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Synthesis and Characterization of Tulipalin-Based Polymers

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2-hydroxyethyl methacrylate (HEMA) terminated poly(DL-lactide) macromonomers (HEMA-PDLLA) were synthesized and copolymerized with α-methylene-γ-butyrolactone (MBL) to produce their graft copolymers of poly(tulipalin A) (PT) and poly(DL-lactide) (PDLLA) (PT-*g*-PDLLA). HEMA-PDLLA were synthesized by ring opening polymerization (ROP) of DL-lactide in the presence of 2-hydroxyethyl methacrylate. The thermal stabilities of PT-*g*-PDLLA copolymers were investigated by Thermogravimetry analysis. There were two stages in weight loss of each copolymer by recorded at 270-300 ºC are attributed to the decomposition of poly(DL-lactide). Two isolated Tg were shown in each case, corresponding to the poly(DL-lactide)-rich domain and PT-rich domain were also investigated by differential scanning calorimetry.

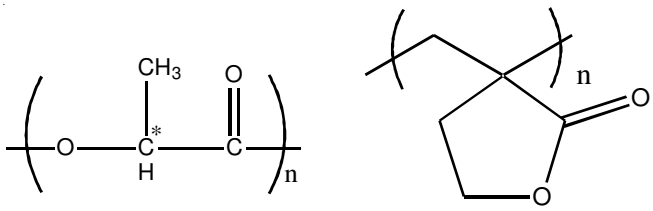
Keywords: Poly(tulipalin A), Ring opening polymerization, Copolymer, Decomposition.

INTRODUCTION

In recent years, sustainable production in human societies has become a controversial issue in relation to the protection of climate change, conservation of the global environment and preservation of natural resources. In particular, surfeit dependence on fossil resources as the source of energy and materials has caused the increase in atmospheric carbon dioxide content followed by global warming. Therefore, fossil resources ought to be replaced by renewable resources such as wind power, solar energy and biomass as quickly as possible. Since biomass resources are made by photosynthetic carbon dioxide assimilation of plants, their production is compatible with natural recycling system and the incineration of biomass-derived materials does not newly increase the atmospheric carbon dioxide concentration. This concept of maintaining the carbon dioxide level in our human activities is called "carbon neutral". In our efforts to cut the carbon dioxide emission, the feature of "carbon neutral" is important as "carbon offset" in which the increase of carbon dioxide is compensated by the decrease achieved by other activities. The substitution of fossil resources to biomass resources is also effective for the conservation of the former resources. Thus, in the industrial society based on use of biomass both sustainable production and preservation of global environment can be consistently maintained in a permanent manner[1].

These polymers are generally classified into three categories. The first is natural polymers such as polysaccharides, proteins *etc.*, which are directly obtained from biomass resources and used in the original polymeric form. The second is bio-synthetic polymers such as bacterial polyesters, polyamino acids *etc.*, which are synthesized by the microbial fermentation or transgenic plant technology. The third is chemo-biotic polymers such as aliphatic polyesters and polyamides, vinyl polymers *etc.*, which are synthesized from biomass-derived feedstock by polymerization techniques. Among these bio-based polymers, biosynthetic and chemo-biotic types that are prepared by using novel biotechnologies have attracted much attention[1].

One of the characteristic bio-based polymers showing high thermal stability is poly(tulipalin A) (PT) (Fig. 1) synthesized from a monomer called tulipalin A (α-methylene-γ-butyrolactone) (MBL). Several compounds containing an α-methylene-γ-butyrolactone moiety have been isolated from various plants[2-5]. The simplest member of these butyrolactones is tulipalin A found in tulips. It was successfully polymerized by radical mechanism (using AIBN)[6-8] and group-transfer polymerization[9] and also copolymerized by photocopolymerization with methoxystyrene[10]. Poly(tulipalin A) consists of a five-member ring with an oxygen and a carbonyl group, possessing structural similarities to methyl methacrylate. The reactivity of tulipalin A in radical polymerization was found to be a little higher than that of methyl methacrylate because of the planar structure of tulipalin A[11]. The planarity favors delocalization of the spin density of the chain-end radical and reduces steric hindrance around it.



Polylactides (PLA) Poly(tulipalin A) (PT)

Fig. 1. Structures of PLA and PT[26]

Polylactides (PLA) are major bio-based polymers synthesized from lactic acids that can be synthesized from renewable resources such as corn or sugarcane[12,13].

