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Synthesis of an $(AB)_4$-type Star Block Copolymer of L-lactide and Cyclohexene Oxide from a Tetra-Arm Telechelic Macrophotoinitiator

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Abstract: A multi-step reaction process was applied for the synthesis of a novel and well-defined star-shaped telechelic macrophotoinitiator with four poly(L-lactide) (PLLA) arms connected to photoinitiating benzoin groups at the chain ends $(PLLA\text{-}PI)_4$. To achieve this, 2,2-bis(hydroxymethyl)-1,3-propanediol was used as the initiator which constitutes the core of the star-shaped polymeric scaffold. Benzoin photoreactive end groups of the telechelic $(PLLA\text{-}PI)_4$, capable of entering into further polymerization, allowed its use as a polymeric photoinitiator in photoinduced free radical promoted cationic polymerization of cyclohexene oxide (CHO) monomer at λ=350 nm to produce an $(AB)_4$-type star-shaped block copolymer composed of both esteric L-lactide and etheric cyclohexene oxide chains on each arm, $(PLLA\text{-}PCHO)_4$. Structural analysis and characterization of all intermediate and final compounds were done by a series of analytical and spectral methods. Molecular weights of the prepared polymers up to telechelic macrophotoinitiator $(PLLA\text{-}PI)_4$ were determined based on ^{1}H-NMR ($M_{n\ H\text{-}NMR}$), GPC ($M_{n\ exp}$) analyses and theoretical calculations ($M_{n\ theo}$) and were found to be in good agreement with each other. Thermal properties and degradations of the prepared polymers were examined by thermogravimetric and differential thermal analyses (TG/DTA). The melting temperature for $(PLLA\text{-}PCHO)_4$ was found higher compared to the other homo-type polymers in the literature. The thermogravimetric (TG) analyses showed that incorporation of the thermally stable PCHO block into the structure via photopolymerization improved its stability by increasing its decomposition temperature compared to the prepolymers.

Keywords: Poly(L-lactide), ring opening polymerization (ROP), star-shaped telechelic macrophotoinitiator, photoinduced polymerization, star block copolymer

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INTRODUCTION

Telechelic polymers are defined as macromolecules comprising functional end-groups having utility in further polymerization or other reactions. In general, when a polymer chain is functionalized with the same group at both ends, the term of telechelic polymer is used. The idea of telechelics has recently been extended from classical linear polymers to many other types of polymers such as star, dendritic, and hyperbranched comprising functional end groups (1,2). The telechelic polymers can be synthesized by a wide variety of polymerization methods such as free radical (3), cationic (4), anionic (5), and step-growth (6) polymerization. Recent advances in controlled/living polymerization techniques (ATRP, RAFT, NMP, and ROP) allow the synthesis of well-defined telechelic polymers (2, 6-8). If these controlled/living polymerization techniques are combined with a coupling, addition or conjugation method, telechelic polymers with low polydispersity and desired chain lengths can be obtained (9,10). Among the combining methods, ROP with click chemistry is often favored as it provides a well control of functionality, polydispersity, and molecular weight during the preparation of well-defined biodegradable linear or star telechelic polymers. For example, Yilmaz and coworkers have synthesized a star-shaped telechelic PCL with terminal azido groups and then clicked it with ethynylferrocene groups (11).

Yang and co-workers have synthesized a well-defined star-shaped telechelic hydrophobic PCL with alkyne terminal groups and then coupled it with an azido-terminated PEG via "click chemistry" to prepare well-defined novel amphiphilic PCL/PEG copolymer conetworks (12).

Synthesis of well-defined polymers having photoreactive end groups, often called macrophotoinitiators or polymeric photoinitiators, has recently received great interest in the field of polymer chemistry because they can be used as cross-linkers, chain extenders, and precursors to prepare block, graft, and star type polymers or polymer networks (13-15). They are also important due to their unique structure which accommodates properties of both macromolecular and small molecular photoinitiators in a single body. Compared to the small photoinitiator molecules, macrophotoinitiators have not only better reactivity but also lower migration rate and lower volatility (16-18). Practically, macrophotoinitiators are used as photoreactive agents in photopolymerization to synthesize copolymers such as block and graft (19-21). Recently, we have successfully applied the combination of ROP and click chemistry to prepare well-defined macrophotoinitiators whose core were connected to both photoreactive group(s) such as benzoin and polymer chain(s) such as PCL or PLLA (22-24). Next, these polymers were used as precursors in photopolymerization for the preparation of different types of block copolymers.

