 as the macroinitiator at different feed ratio of LLA and PMPA (Table 2) in the presence of $Sn(Oct)_2$ as a catalyst. The products were obtained as colorless solids in contrast to a viscous liquid PMPA-2. The synthesized copolymers were analyzed through NMR and GPC primarily to verify successful synthesis of the copolymers. Different lactide-to-macroinitiator feed ratio were used to synthesize copolymers to check the effects of the composition and block length on polymer properties. Molecular weight distributions were relatively narrow in addition to high yields of ring-opening polymerization of lactide.

In the ^{1}H NMR spectra of the PLLA-*b*-PMPA-*b*-PLLA as shown in Figure 1, the signal due to the hydroxyl terminal of the original PMPA-diol shown at 3.52 (peak E) has completely been replaced by the signal of the hydroxyl terminal of PLLA detected at 4.34 ppm (peak T) as the PLLA chains have grown from the hydroxyl tails of the PMPA-diol. Triblock copolymers exhibited a quartet peak at 5.2 ppm, which was a characteristic peak of the methine proton in PLLA blocks in addition of PMPA blocks. Another characteristic double peak for methyl proton in PLLA block appeared at around 1.6 ppm.[8] These observations indicated that PLLA had been incorporated into the polymer chains successfully.

The 125 MHz ^{13}C-NMR spectrum of the PLLA-*b*-PMPA-*b*-PLLA revealed the signals, C9 ($\delta = 169.4$ ppm), C8 ($\delta = 16.7$ ppm) and C7 ($\delta = 69.1$ ppm) derived from the carbonyl, methyl and methylene carbons in the PLLA repeating units, respectively (Figure 5). Besides the clear signals for PMPA repeating units, no other signals were found which could be formed by the transesterification reaction.[9]

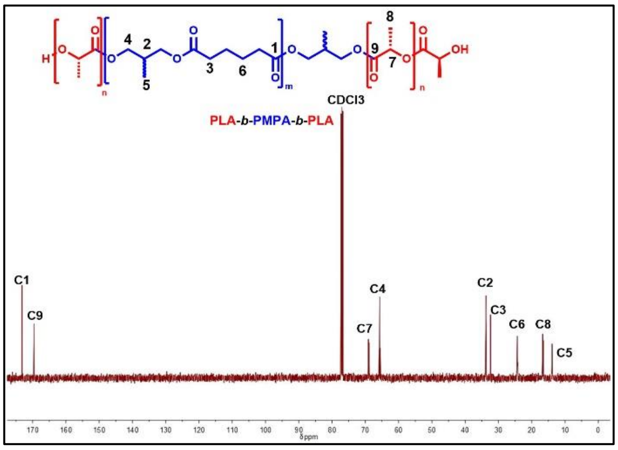


Figure 5. ^{13}C-NMR spectrum of PLLA-*b*-PMPA-*b*-PLLA (TPE100) ($CDCl_3$, r.t., 125 MHz).

Figure 6 shows the typical GPC curves of the PLLA-*b*-PMPA-*b*-PLLAs and the PMPA-diol used as the macroinitiator. The GPC curves shifted from lower molecular weight region to higher molecular weight region with increasing feed $[LLA]_0$/[PMPA-2] ratio and indicated the successful block copolymerization. This shifting was linearly correlated with the change of lactide/PMPA feed ratio which suggested efficient copolymerization with no residual macroinitiator.

Table 2. The ROP of L-LA catalyzed by Sn(Oct)$_2$ using PMPA-2 as macroinitiator [a]

Sample	Feed Ratio [LLA]$_0$: [PMPA-2]	Yield [%]	$M_{n(GPC)}$[b] (×10^3) [g mol^{-1}]	$M_{n(NMR)}$[c] (×10^3) [g mol^{-1}]	M_w/M_n[b]	f_{LLA}[c] [mol%]
TPE100	100:1	91	22.8	20.0	1.3	53.7
TPE75	75:1	91	20.3	18.6	1.4	46.0
TPE50	50:1	91	18.7	17.3	1.4	40.6
TPE25	25:1	90	16	15.3	1.3	32.8
PLLA-1[143]	50:1[d]	97	5	5.7	1.4	-
PLLA-2[143]	25:1[d]	97	3	3.1	1.4	-

[a] PMPA-2 (M_n = 10.8×10^3 gmol^{-1}, M_w/M_n = 1.61, T_g = -27.7 °C), Cat = Sn(Oct)$_2$ (4 ×10^{-3} mmol), [LLA]$_0$: [Cat] = 400 : 1, temp = 100 °C, time = 24 hrs. [b] Determined by GPC in THF calibrated with standard polystyrene. [c] Determined by ^{1}H-NMR analysis. [d] BnOH was used as macroinitiator instead of PMPA-2.

Table 2 summarized all the properties analyzed by GPC and NMR characterization. The homopolymers PLLA-1 and PLLA-2, with similar chain length to those of the PLLA segments in TPE100 and TPE50, were previously synthesized by ROP using BnOH as initiator and Sn(Oct)$_2$ as catalyst for comparison.[7] The M_w/M_n of synthesized copolymers were narrower than that of the macroinitiator (PMPA-2, M_w/M_n = 1.8) and PLLA block length increased when LLA/PMPA feed ratio was changed from 25 to 100 indicating their controllable PLLA block length.