Polylactides show low thermal stability and several approaches have been examined to improve their inferior properties using copolymerization and polymer blend techniques. Almost all the polymers examined for blending and copolymerization with PLA, however, have been those derived from petroleum feedstock[14-21]. Furthermore, polymerization mechanisms of these two polymers are different: polylactide is polymerized by ring opening polymerization with coordination metal catalysts, while PT is polymerized by radical addition, making it difficult to perform random copolymerization of the two monomers. For increasing their compatibility, graft or block copolymers of PLA and PT should preferably be prepared. In the presence of the graft and block copolymers, the compatibility of the component polymers can also be improved. For PLA, less study has been done to prepare such block and graft copolymers with vinyl polymers. Previously, macromers have been widely used for producing well defined graft copolymers, for which the graft length and ratio can be controlled in advance by choosing the molecular weight and composition of the macromers, which can readily be adjusted by controlling the monomer/initiator ratio in the feed[22-25]. In this study, 2-hydroxyethyl methacrylate (HEMA) terminated poly(DL-lactide) macromonomers (HEMA-PDLLA) were synthesized and copolymerized with α-methylene-γ-butyrolactone to produce their graft copolymers (PT-*g*-PDLLA). The thermal stabilities of PT-*g*-PDLLA copolymers were investigated by TGA. Miscibility and the morphological structure of the two component polymers were also investigated by differential scanning calorimetry (DSC) and atomic force microscopy (AFM).

EXPERIMENTAL

DL-Lactide was supplied by Musashino Kagaku Co., Ltd (Saitama, Japan). Tulipalin A (α-methylene-γ-butyrolactone) (MBL) and 2-hydroxyethyl methacrylate (HEMA) were purchased from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan) and distilled under reduced pressure before use. Stannous octoate [$Sn(Oct)_2$] was purchased from Nacalai Tesque Co., Ltd (Kyoto, Japan). It was dissolved in a distilled toluene in a concentration of 0.05 g/mL. 2,2'-Azoisobutyronitrile (AIBN) was purchased from Nacalai Tesque Co., Ltd (Kyoto, Japan) and recrystallized from methanol. Dimethyl sulfoxide (DMSO) was purchased from Kanto Chemical Co., Ltd (Tokyo, Japan) and dehydrated with 3 Å molecular sieves (Nacalai Tesque Co., Ltd) without distillation. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was received from Central Glass Co (Ube, Japan).

500 MHz ^{1}H NMR spectra were measured on a Brucker ARX spectrometer. Samples were dissolved in deuterated chloroform ($CDCl_3$) or deuterated N,N-dimethylformamide (DMF-d_6) containing tetramethylsilane (TMS) as the internal reference. Gel permeation chromatography (GPC) with chloroform eluent was carried out with Shimadzu analyzer system consisting of an LC-10ADvp pump, an RID6A detector. Samples were eluted out at 40 ºC from a combination of TOSOH TSKgel Super HZM-N and Super HZ-H columns with chloroform as the mobile phase at a flow rate of 0.4 mL/min. The molecular weights were calibrated with polystyrene (PS) standards. Differential scanning calorimetry (DSC) was performed on a Shimadzu DSC-50 thermal analyzer under a nitrogen flow of 20 mL/min at a heating rate of 20 ºC/min in a temperature range from -20 to 220 °C. Thermogravimetry analysis (TGA) was performed on an analyzer system of TA Instruments under a nitrogen flow of 40 mL/min at a heating rate of 20 ºC/min in a temperature range from 30 to 700 °C. Atomic force microscope (AFM) was operated in the tapping mode using a Digital Instruments Multimode AFM equipped with a Nanoscope IIIa scanning probe microscope controller at a scan rate of 1 Hz in ambient atmosphere and temperature. Both hight and phase images were recorded simultaneously using the retrace signal.