Depending on the telechelic definition as stated above, if a macrophotoinitiator contains the same photoactive groups at the chain-ends, it can be considered as telechelic macrophotoinitiator. Degirmenci group previously synthesized a well-defined telechelic macrophotoinitiator of polystyrene with two benzoin groups at the both ends of the polymer chain via the combination of ATRP and click chemistry (9), and then used this as a prepolymer in photopolymerization to synthesize a linear ABA type tri-block copolymer. Even though there exist various studies about the telechelic polymers in the literature as shown above, to the best of our knowledge, very few linear-type telechelic macrophotoinitiators and no star-type telechelic macrophotoinitiator have been reported so far. Thus, here we report synthesis, characterization, and thermal analyses of a novel well-defined star-shaped telechelic macrophotoinitiator of PLLA with benzoin photoreactive end groups $(PLLA\text{-}PI)_4$ and an $(AB)_4$-type star block copolymer $(PLLA\text{-}PCHO)_4$ which was prepared by the photoinitiated free radical promoted cationic polymerization of CHO monomer with the $(PLLA\text{-}PI)_4$. As far as we are concerned, the synthesis of such type of telechelic PLLA macrophotoinitiator $(PLLA\text{-}PI)_4$ and star block copolymer $(PLLA\text{-}PCHO)_4$ have not been reported yet.

MATERIALS AND METHODS

Materials and Instrumentation

Azido end-functional benzoin photoinitiator ($PI\text{-}N_3$), namely 2-oxo-1,2-diphenylethyl-2-azidopropanoate, was synthesized according to the reported method (22,25). Benzoin (Aldrich) was recrystallized from ethanol. Other reagents used in the synthesis of ($PI\text{-}N_3$) such as 2-bromopropanoyl bromide (Aldrich) and sodium azide (NaN_3) (Merck) were used as received from the commercial suppliers. Cyclohexene oxide (CHO) (Aldrich) was purified by distillation over calcium hyride (CaH_2) under reduced pressure and L-lactide (LLA) (Aldrich) was recrystallized from toluene. Pentaerythritol (Aldrich), the initiator for ROP, was used without further purification. 1-Ethoxy-2-methylpyridinium hexafluorophosphate ($EMP^+PF_6^-$) was synthesized by following the published process (26). Solvents, dichloromethane (CH_2Cl_2), toluene, dimethylformamide (DMF), and tetrahydrofuran (THF), were dried by distilling over the proper drying agents under N_2 before use. All other reagents and solvents were used as received from the commercial sources unless otherwise stated.

An Agilent 400 MHz NMR spectrometer was used to record NMR measurements at ambient temperature and the data were processed with MestReNova 12 software. Fourier transform infrared (FT-IR) analyses were carried out using a Perkin-Elmer Spectrum Two FT-IR spectrometer. The number and average molecular weights (M_n and M_w) and molecular weight distributions (M_w/M_n) of the polymers were determined by gel permeation chromatography with a Viscotek GPCmax VE 2001 Autosampler system having Viscotek VE 3580 refractive index (RI) detector. Three Viscotek GPC columns (T3000, LT4000L and LT5000L), (7.8 mm internal diameter, 300 mm length) and a Viscotek guard column (CLM3008, 4.6 mm internal diameter, 10 mm length) were used in series. The effective molecular weight ranges were 456–42800, 1050–107000, and 10200–2890000, respectively. THF was used as an eluent at flow rate of 1.0 mL/min at 35°C. Detector was calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC 4.7.0 software. Molecular weights were calculated with the aid of polystyrene standards. The experimental molecular weights ($M_{n\ exp}$) of $(PLLA\text{-}OH)_4$, $(PLLA\text{-}alkyne)_4$ and $(PLLA\text{-}PI)_4$ were calculated from GPC with the help of polystyrene calibration curve using a correction coefficient, $M_{n\ exp} = 0.58 \times M_{n\ GPC}$ (27). A Perkin-Elmer model Lambda 25 spectrophotometer and a Perkin–Elmer model LS 55 spectrometer were used to record UV-vis and Fluorescence spectra, respectively. An S II EXSTAR TG/DTA 7300 thermal analysis systems under N_2 flow with a heating rate of 10 °C $min^{-1}$was used to determine the thermal stabilities and the glass transition temperatures of the polymers.