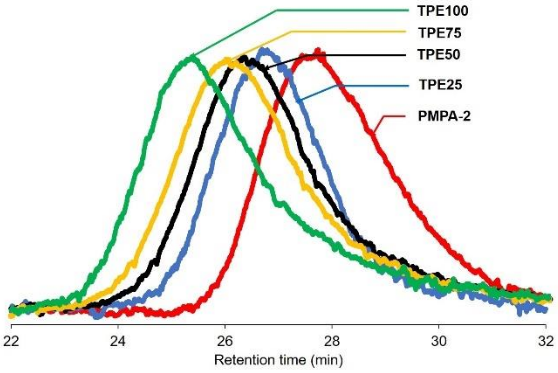


Figure 6. GPC curves of PLLA-*b*-PMPA-*b*-PLLA samples (TPE100,75,50 and 25) and PMPA-2.

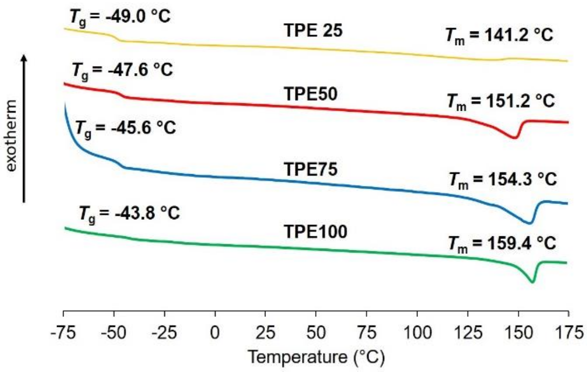


Figure 7. DSC curves of PLLA-*b*-PMPA-*b*-PLLA samples (TPE100, 75, 50 and 25) collected in the 2nd heating scan. Both the cooling and heating rates are 10 °C/min.

Besides GPC, molecular weights of the triblock copolymers were also estimated from the NMR spectra by comparing NMR peak intensities of respective main chains with that of the end group as included in Table-2. Both GPC and NMR data were in good agreement and approved the successful synthesis of PLLA-*b*-PMPA-*b*-PLLA.

3.3 Thermal Properties of PLLA-*b*-PMPA-*b*-PLLA

The thermal properties and crystallization behavior of the triblock copolymer, PLLA-*b*-PMPA-*b*-PLLA are investigated and summarized in Table 3 and the relative calorimetric curves are reported in Figure 7. At first, the copolymers were analyzed by DSC in order to compare their crystallization and melting behavior. The low T_g values of the copolymers at around −43.8-−49.0 °C was corresponding to the T_g value of the PMPA soft segment, although these values are little higher than pure PMPA-2 (−51.3 °C) due to the restriction by PLLA segment. Only one T_g indicated that PLLA and PMPA segments are partly miscible in the copolymer.

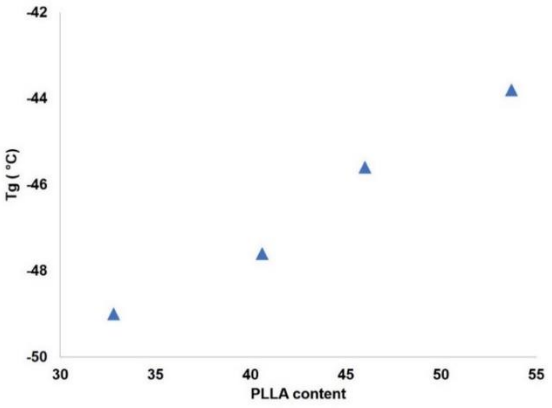


Figure 8. T_g vs PLLA content of copolymers.

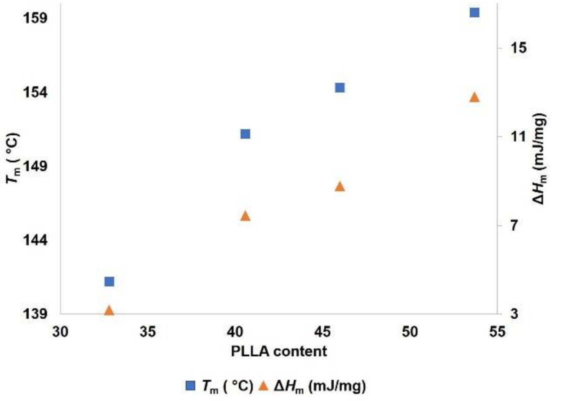


Figure 9. T_m (°C), ΔH_m (mJ/mg) vs PLLA content of copolymers.

Figure 8 shows the plot of T_g of the block copolymers as a function of the PLLA content, exhibiting a clear linear relationship. No crystallization peak was observed in the thermal curve of the copolymers. This could come from enhanced crystallization of the PLLA segment in the preceding cooling process due to high mobility of the PMPA segment. The melting points, T_m, were observed at 159.4, 154.3, 151.2 and 141.2 °C for the TPE100, 75, 50 and 25, respectively, which must come from the PLLA segment as PMPA was amorphous with no melting peak. These T_m values showed linear relationship with the PLLA content where the melting peak shifted to the higher temperature when the block length of PLLA segment was increased. T_m and ΔH_m of the copolymers are plotted as a function of the PLLA contents in Figure 9. Higher PLLA content resulted in higher ΔH_m values and thus showed linear relationship with each other. The embedded PMPA segment could not occupy the crystal space of the PLLA segment. So, the melting and crystallization behavior of PLLA was almost unaffected by the PMPA segment in the copolymers.

