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Synthesis and characterization of polylactide–poly(methyl methacrylate) copolymer by combining of ROP and AGET ATRP

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ABSTRACT

Block copolymers of polylactide (PLA) and poly(methyl methacrylate) (PLA–PMMA) were synthesized by the combination of ring-opening polymerization (ROP) and activator generated by electron transfer for atom transfer radical polymerization (AGET ATRP), where PLA was prepared as macroinitiator with active bromo end group (PLA–Br). Tin octoate ($Sn(oct)_2$) and benzyl alcohol were applied as the initiation system for ROP of lactide. During AGET ATRP, copper (II) chloride ($CuCl_2$) with *N*,*N*,*N*′,*N*″,*N*″-pentamethyl-diethylenetriamine (PMDETA) was used as the catalyst system including $Sn(oct)_2$ as reducing agent. At the feed ratio [PLA–Br]/[$CuCl_2$]/[PMDETA]/[$Sn(oct)_2$]/[MMA] of 1/1/9.6/0.45/100, the mole fraction of the PMMA block was 0.6 as determined by ^{1}H NMR. Thermal stability of PLA was enhanced by incorporating of PMMA as block copolymers. In addition, blend between of PLA and PLA–PMMA copolymer was investigated and 5 phr of PLA–PMMA showed optimum condition to decrease in Young's modulus and increase in impact strength.

1. Introduction

Polylactide (PLA) is thermoplastic polyester which is obtained from renewable resources. PLA is a crystalline thermoplastic with clear and transparent appearance. In addition, PLA has relatively high strength and modulus, biocompatibility, and biodegradability. Therefore, PLA is a good candidate in both of the industrial packaging field and the biocompatible/bioabsorbable medical device market. Limitations of PLA are brittleness, insufficient impact strength and low thermal stability. In order to improve its properties, various studies have been conducted by blending with non-biodegradable resins [1], preparing as copolymers, or as functionalized polymers [2]. For example, when PLA was blended with a rubbery polymer in order to improve impact strength, in spite of an increase in toughness, the blend showed varying degrees of success [3,4]. In addition, transparency of PLA was diminished, and blending capacity was limited by compatibility/miscibility between the rubbery polymer and PLA [5].

Chemical modification of polymer by preparing as copolymer can attract much interest due to the controllability of the structural architecture, its properties, and molecular weight which depend on the molecular composition of copolymer. Many studies of PLA copolymers were reported using various methods, for example, (i) two-step method by combining PLA and PEG to obtain PLA–PEG amphiphilic block copolymer for drug carriers [6], and (ii) by introducing a reactive functional monomer on the TPO chain before it was reacted with PLA in order to enhance miscibility of PLA/TPO blends [7].

In view of the foregoing, PLA was modified mainly to improve structural or mechanical properties but its clarity was rarely of concern. To retain transparency of PLA, PLA and PMMA blends were prepared by mixing with impact modifier which consists of methyl methacrylate unit as shell layer and the polymer having alkyl acrylate unit as core [8]. Cygan and Brake [9] reported an improvement in impact strength of PLA by using methyl methacrylate–butadiene–styrene (MBS) copolymer as impact modifier. Transparency of the compound was controlled by proper balance between the impact modifier and PLA. PMMA or acrylic polymers are good candidates in maintaining transparency of the compound. Fujii et al. [8] investigated blending of PLA and PMMA with core–shell type of acrylic copolymer as impact modifier. The results showed an improvement in impact strength including transparency and heat resistance.

In order to improve simultaneously the impact property and clarity of the compound, diblock copolymers of PLA and PMMA were designed. In the past, the preparation of PLA–PMMA copolymer was carried out through functionalization of PLA with the end group of active methyl methacrylate (MMA) monomer and subsequent polymerization by free radical initiator [10] or atom transfer radical polymerization (ATRP) [11]. Recently, ATRP has

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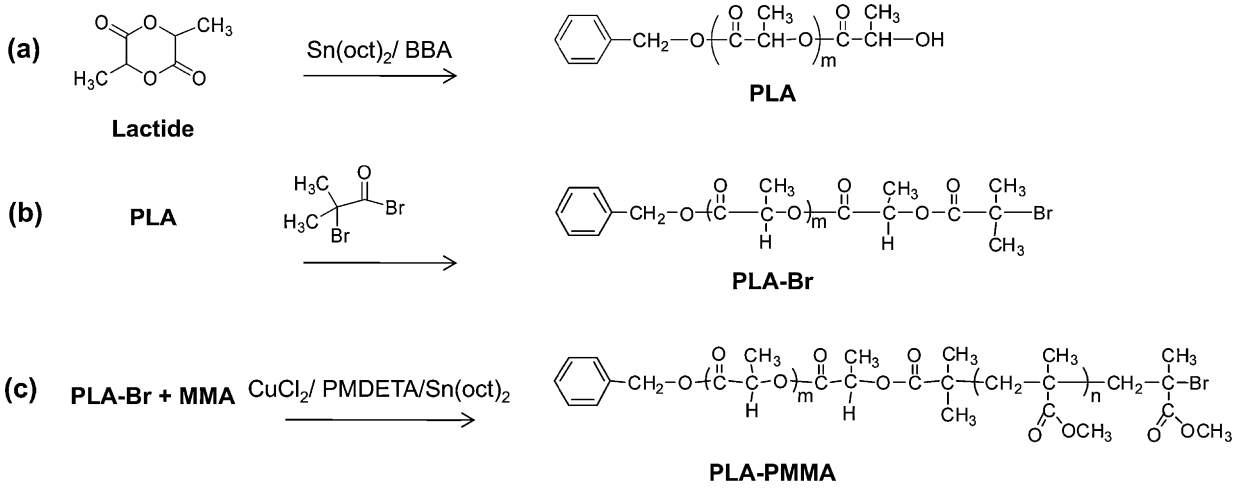