Synthesis of HEMA-PDLLA macromonomers[26]: Macromonomers of HEMA-terminated poly(DL-lactide) (HEMA-PDLLA) having various lactide chain lengths were synthesized by ring opening polymerization (ROP) of DL-lactide using 2-hydroxyethyl methacrylate as the initiator in the presence of $Sn(Oct)_2$ as the catalyst. In a typical polymerization, DL-lactide was placed in a test tube and dried in vacuum at room temperature for 1 h. A catalytic amount of $Sn(Oct)_2$ (0.2 mol % relative to DL-lactide as a toluene solution) was added to the test tube under a nitrogen atmosphere and the mixture was dried in vacuum at room temperature for 3 h. Immediately after 2-hydroxyethyl methacrylate had been added to the test tube under a nitrogen atmosphere, the mixture was heated at 130 °C for 3 h and then allowed to cool down to room temperature. The resulting product was dissolved in tetrahydrofuran (THF), reprecipitated into an ice-cold water and dried under vacuum at 50 °C for 24 h. The degree of polymerization (DP) of the obtained HEMA-PDLLA was determined by the ^{1}H NMR spectroscopy.

Copolymerization of MBL with HEMA-PDLLA[26]: The graft copolymers (PT-*g*-PDLLA) having various PDLLA/PT compositions were synthesized by free-radical copolymerization of HEMA-PDLLA and MBL using AIBN as the radical initiator. The molar ratios of MBL to the poly(DL-lactide) lactate units in the feed were adjusted to 2:8, 5:5 and 8:2. In a typical polymerization, the mixture of HEMA-PDLLA, MBL and AIBN (1 mol % with respect to the vinyl group) were dissolved in DMSO (5 mL) in a test tube. The tube was repeatedly degassed by freeze-thaw cycles and finally sealed under nitrogen. The tube was heated at 60 °C for 24 h and then allowed to cool down to room temperature. The resulting polymer was well washed with methanol and dried under vacuum at 80 °C for 12 h.

Determination of reactivity ratios of MBL and HEMA-PDLLA[26]: The copolymerization reactivity ratios of MBL and

HEMA-PDLLA (degree of polymerization = 7) were examined by the Kelen-Tüdos method[27]. The copolymerization of MBL and HEMA-PDLLA was carried out in DMSO-d_6 with AIBN (1 mol % with respect to the vinyl group) as the initiator at 60 ºC in a NMR tube for 1 h. Compositions of the monomers and copolymers were determined by ^{1}H NMR. The integrations of the signals at 5.704 ppm (the double bond protons of MBL) and 5.733 ppm (the double bond protons of 2-hydroxyethyl methacrylate) were used to estimate the corresponding monomer concentration.

RESULTS AND DISCUSSION

Synthesis of HEMA-PDLLA macromonomers: Fig. 2 shows the synthetic procedure of HEMA-PDLLA in which 2-hydroxyethyl methacrylate was used as the initiator of ring opening polymerization of DL-lactide[26]. The formation of HEMA-PDLLA was confirmed by the ^{1}H NMR spectrum (Fig. 3). The proton signals from the 2-hydroxyethyl methacrylate residues (a, b, c and d) and lactyl units (e, f, g, h and i) are detected. The relative peak intensity of the methine proton of the lactyl units at δ 5.2 ppm and the double bond protons of the 2-hydroxyethyl methacrylate residue at δ 5.8-6.1 ppm was used to determine degree of polymerization and molar mass of the poly(DL-lactide) chains.

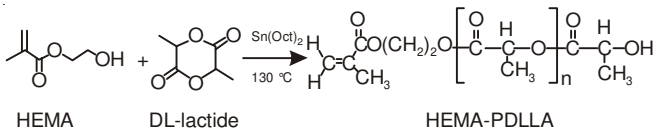


Fig. 2. Synthesis of HEMA-PDLLA macromers

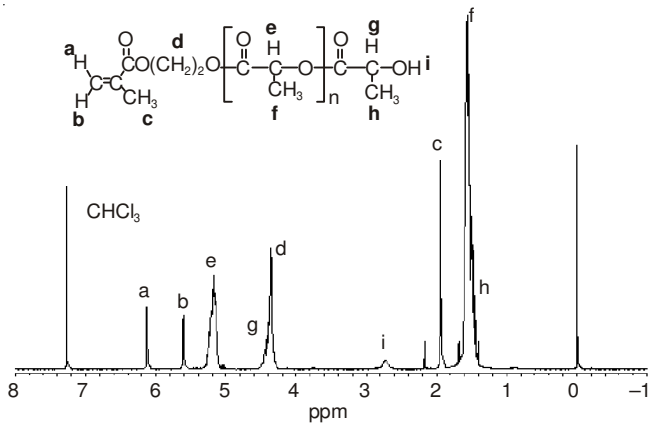


Fig. 3. ^{1}H NMR spectrum of a HEMA-PDLLA macromer (M500) in $CDCl_3$

Synthesis and characterization of PT-g-PDLLA copolymers: Fig. 4 shows the synthetic procedure of PT-*g*-PDLLA in which the copolymers having various PDLLA/PT compositions and graft chain lengths were prepared by free radical copolymerization of HEMA-PDLLA and MBL[26].