Preparation of tetra-arm star-shaped poly(L-lactide) by ring opening polymerization $(PLLA\text{-}OH)_4$

2,2-Bis(hydroxymethyl)-1,3-propanediol (188.8 mg, 1.39 mmol), L-lactide (10 g, 69.4 mmol), and $Sn(Oct)_2$ (95%) (5.26 mg, 12.3×10^{-3} mmol, 0.05% $w/w_{monomer}$) were placed in a Schlenk flask with a ratio of 1/50 (initiator/monomer). The flask was vacuumed for 30 min to dry the reaction mixture and then charged with N_2 gas. The reaction was stirred for 10 h at 130 °C under N_2 until the reaction bulk was viscous enough to stop stirring bar. The reaction mixture was solidified by immersing it in an ice-water bath. The glassy solid polymer was then dissolved in dichloromethane and the resulting solution was added drop wise to 250 mL of cold methanol. The title polymer $(PLLA\text{-}OH)_4$ was obtained as a white solid after the filtration of the mixture by a Gooch crucible. Yield: 9.5 g, 93%, $M_{n\ theo} = 6838$, $M_{n\ H\ NMR} = 6626$, $M_{n\ exp} = 6600$, $M_w/M_n = 1.06$.

Preparation of alkyne end-functional tetra-arm star-shaped poly(L-lactide) $(PLLA\text{-}alkyne)_4$

To a two-necked round-bottom reaction flask were placed $(PLLA\text{-}OH)_4$ (2g, 0.30 mmol based on NMR calc), 4-pentynoic acid (98%) (237 mg, 2.37 mmol), DMAP (36.5 mg, 0.30 mmol), and DCC (610 mg, 3.00 mmol). The flask was vacuumed and then flushed with Ar atmosphere and then 45 mL of dry dichloromethane was added. The reaction was stirred for 3 days at rt under Ar. The reaction mixture was concentrated with a rotary evaporator and then the insoluble part was removed by filtration through No:1 Whatman filter paper. The title polymer was reprecipitated by the dropwise addition of the filtrate into 250 mL of cold methanol. The white polymer solid, $(PLLA\text{-}alkyne)_4$, was then filtered by a pore-4 Gooch crucible and dried under vacuum. Yield: 2.0 g, 96%, $M_{n\ theo} = 7158$, $M_{n\ H\ NMR} = 7119$, $M_{n\ exp} = 7000$, $M_w/M_n = 1.06$.

Preparation of benzoin end-functional tetra-arm star-shaped telechelic poly(L-lactide) macrophotoinitiator by click chemistry $(PLLA\text{-}PI)_4$

To a Schlenk flask equipped with a stirring bar were added $(PLLA\text{-}alkyne)_4$ (514 mg, 0.1 mmol based on NMR calc), $PI\text{-}N_3$ (186 mg, 0.6 mmol), CuBr (172 mg, 1.2 mmol), and bipyridine (375 mg, 2.4 mmol) and 20 ml of dry THF under Ar. The dark-brown suspension was degassed by three freeze-pump-thaw cycles. After 24 h stirring at room temperature, the reaction suspension looking like pale brown ash was diluted with THF and filtered through a short silica gel column to remove excess CuBr and other particulate matters. Dropwise addition of the filtrate to cold methanol resulted in solid precipitation which was filtered through a pore-4 Gooch crucible and dried under vacuum to give $(PLLA\text{-}PI)_4$ as a white polymer. Yield: 580 mg, 96%, $M_{n\ theo} = 8396$, $M_{n\ H\text{-}NMR} = 8312$, $M_{n\ exp} = 8200$, $M_w/M_n = 1.12$.

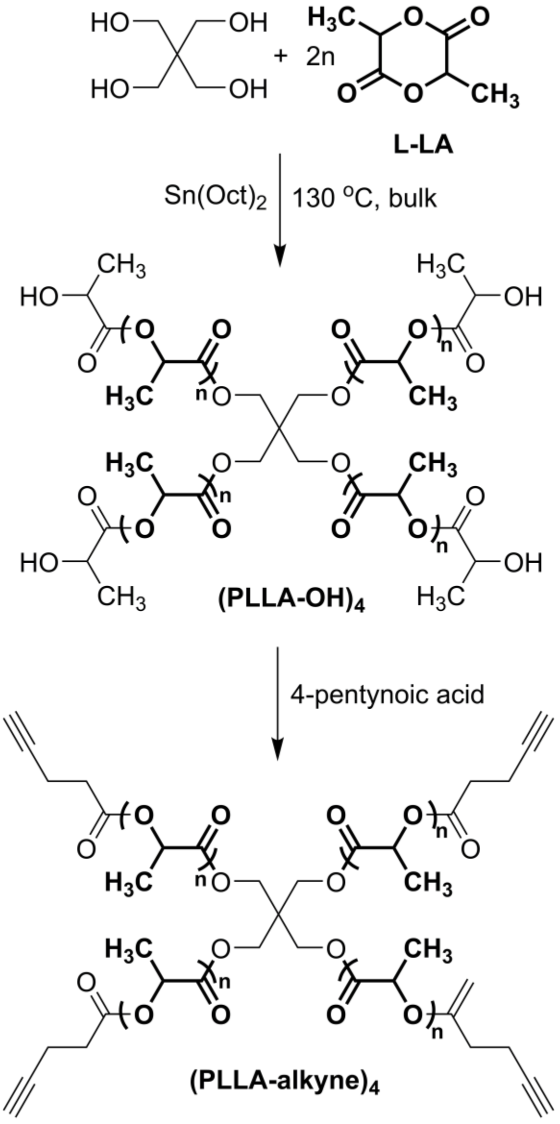
Preparation of $(AB)_4$-type star block copolymer by photoinduced free radical promoted cationic polymerization $(PLLA\text{-}PCHO)_4$