Thermogravimetry (TG) analysis of the PLLA-*b*-PMPA-*b*-PLLAs was used to further study the differences in their thermal stability (Figure 10). Their thermal degradation process could be divided into two steps. The first degradation stage started at around 200 - 230 °C can be attributed to the degradation of PLLA block, followed by the degradation of the PMPA segment started at around 240 – 270 °C. The weight loss at the first stage increased with increasing PLLA contents in the triblock copolymers. The copolymers containing shorter PLLA block showed higher T_{d5} value but lower than that of PMPA macroinitiator. The residual Sn catalyst in the triblock copolymers could cause their relatively low thermal stabilities. It is reported that acylation process of the terminal hydroxy group could improve the T_{d5} value about 40-50 °C in case of PLLA.[10-12] The T_g values of the present PLLA-*b*-PMPA-*b*-PLLAs are significantly lower than those of PLLA-*b*-PMPS-*b*-

PLLAs[7] reflecting lower T_g of PMPA than that of PMPS. The T_m values of the PLLA-*b*-PMPA-*b*-PLLAs were relatively high in comparison with those of the PMPS analogs with similar compositions.

Table 3. Thermal properties of the synthesized triblock copolymers, PLLA-*b*-PMPA-*b*-PLLA

Sample	**Feed Ratio $[LA]_0$: [PMPA-2]**	**f_{LLA} [mol%]**	**T_g[a] [°C]**	**T_m[a] [°C]**	**ΔH_m[a] [J/g]**	**T_{d5} [°C]**
TPE100	100:1	53.7	-43.8	159.4	12.8	245.1
TPE75	75:1	46.0	-45.6	154.3	8.77	251.5
TPE50	50:1	40.6	-47.6	151.2	7.44	256.0
TPE25	25:1	32.8	-49.0	141.2	3.18	256.7

[a] Determined by DSC at 2nd heating scan. [b] Decomposition temperature losing 5% of sample weight.

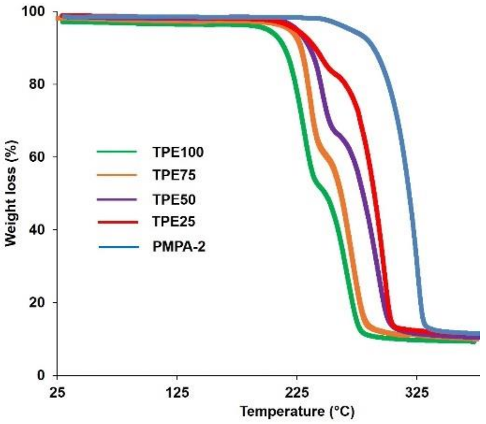


Figure 10. TG curves of PLLA-*b*-PMPA-*b*-PLLAs (TPE100, 75, 50 and 25) and PMPA-2.

3.4 Mechanical properties of the copolymer films

Enough mechanical properties are much needed for practical use as newly emerged polymeric materials. So, the tensile properties of TPE100, 75, 50 and 25 were assessed to understand their mechanical behavior. For that purpose, each of the copolymers was casted into thin self-standing film (thickness: approximately 0.1 mm) from toluene solution and cut into a nonstandard dumbbell shape. The soft segment, PMPA could not be shaped accordingly because of its viscous nature. Figure 11(a) plots the typical tensile curves of the copolymers. The Young's modulus, tensile stress and elongation at break (%) are listed in table 4.

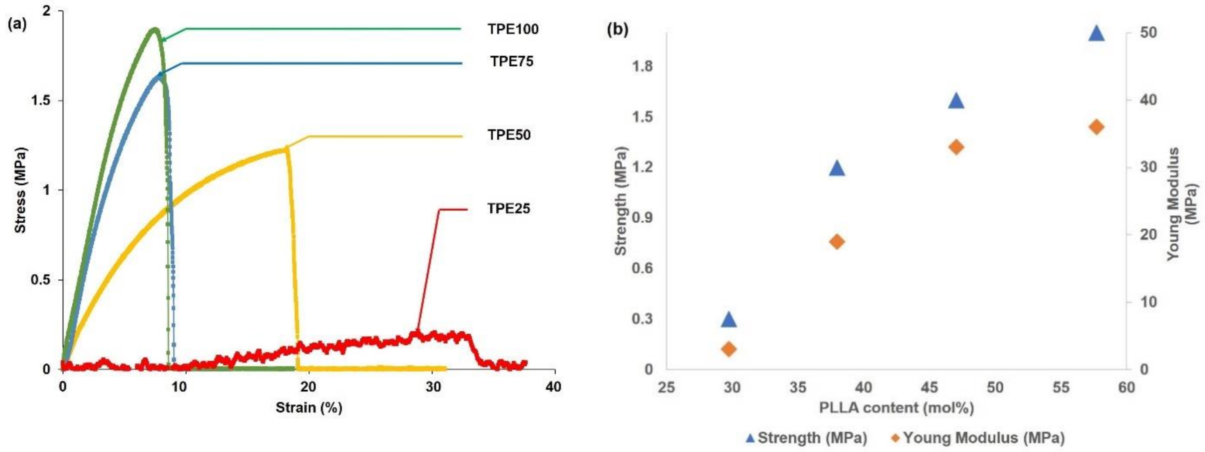


Figure 11. Comparison of tensile properties of the copolymer films of TPE100, TPE75, TPE50 and TPE25 (a) Stress-strain curves (b) Plots of tensile strength and Young Modulus vs. PLLA content.