Monomer reactivity ratios: To investigate the copolymerization behavior of MBL and HEMA-PDLLA, their reactivity ratios were determined by using MBL and HEMA-PDLLA (M500) as M_1 and M_2, respectively. Fig. 5 shows the mole fractions of MBL in the feed *versus* the mole fractions of MBL in the copolymer. The monomer reactivity ratios were determined by Kelen-Tüdos method; *i.e.*, from the linear plots of the following eqation (eqn. 1).

$$\eta = (r_1 + r_2/a)\xi - r^2/\alpha \quad (1)$$

where α, η and ξ refer to the following equations, respectively.

$$\alpha = \sqrt{F'_{min} F'_{max}} \quad (2)$$

$$\eta = z(y-1)/(\alpha z^2 + y) \quad (3)$$

$$\xi = y/(\alpha z^2 + y) \quad (4)$$

The values y, z and F' refer to the following equations, respectively

$$y = dm_1/dm_2 = (m_1^0 - m_1)/(m_2^0 - m_2) \quad (5)$$

$$z = [\log(m_1/m_1^0)]/[\log(m_2/m_2^0)] \quad (6)$$

$$F' = y/z^2 \quad (7)$$

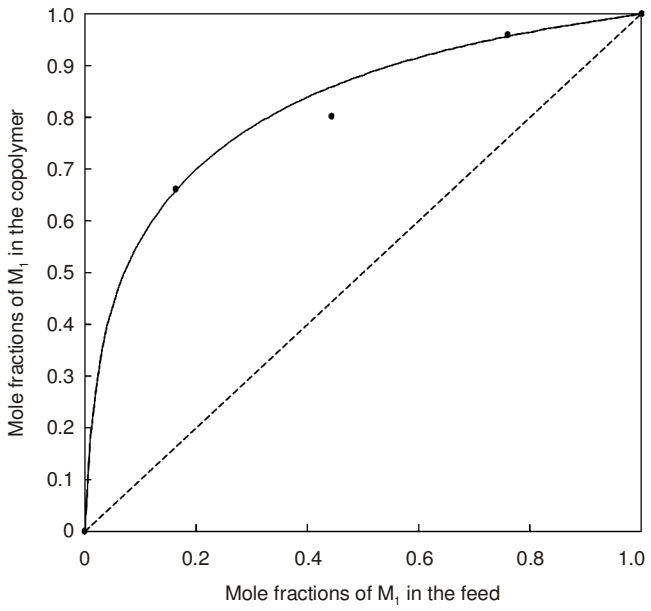


Fig. 5. Copolymerization curve of MBL (M_1) and HEMA-PDLLA macromer (M500) (M_2); the points represent experimental date and the line represents the theoretical composition curve calculated from the reactivity ratios determined

where m_i^0 and m_i are mole fractions of MBL (i = 1) and HEMA-PDLLA (i = 2) in the feed and the resultant copolymer,

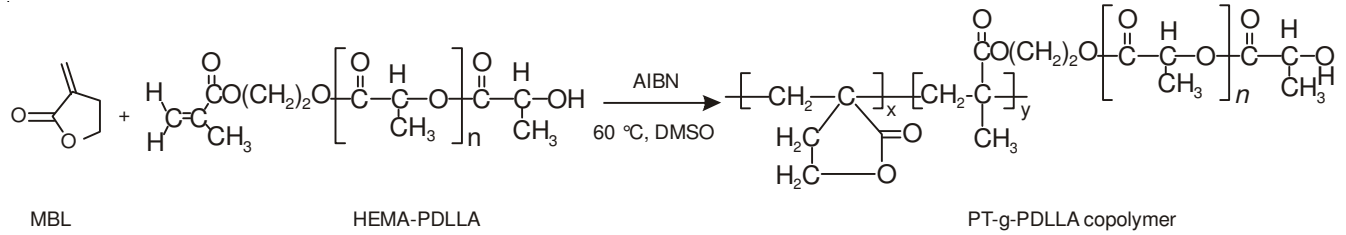


Fig. 4. Synthesis of PT-g-PDLLA copolymers

respectively. The reactivity ratios of MBL (r_1) and HEMA-PDLLA (r_2) were determined to be as $r_1 = 6.81$ and $r_2 = 0.04$. This result indicates that the MBL units are more involved in the copolymer than the 2-hydroxyethyl methacrylate units. Namely, MBL are more easily incorporated in the copolymer in the early stage of the polymerization and HEMA-PDLLA is incorporated in the copolymer in the last stage, making the polymer chains to possess various numbers of side chains.