The macrophotoinitiator $(PLLA\text{-}PI)_4$, onium salt ($Ph_2I^+PF_6^-$ or $EMP^+PF_6^-$) and 1 mL of cyclohexene oxide (CHO) were placed in a Pyrex tube and the mixture was degassed by bubbling N_2 for 6 min. The tube was tightly sealed and put in a merry-go-round type photoreactor with 15 lamps (Philips 8W/08) emitting light nominally at 350 nm at rt. The transparent clear bulk solution became quite viscous after subjected to irradiation for 45 min. The viscous solution was diluted with dichloromethane and added dropwise to cold methanol. The precipitation formed was filtered with a pore-4 Gooch crucible and dried under vacuum to give $(AB)_4$-type star block copolymer of $(PLLA\text{-}PCHO)_4$. Conversions were determined gravimetrically.

RESULTS AND DISCUSSION

Synthesis of $(PLLA\text{-}OH)_4$ and $(PLLA\text{-}alkyne)_4$

Ring opening polymerization (ROP) of lactides such as L-lactide (LLA) with stannous-2-ethylhexanoate, $Sn(Oct)_2$ catalyst, and an –OH functionalized initiator is a very convenient method for synthesizing polylactides with well-defined structures (24). Here, we have applied ROP to prepare a tetra-arm star-shaped poly(L-lactide) with controlled molecular weight and low molecular weight distribution. The ROP of LLA was accomplished using 2,2-bis(hydroxymethyl)-1,3-propanediol as the initiator and $Sn(Oct)_2$ as the catalyst by taking the molar ratios of [Initiator]/[LLA]: 1/50 under inert atmosphere at 130 °C (Scheme 1). The resulting $(PLLA\text{-}OH)_4$ was then reacted with 4-pentynoic acid via condensation reaction to obtain the first click couple compound $(PLLA\text{-}alkyne)_4$. The results and conditions of the synthesized $(PLLA\text{-}OH)_4$ and $(PLLA\text{-}alkyne)_4$ are summarized in Table 1.



Scheme 1. Synthesis of (PLLA-OH)$_4$ and (PLLA-alkyne)$_4$.

Table 1: Results and conditions of the (PLLA-OH)$_4$[a], (PLLA-alkyne)$_4$[b], and (PLLA-PI)$_4$[c]

Run	Polymer	Temp (°C)	Conversion (%)	$M_{n\ theo}$ (g/mol)	$M_{n\ H\ NMR}$[d] (g/mol)	$M_{n.exp}$[e] (g/mol)	M_w/M_n[f]
1	(PLLA-OH)$_4$	130	93	6838	6626	6600	1.06
2	(PLLA -alkyne)$_4$	rt	96	7158	7119	7000	1.06
3	(PLLA -PI)$_4$	rt	96	8396	8312	8200	1.12

- [a] Prepared by ROP of LLA in bulk, [I]/[LLA] = 1/50
- [b] Prepared from the reaction between (PLLA-OH)$_4$ and 4-pentynoic acid
- [c] Prepared via "click" reaction between (PLLA-alkyne)$_4$ and PI-N$_3$
- [d] Determined by ^{1}H NMR measurements
- [e] Determined by GPC measurements. GPC values corrected with the polystyrene calibration curve using a correction coefficient, $M_{n\ exp} = 0.58 \times M_{n\ GPC}$ (27)
- [f] Determined by GPC analysis with polystyrene standards

As can be seen from Table 1, the molecular weight distribution of (PLLA-OH)$_4$ is low and the theoretical molecular weight determined according to the following equation is in good agreement with the measured values by GPC and ^{1}H-NMR analyses. A similar situation was also observed in the case of (PLLA-alkyne)$_4$.