All the copolymers were semicrystalline with chain of amorphous soft segment, so they performed as typical flexible semicrystalline plastics, exhibiting elastic deformation. Modulus and tensile stress at yield are influenced mainly by crystallinity. The copolymers showed stress value from 0.3 to 2.0 MPa which increased in the following order: TPE25 < 50 < 75 < 100 in well agreement with the crystallinity order.

Table 4. Mechanical properties of the triblock copolymers

Sample	**FPLLA[a] [mol%]**	**Young modulus [MPa]**	**Strength[b] [MPa]**	**Strain at break [%]**	**Sample**	**FPLLA[a] [mol%]**
TPE100	53.7	36	2.0	10	TPE100	53.7
TPE75	46.0	33	1.6	10	TPE75	46.0
TPE50	40.6	19	1.2	18	TPE50	40.6
TPE25	32.8	3	0.3	34	TPE25	32.8

[a] Calculated from ^{1}H NMR. [b] Strength is defined as the stress at the strain at break. Determined by tensile tester with elongation rate 3.5 mm/min. Number of measurement times 3.

Molecular weight and PLLA chain length are important factor for modulus and strength value. The highest strength value of TPE100 can be explained by its molecular weight and crystallinity. All the copolymers showed much lower young modulus than typical PLLA.[13] Therefore, these triblock copolymers are much softer than PLLA. From Figure 11 (b), it is seen that both strength and modulus series maintained almost linear relationship with PLLA content in the copolymers. These trends are similar to those of the previously synthesized PLLA-*b*-PMPS-*b*-PLLA by our group. Lower Young modulus and strength values of the newly synthesized PLLA-*b*-PMPA-*b*-PLLA in this work than those of the previous PLLA-*b*-PMPS-*b*-PLLA reveals that the former is softer than the latter.[7]

3.5 Biodegradability of the synthesized copolymers

The enzymatic degradation of the triblock copolymers was evaluated using two different enzymes, i.e., proteinase K and Lipase PS. This is due to the difference in specificity of the enzymes for the kinds of polymers. Chemical structure, molecular weight, the specific solid-state morphology, crystallinity etc. can also greatly influence the rate of enzymatic degradation of polyesters.[14] Proteinase K as hydrolytic catalyst proved its high efficiency for the degradation of PLLA.[15] Lipase PS was reported to be very competent for the degradation of poly(alkanediyl dicarboxylate). [16-18]

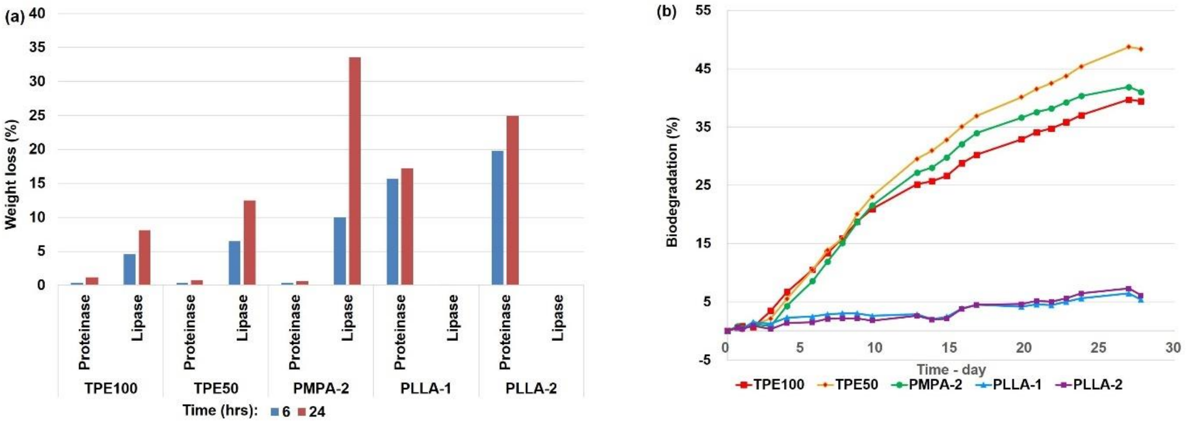


Figure 12. Comparison of (a) weight loss % due to enzymatic degradation using proteinase K and lipase PS (b) seawater biodegradation % of the copolymers, PMPA-2 and PLLA homopolymers.