Fig. 6 shows the DSC curves of the copolymers whose side chains are of 1100 Da in M_n (C1100 series). Two isolated T_g were shown in each case, corresponding to the poly(DL-lactide)-rich domain and PT-rich domain. It was therefore indicated that in this C1100 series the component poly(DL-lactide) and PT are immiscible. Similar results were obtained for the copolymers of the C2000 and C7000 series having the longer poly(DL-lactide) grafts.

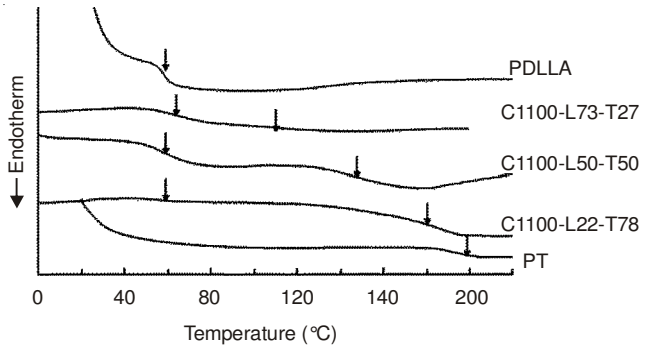


Fig. 6. DSC curves in the second heating run for PT-*g*-PDLLA copolymers of C1100 series

The thermal stabilities of PT-*g*-PDLLA copolymers were investigated by TGA. Table-1 shows the TGA curves of the copolymers of the C500 series. There were two stages in weight loss of each copolymer of this series. The weight losses recorded at 270-300 ºC are attributed to the decomposition of poly(DL-lactide). They are almost close to the weight composition of poly(DL-lactide) as summarized in Table-1. Fig. 7 shows the changes in decomposition temperature (T_d) of poly(DL-lactide) (Fig. 7 (a)) and PT (Fig. 7 (b)) as a function of poly(DL-lactide) graft content. When the poly(DL-lactide) graft content is higher, the poly(DL-lactide) and PT degradation

TABLE-1
COMPARISON OF THE WEIGHT RATIOS IN THE COPOLYMERS DETERMINED BY ^{1}H NMR AND TGA

Code	PDLLA/PT determined by ^{1}H NMR	PDLLA/PT determined by TGA
C7000-L78-T22	72/28	71/29
C7000-L54-T46	46/54	39/61
C7000-L25-T75	20/80	24/76
C2000-L76-T24	70/30	67/33
C2000-L43-T57	36/64	30/70
C2000-L21-T79	16/84	22/78
C1100-L73-T27	67/33	57/43
C1100-L50-T50	42/58	36/64
C1100-L22-T78	17/83	23/77
C500-L76-T24	70/30	57/43
C500-L65-T35	58/42	39/61
C500-L45-T55	38/62	39/61
C500-L22-T78	17/83	24/76