Scheme 1. Synthesis of PLA–PMMA copolymer.

gained rapidly increasing popularity due to the relatively mild reaction conditions, availability of plenty of monomers, initiators, catalysts, specific functionalities and various architectures [12]. However, the typical catalyst of ATRP, which is a transition metal complex, can easily be oxidized to the higher oxidation state. Therefore, ATRP needs some requirements such as special handling procedure under inert atmosphere, where oxygen or other oxidizing agents should be removed. Matyjaszewski and Jakubowski [13] presented a new procedure by using initiator with a radically transferrable atom or group, catalyst complex, and reducing agent. This method is named as activator generated by electron transfer for atom transfer radical polymerization (AGET ATRP).

In this study, we report an alternative route for the synthesis of diblock copolymer of PLA and PMMA through the combination of ring opening polymerization (ROP) and activator generated by electron transfer for atom transfer radical polymerization (AGET ATRP), where PLA was modified as macroinitiator for AGET ATRP (Scheme 1).

2. Experimental

2.1. Materials

L-Lactide was supplied by Cheil Industries in Korea and recrystallized from diethyl ether and vacuum dried prior to use. CuBr (99.999%, Aldrich) was used as received. *N*,*N*,*N*′,*N*″,*N*″-pentamethyl-diethylenetriamine (PMDETA) was purchased from Tokyo Chemical Industry Corp. (Japan). 2-Bromoisobutyryl bromide (98%), tin (II) 2-ethylhexanoate, ammonium bicarbonate (minimum 99%), and 4-tert-butylbenzyl alcohol (BBA, 98%) were purchased from Aldrich. Methyl methacrylate (99%, Aldrich) was purified following the procedure reported in the literature [14]. Polylactide (PLA) pellets for compounding were a kind gift from NatureWorks LLC, USA.

2.2. Instruments and equipments

^{1}H NMR and ^{13}C NMR spectra were obtained with a Varian Inova 400 at 400 MHz under ambient temperature, using chloroform-d and tetramethylsilane (TMS) as the corresponding solvent and the internal chemical shift standard, respectively. Fourier Transform Infrared (FTIR) spectra were obtained from a Bruker Equinox 55 spectrometer. The number-average molecular weight (M_n) of the obtained polymer was measured by gel permeation chromatography (GPC) analysis on a Water Breeze HPLC System. Thermogravimetric analysis (TGA) was performed with a TA instruments Q50 thermogravimetric analyzer in the range of ambient temperature to 700 °C at a heating rate of 10 °C/min, under nitrogen flow.

Differential scanning calorimetry (DSC) was conducted using Perkin Elmer, Jade DSC, where nitrogen gas was purged into the DSC cell with a flow rate of 19.8 mL/min. Measurements were carried out by using 2–4 mg of samples in sealed aluminum pan. The samples were first heated from 25 °C to 175 °C at the heating rate of 10 °C/min and were annealed for 5 min at this temperature to erase previous thermal history, followed by cooling to 25 °C with the same rate. The second heating was subsequently made to 175 °C at the heating rate of 10 °C/min. In case of PLA–PMMA copolymers, the maximum temperature was 240 °C. The thermograms of the first and second DSC heating run were both recorded. The glass-transition temperature (T_g) was taken as the temperature at the midpoint of the corresponding heat-capacity jump in the second heating run. The melting temperature (T_m) of each sample was determined from the maximum of the endothermic peaks, and cold crystallization temperature of each sample was determined from the maximum of the exothermic peaks in the second heating run. Young's modulus was measured under uniaxial elongation at room temperature in accordance with the ASTM D638 standard using a UTM from Hounsfield Test Equipment. Each sample had a dog-bone shape, and the average of at least five measurements was reported. Notched Izod test (CEAST, code 65451000) of the blends was performed in accordance with the ASTM D256 standard at room temperature.

2.3. Ring-opening polymerization of lactide

L-Lactide (3 g, 21 mmol) was weighed into a round bottom flask, where toluene (10 mL) was added. The reaction vessel was immersed in oil bath with controlled temperature at 120 °C, and the reaction was set up as reflux reaction under nitrogen atmosphere. After benzyl alcohol (0.21 mmol) was added to lactide, the initiator (0.21 mmol) was added in the form of a 1 M solution in toluene. After 24 h, the reaction was stopped by precipitation in cold methanol, and the products were dried in vacuum.

FTIR (KBr, cm^{-1}): 3440 (OH stretch), 2947 (C–H stretch), 1769 (C=O stretch), 1454 (C–H bend), 1213–1000 (C–(C=O)–O stretch).

^{1}H NMR in $CDCl_3$ (δ, ppm): 7.4 (H of benzyl end group), 5.15 (H of methine), 4.3 (H of methine end group), 1.54 (CH_3).