Degradation behaviors of the copolymers were monitored in view of weight loss (%) for both enzymes. Figure 12a shows the loss of weight of the PMPA soft polymer, PLLA homopolymers (PLLA-1: M_n = 5000 g/mol; PLLA-2: M_n = 3100 g/mol) and PLLA-*b*-PMPA-*b*-PLLA triblock copolymers during proteinase K and lipase PS catalyzed enzymatic hydrolysis. The weight loss was measured after 6 hrs and 24 hrs. The results of PLLA-1 and PLLA-2 are the same data in our previous report.[7] It is observed that for all samples, (%) loss of weight was increased with time from 6 hrs to 24 hr in the presence of both enzymes. There was no significant weight loss even after 24 hours for the homopolymer PLLA-1 and PLLA-2 immersed in the buffer solution with lipase PS, while proteinase K degraded those PLLA homopolymers by 15-25% (Figure 12a).[7] Table 5 represents comparative study of weight loss (%) of previously reported biodegradable PLLA-*b*-PMPS-*b*-PLLA and newly synthesized PLLA-*b*-PMPA-*b*-PLLA copolymers by proteinase K and Lipase enzymes. For the case of PMPA homopolymer, the rate of degradation is about 50 times higher by lipase PS compared to proteinase K and PMPA is more degradable by lipase PS than PMPS. Despite the significant PLLA contents in TPE50 and 100, they showed low degradation of less than 2% by proteinase K, indicating the hindrance of PLLA degradation by PMPA. Similar tendency was observed for the previous PLLA-*b*-PMPS-*b*-PLLA triblock copolymers.[7] On the other hand, triblock copolymers exhibited considerable degradation by lipase PS. It may cause due to the presence of PMPA segment which lost

33.54% of its weight in one day by lipase. TPE50 showed higher degradation rate than that of TPE100 by lipase PS. This might be explained by the effect of the molecular weights and PMPA-contents of the copolymers. The high activity of lipase for PMPA segment could dominate the overall degradation of the triblock copolymers by lipase PS.

Table 5. Rough comparison of weight loss (%) of different polymers by enzyme

Sample	**Weight loss by Proteinase K in 24 hrs (%)**	**Weight loss by Lipase PS in 24 hrs (%)**
TPE100	1.13	8.11
TPE50	0.48	12.48
PMPA	0.58	33.54
PLLA-1	17.21	0.01
PLLA-2	24.92	0.06
PLLA-*b*-PMPS-*b*-PLLA ([LLA]/[PMPS] = 100) [143]	2.94	1.52
PLLA-*b*-PMPS-*b*-PLLA ([LLA]/[PMPS] = 50) [143]	0.69	2.08
PMPS [143]	1.03	3.66

In the case of proteinase K, our previously reported polymer PLLA-*b*-PMPS-*b*-PLLA showed the highest weight loss (%) in one day among the present PLLA-*b*-PMPA-*b*-PLLA (TPE100 and 50) and PLLA-*b*-PMPS-*b*-PLLA copolymers. On the other hand, PLLA was reported to be mostly degraded by proteinase K in different conditions from our work.[19]

Due to the vulnerable consequence of pollution by the waste plastic debris in the sea water, recently marine biodegradation test for the plastic polymers has been widely practiced by the researchers to ensure a healthy environment for the sea animals.[18] Figure 12b represents the resultant biodegradation (%) of PMPA, PLLA homopolymers and synthesized triblock copolymers plotted against the number of days when these samples were exposed to the seawater. This test was based on the amount of O_2 consumption caused by the microorganism in the seawater with samples which was monitored every day for total 28 days in a row for each sample. Biodegradation BOD test was carried out at 27 °C with the seawater collected at Osaka port area. From the very early stage of experiment, O_2 consumption started for all samples and gradually increased. In our previous study, PLLA-2 about 11% after 28 days was more degraded than PLLA-1 (about 4% after 28days), while the present degradation test showed their similar degradation of about 6%. This could come from the difference of seawater, the one used for the former test was collected in March and the one used for the latter test was collected in June. PMPA was found to be highly biodegradable in seawater, which reached 40% of biodegradation within 28 days. The TPE50 and 100 also exhibited high biodegradabilities similar to that of PMPA.

Tsuji and his co-workers carried out comparative degradation of PCL, PLLA and poly(3-hydroxybutyrate) (PHB) at 25 °C in the controlled seawater and reported no significant degradation for PLLA films. They concluded as the pore formation and surface erosion mechanism to be responsible for the degradation of PCL and PHB films in controlled seawater.[20] Among some so-called biodegradable polyesters PCL, PLLA, PHB, poly(butylene adipate terephthalate) (ecoflex) and poly(lactic-*co*-glycolic acid) (PLGA), PLGA showed the highest and 100% degradation in 270 days in controlled seawater degradation test conducted for 365 days.[21]

Although the results of the biodegradation tests in seawater are considerably dependent on the conditions such as used seawater i.e. tide, preservation of seawater, sampling place, population of microorganism, seawater temperature and so on[22], the biodegradabilities of the present copolymers and PMPA in seawater were roughly compared with those of the other reported examples depending on the time required to degrade fully in seawater under certain testing conditions assuming linear relationship between biodegradation with time (Table 6). Among all the polymers mentioned in the Table 6, the PLLA-*b*-PMPA-*b*-PLLA and PMPA synthesized in this work indicated comparable biodegradability in seawater to those of PHBs. Thus, PLLA-*b*-PMPA-*b*-PLLA and PMPA seems more biodegradable than PMPS, PBS, PCL and PLLA, comparable to PHB[22]. The high biodegradability of TPE100 and TPE50 can be attributed to the influence of the PMPA soft segment. TPE50 containing higher PMPA-content (mol%) showed the slightly faster degradation than TPE100 with lower PMPA-content. The upward trend line of biodegradation (%) was followed by every sample up to 27 days.

Table 6. Rough comparison of biodegradation (%) of different biodegradable polymers by seawater.