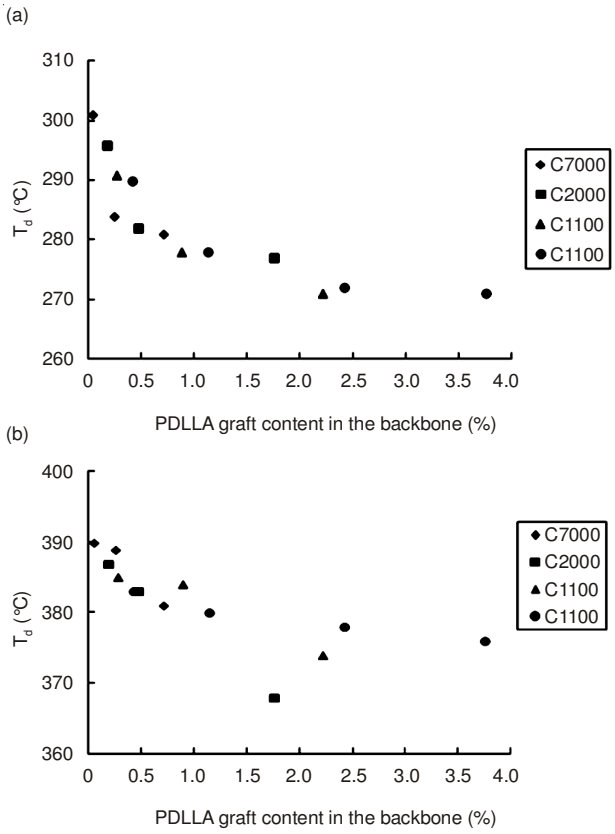


Fig. 7. T_d of (a) PDLLA and (b) PT *vs*. the graft content of poly(DL-lactide) (PDLLA) in the copolymer backbone for the whole series

is more highly induced at lower temperature. This result indicates that the thermal degradation of the poly(DL-lactide) grafts affects the degradation of PT backbones. Table-2 summarizes the thermal date of the copolymers.

Morphologies of the copolymers: Fig. 8 shows AFM phase images of the typical copolymers. Micro phase separation was observed in C500-L76-T24 and C1100-L73-T27 consisting of rather long poly(DL-lactide) grafts (Fig. 8 (a) (b)). Here, the PT-rich phase is shown dark and poly(DL-lactide)-rich phase is shown bright. These results support the structural images based on the T_g changes of the copolymers.

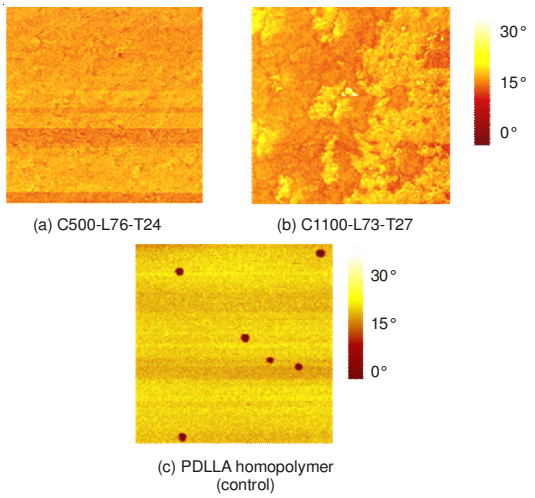


Fig. 8. AFM phase images of the typical copolymers

TABLE-2
THERMAL DATA OF THE COPOLYMERS

Code	T_g(PDLLA[a] -rich phase) (ºC)	T_g (PT[a] -rich phase) (ºC)	T_d(PDLLA[b]-rich phase) (ºC)	T_d (PT[b]-rich phase) (ºC)
C7000-L78-T22	58	161	281	381
C7000-L54-T46	48	192	284	389
C7000-L25-T75	51	195	301	390
C2000-L76-T24	59	149	277	368
C2000-L43-T57	50	183	282	383
C2000-L21-T79	37	188	296	387
C1100-L73-T27	64	108	271	374
C1100-L50-T50	58	143	278	384
C1100-L22-T78	54	182	291	385
C500-L76-T24	61[c]	-	271	376
C500-L65-T35	84[c]	-	272	378
C500-L45-T55	125[c]	-	278	380
C500-L22-T78	170[c]	-	290	383

[a]Determined by DSC; [b]Determined by TGA; [c]A single T_g was observed

Conclusions

• In this study, 2-hydroxyethyl methacrylate (HEMA) terminated poly(DL-lactide) macromonomers (HEMA-PDLLA) were synthesized and copolymerized with MBL to produce their graft copolymers (PT-*g*-PDLLA).

• To investigate the copolymerization behavior of MBL and HEMA-PDLLA, their reactivity ratios were determined by using MBL and HEMA-PDLLA.

• α-Methylene-γ-butyrolactone (MBL) are more easily incorporated in the copolymer in the early stage of the polymerization and HEMA-PDLLA is incorporated in the copolymer in the last stage, making the polymer chains to possess various numbers of side chains.

• The DSC curves of the copolymers whose side chains are of 1100 Da in M_n (C1100 series). Two isolated Tg were shown in each case, corresponding to the poly(DL-lactide)-rich domain and PT-rich domain.

• The AFM phase images of the typical copolymers were shown dark of PT-rich phase and poly(DL-lactide)-rich phase is shown bright. This result supported the phase-separated morphologies in the latter while the single phase in the former.

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