Sample	Biodegradation in seawater per day (%)	Approx. biodegradation in a year (%)	Time required to degrade 100%
PLLA-*b*-PMPA-*b*-PLLA	1.80	657	less than 2 months
PMPA	1.52	555	2 months 6 days
PLLA-*b*-PMPS-*b*-PLLA[7]	0.37	135	9 months
PMPS	0.20	73	About 1.5 years
PLLA[21]	-	-	-
PHB[20]	0.02	7.3	14 yrs
PCL[21]	0.35	128	9.5 months
Ecoflex[22]	0.00	0.5	200 yrs
PBS[23]	0.01	3.65	28 yrs
PLGA[22]	0.37	135	9 months

"-" = did not degrade significantly.

4. Conclusions

Very common and relatively cheap monomers, MP, AA and LLA were used to synthesize biodegradable thermoplastic elastomers which can potentially be used for various applications i.e. to produce fibers, film, vehicle interiors, appliance components, foot wares, food/beverage packaging, etc. A series of triblock copolymers, PLLA-*b*-PMPA-*b*-PLLA, composed of the soft PMPA midblock and hard PLLA end blocks with different molecular weight, was synthesized by the ROP of LLA using PMPA-diol as a macroinitiator using $Sn(Oct)_2$ as a catalyst. The triblock copolymers exhibited T_g at below -40 °C for the soft segment and T_m at 141-159.5 °C for the PLLA segment. The triblock copolymer and PMPA were found to have high biodegradability in seawater along with satisfactorily high degradation by enzymatic hydrolysis. Thus, the newly synthesized copolymers can have big contribution to balance the ecosystem of our environment.

5. References

1 T. Debuissy, E. Pollet and L. Avérous, *Polymer (Guildf).*, 2016, **99**, 204–213.

2 T. Polen, M. Spelberg and M. Bott, *J. Biotechnol.*, 2013, **167**, 75–84.

3 D. R. Vardon, M. A. Franden, C. W. Johnson, E. M. Karp, M. T. Guarnieri, J. G. Linger, M. J. Salm, T. J. Strathmann and G. T. Beckham, *Energy Environ. Sci.*, 2015, **8**, 617–628.

4 L. Jun, Y. Zhang, Y. Hao, L. Cheng and J. J. Zhang, *J. Appl. Polym. Sci.*, 2009, **112**, 2247–2254.

5 M. Suzuki, C. Setoguchi, H. Shirai and K. Hanabusa, *Chem. - A Eur. J.*, 2007, **13**, 8193–8200.

6 R. Shamsi, M. Mahyari and M. Koosha, *J. Appl. Polym. Sci.*, , DOI:10.1002/app.44567.

7 L. Zahir, T. Kida, R. Tanaka, Y. Nakayama, T. Shiono, N. Kawasaki, N. Yamano and A. Nakayama, *Polym. Degrad. Stab.*, 2020, **181**, 109353.

8 Y. Nishiwaki, K. Masutani, Y. Kimura and C. Lee, *J. Polym. Sci.*, 2020, **58**, 860–871.

9 B. Gupta, N. Revagade and J. Hilborn, *Prog. Polym. Sci.*, 2007, **32**, 455–482.

10 Y. Fan, H. Nishida, Y. Shirai and T. Endo, *Polym. Degrad. Stab.*, 2004, **84**, 143–149.

11 H. Nishida, T. Mori, S. Hoshihara, Y. Fan, Y. Shirai and T. Endo, *Polym. Degrad. Stab.*, 2003, **81**, 515–523.

12 Y. Nakayama, N. Matsubara, Z. Cai, T. Shiono, K. Inumaru and H. Shirahama, *Polym. Degrad. Stab.*, 2017, **141**, 97–103.

13 Y. Nakayama, K. Aihara, H. Yamanishi, H. Fukuoka, R. Tanaka, Z. Cai and T. Shiono, *J. Polym. Sci. Part A Polym. Chem.*, 2015, **53**, 489–495.

14 D. N. Bikiaris, G. Z. Papageorgiou, D. J. Giliopoulos and C. A. Stergiou, *Macromol. Biosci.*, 2008, **8**, 728–740.

15 N. Hegyesi, Y. Zhang, A. Kohári, P. Polyák, X. Sui and B. Pukánszky, *Ind. Crops Prod.*, 2019, **141**, 111799.

16 C. Tsutsumi, N. Hayase, K. Nakagawa, S. Tanaka and Y. Miyahara, *Macromol. Symp.*, 2003, **197**, 431–442.

17 Y. Tokiwa and B. P. Calabia, *J. Polym. Environ.*, 2007, **15**, 259–267.

18 Y. Picó and D. Barceló, *ACS Omega*, 2019, **4**, 6709–6719.

19 M. Zenkiewicz, A. Richert, R. Malinowski and K. Moraczewski, *Polym. Test.*, 2013, **32**, 209–214.

20 A. Nakayama, N. Yamano and N. Kawasaki, *Polym. Degrad. Stab.*, 2019, **166**, 290–299.

21 H. Tsuji and K. Suzuyoshi, *Polym. Degrad. Stab.*, 2002, **75**, 347–355.

22 A. R. Bagheri, C. Laforsch, A. Greiner and S. Agarwal, *Glob. Challenges*, 2017, **1**, 1700048.

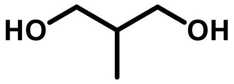
23 K. I. Kasuya, K. I. Takagi, S. I. Ishiwatari, Y. Yoshida and Y. Doi, *Polym. Degrad. Stab.*, 1998, **59**, 327–332.

Chapter-V

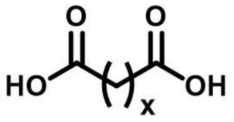
Summary

ABA type triblock copolymers consisting of PLLA hard end blocks and biodegradable aliphatic polyester soft midblock can work as fully biodegradable thermoplastic elastomer (TPE) to mitigate the problem of white pollution.

From that point of view, a series of TPEs have been systematically synthesized incorporating different soft blocks from 2-methyl-1,3-propanediol (MP) and dicarboxylic acid with PLLA and their thermal, mechanical and biodegradation properties were investigated in this study.



2-methyl-1,3-propanediol
(MP) (small excess)



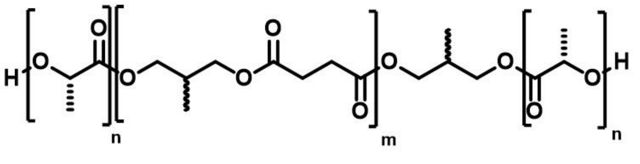
x=2, succinic acid (SA)
x=3, glutaric acid (GA)
x=4, adipic acid (AA)

Chapter I: General introduction

The source, manufacturing process, application, physical and chemical properties and degradation mechanism of PLLA were described. The synthesis, structure and properties of so far reported having polylactide blocks were briefly reviewed.

The purpose of this work was described and outline of each chapter was introduced.

Chapter II: Synthesis of Biodegradable Thermoplastic Elastomer from 2-Methyl-1,3-propanediol, Succinic Acid and L-Lactide



PLLA-*b*-PMPS-*b*-PLLA (TPE-S)

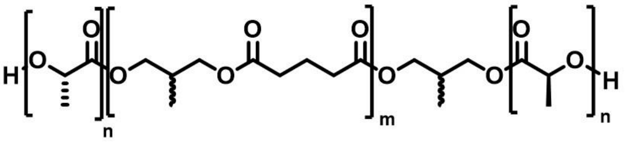
In this chapter, succinic acid was chosen as a diacid because it can be produced from biomass and the resulting polyesters can be biodegradable. PMPS was prepared from polycondensation of MP and SA. Triblock copolymers, PLLA-*b*-PMPS-*b*-PLLA(TPE-S) were synthesized using PMPS as a macroinitiator in the ROP of LLA.

From the analysis of thermal property, the TPE-Ss exhibited T_g at below -20 °C for the soft segment PMPS and T_m at 133-159.5 °C for the PLLA segment. The T_g is much lower than room temperature and thus this copolymer can act as thermoplastic elastomer.

The elongation at break of the synthesized TPE-Ss were much higher than PLLA homopolymer. So , the brittleness of PLLA could be improved. The TPE-S with LLA to PMPS feed ratio 75 to 1 containing 53% PMPS showed the highest elongation at break up to 62% with good elastic properties.

The presence of PMPS soft block in different content in the TPE-S demonstrated significant influence on the biodegradation behavior of the synthesized TPE-S. All the copolymers were biodegradable in enzymes and seawater.

Chapter III: Synthesis of Biodegradable Thermoplastic Elastomer from 2-Methyl-1,3-propanediol, Glutaric Acid and L-Lactide



PLLA-*b*-PMPG-*b*-PLLA (TPE-G)

In order to evaluate the effect of the kinds of diacid on the properties of the resulting polymers, glutaric acid was selected in this chapter.

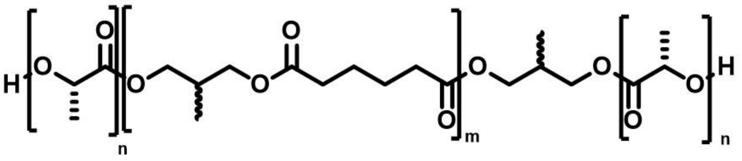
The triblock copolymers, TPE-Gs with different feed ratios were synthesized by $Sn(Oct)_2$ catalyzed ROP of LLA where PMPG as macroinitiator was synthesized using very common and relatively cheap monomers, MP and GA.

From DSC analysis, as a suitable soft segment PMPG showed T_g value around −40 °C. The copolymers showed T_g at around −42 to −48 °C from PMPG segment and T_m at 152 to 130 °C from PLLA segment.

From the tensile tests, TPE-Gs showed lower elongation at break compared to the PMPS derivatives. The softness of the copolymers gradually increased when the PMPG content in the copolymers increased.

Finally, from the biodegradation tests, the copolymers and PMPG showed relatively high degradability by seawater and similar enzymatic degradability to those of the PMPS derivatives.

Chapter IV: Synthesis of Biodegradable Thermoplastic Elastomer from 2-Methyl-1,3-propanediol, Adipic Acid and L-Lactide



PLLA-*b*-PMPA-*b*-PLLA (TPE-A)

Adipic acid is widely used diacid in the synthesis of polyamides, polyurethanes and polyesters.

In this chapter, very common and relatively cheap monomers, MP, AA and LLA were used to synthesize biodegradable thermoplastic elastomers which can potentially be used for various applications i.e. to produce fibers, film, vehicle interiors, appliance components, foot wares, food/beverage packaging, etc.

PLLA-*b*-PMPA-*b*-PLLA (TPE-A), composed of the soft PMPA midblock and hard PLLA end blocks with different molecular weight, was synthesized by the ROP of LLA using PMPA-diol as a macroinitiator using $Sn(Oct)_2$ as a catalyst.

From the DSC analysis, the triblock copolymers exhibited T_g at below −40 °C for the soft segment and T_m at 141-159.5 °C for the PLLA segment.

The triblock copolymer and PMPA were found to have very high biodegradability in seawater along with satisfactorily high degradation by enzymatic hydrolysis compared to PMPS and PMPG derivatives.

In conclusion, TPE-A seems to be the most promising among the three types of TPEs synthesized in this study because its low T_g and particularly high biodegradability.

List of Publication

Chapter II

Synthesis of Biodegradable Thermoplastic Elastomer from 2-methyl-1,3-propanediol, Succinic Acid and L-lactide

Lamya Zahir, Takumitsu Kida, Ryo Tanaka, Yuushou Nakayama, Takeshi Shiono, Norioki Kawasaki, Naoko Yamano, Atsuyoshi Nakayama, Polymer Degradation and Stability, 2020 (181) 109353.

Chapter III

Synthesis, Properties, and Biodegradability of Thermoplastic Elastomers made from 2-Methyl-1,3-propanediol, Glutaric Acid and Lactide

Lamya Zahir, Takumitsu Kida, Ryo Tanaka, Yuushou Nakayama, Takeshi Shiono, Norioki Kawasaki, Naoko Yamano, Atsuyoshi Nakayama, Life, 2021 (11) 43.

Chapter IV

Synthesis of Thermoplastic Elastomers with High Biodegradability in Seawater.

Lamya Zahir, Takumitsu Kida, Ryo Tanaka, Yuushou Nakayama, Takeshi Shiono, Norioki Kawasaki, Naoko Yamano, Atsuyoshi Nakayama, Polymer Degradation and Stability, 2021 (184) 109467.

Presentation in Conferences

1. Synthesis of Biodegradable Thermoplastic Elastomers using 2-Methyl-1,3-propanediol, Succinic Acid and Lactide

Lamya Zahir, Takumitsu Kida, Ryo Tanaka, Yuushou Nakayama, Takeshi Shiono, Norioki Kawasaki, Naoko Yamano, Atsuyoshi Nakayama

69th Symposium on Macromolecules , **2020**, Iwate University, Online Virtual Meeting

2. Properties and Biodegradabilities of Thermoplastic Elastomers Synthesized from 2-Methyl-1,3-propanediol, Succinic Acid and Lactide

Lamya Zahir, Takumitsu Kida, Ryo Tanaka, Yuushou Nakayama, Takeshi Shiono, Norioki Kawasaki, Naoko Yamano, Atsuyoshi Nakayama

9th Joint Conference on Renewable Energy and Nanotechnology (JCREN-2020), **2020**, Online Conference

3. Synthesis and Properties of Biodegradable Thermoplastic Elastomers from 2-Methyl-1,3-propanediol, Succinic Acid and Lactide

Lamya Zahir, Takumitsu Kida, Ryo Tanaka, Yuushou Nakayama, Takeshi Shiono, Norioki Kawasaki, Naoko Yamano, Atsuyoshi Nakayama

69th SPSJ Annual Meeting, **2020**.

4. Synthesis of Thermoplastic Elastomers using 2-Methyl-1,3-propanediol, Succinic Acid and Lactide

Lamya Zahir, Ryo Tanaka, Yuushou Nakayama, Takeshi Shiono

8th Joint Conference on Renewable Energy and Nanotechnology (JCREN-2019), **2019**, Makassar, Indonesia

Acknowledgement

The research work presented in this thesis has been carried out at polymer chemistry laboratory, Department of applied Chemistry, Hiroshima University.

First of all, “ALHAMDULILLAH”- for all of HIS blessings for me including this PhD work.

I would like to express my immense gratitude and pleasure to my supervisor Yuushou Nakayama (PhD), Associate Professor, Hiroshima University for his sincere guidance and helpful discussion throughout the journey of my doctoral study. I convey my heartiest gratitude to Professor Takeshi Shiono, PhD for the financial support and intellectual advice to solve my research and daily life issues without which my journey would not be possible. I am very grateful to Ryo Tanaka, PhD, Assistant Professor, Hiroshima University, for his continues support and suggestion during my research work period. I am thankful to Takumitsu Kida (PhD), for his lessons and help in the determination of mechanical properties. I greatly acknowledge the assistance provided by all my very friendly lab members of Polymer Chemistry lab for their immense cooperation and support to both of my lab and daily life activities.

I also owe my deeper gratitude to Prof. Norioki Kawasaki, Prof. Naoko Yamano, Prof. Atsuyoshi Nakayama from Biomedical Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), for the biodegradation tests of my samples.

I have no words to express my gratefulness towards my parents, Dr. Zahirul Haque Khandaker and Jyotshna Fauzia Kulsum, whose inspiration, motivation, sacrifice and prayers made me to start and complete this doctoral study successfully. They are the strength and blessings of each endeavor in my life. I am indebted to Dr. Fahim Arefin Khandaker, my younger brother and his family, for being so much caring and supportive throughout my journey.

Finally, this research work has been made possible due to all out sacrifice endured by my husband Dr. Md. Samiul Islam Chowdhury. His practical advice and help in my experiments, immense care and concern was my strength to complete this doctoral study. I find no words fit to express my gratitude to him.

LAMYA ZAHIR

March 2021