$M_{n\ theo} = [M_0]/[I_0] \times M_m \times \%\ \text{Conv.} + M_I$ (Eq. 1)

where $[M_0]$ and $[I_0]$ are the initial molar concentrations of monomer (LLA) and initiator, and (M_m) and M_I are the molecular weights of the monomer and initiator, respectively. The theoretical molecular weight of (PLLA-alkyne)$_4$ was determined by adding 97 (the molecular weight of the residue of 4-pentynoic acid) to that of (PLLA-OH)$_4$.

The structure of $(PLLA\text{-}OH)_4$ and $(PLLA\text{-}alkyne)_4$ were confirmed by ^{1}H NMR, FT-IR, and GPC analyses. Figure 1 indicates the ^{1}H NMR spectra of $(PLLA\text{-}OH)_4$ and $(PLLA\text{-}alkyne)_4$ polymers. The typical PLLA proton signals at 5.25-5,12 ppm (protons b) and 1.60−1.48 ppm (protons a), and the protons of the initiator in the core were clearly observed for both polymers. ^{1}H-NMR spectrum of $(PLL\text{-}OH)_4$ (Figure 1a) showed that the signals of the methylene protons of the initiator residue (proton c) and the methine protons adjacent to the ω-chain-end hydroxyl groups (proton b′) overlap at 4.34-4.20 ppm while the -CH_3 protons at the last L-lactide unit at the end of the chain (proton a′) appear at 1.37 ppm. However, in the case of $(PLLA\text{-}alkyne)_4$ (Figure 1b), the ω methine proton (b′) and -CH_3 protons (a′) of the last L-lactide unit of $(PLLA\text{-}alkyne)_4$ shifted downfield to where the other b and a protons are, respectively. This is because introduction of the 4-pentynoic acid to the chain end of $(PLLA\text{-}OH)_4$ changed the chemical environment of the last unit and ω methine proton (b′) and -CH_3 protons (a′) are now adjacent to esteric groups rather than hydroxyl groups just like the other repeating units. This clearly shows successful conversion of hydroxyl groups to esteric groups by condensation reaction. The protons of the initiator residue (protons c) in the center of the polymer are not affected by the conversion taking place at the chain ends thus they resonate at the same chemical shift, 4.28 ppm, for both polymers. The successful conversion of the reaction was further supported by the presence of new signals belonging to 4-pentynoic acid protons which were absent in the ^{1}H-NMR spectrum of $(PLLA\text{-}OH)_4$. Neighboring CH_2 protons adjacent to -C≡C- group (protons e) and carbonyl group (protons d) showed triplet peaks at 2.47 and 2.60 ppm, respectively, while the terminal ≡CH proton displayed a singlet at 2.36 ppm. The complete end functionalization of each PLLA arm with alkyne group was also proved by the comparison of the integration values for methylene protons of the initiator (proton c) moiety to those of alkyne (proton d or e) moieties.

The total polymerization degree for 4-arm polymer was found as 46, approximately 12 for each arm, by comparing the integral value of repeating –CH_2– protons of the polymer units to those of terminal –CH-OH (proton b′) or methylene protons of initiator residue (proton c). The ^{1}H NMR molecular weight of $(PLLA\text{-}OH)_4$ and $(PLLA\text{-}alkyne)_4$ were determined according to the equations 2-4 below, respectively;

$$M_{n\ \mathrm{H\,NMR}} = 4 \times (DP_n \times M_m) + M_I \quad \text{(Eq. 2)}$$
$$M_{n\ \mathrm{H\,NMR}} = 4 \times (DP_n \times M_m + 80.1) + M_I \quad \text{(Eq. 3)}$$
$$DP_n = I_{\mathrm{Poly}}/I_I \quad \text{(Eq. 4)}$$

where, $M_{n\ \mathrm{H\text{-}NMR}}$ is the molecular weight of each polymer designated by ^{1}H-NMR; DP_n is the polymerization degree of each polymer arm; M_m is the molecular weight of LLA monomer; M_I is the molecular weight of the initiator moiety in the core of polymers; 80.1 represents the molecular weight of pentynoic acid residue at the end of each PLLA arm after the condensation reaction; I_{Poly} represents the integral value of the signals of two identical –CH– protons in PLLA backbone (b protons); I_I represents the integral value of the signals of -CH_2- protons in the initiator unit at the core of PLLA arms (c protons).

The structure of $(PLLA\text{-}OH)_4$ and $(PLLA\text{-}alkyne)_4$ polymers were also evidenced by FT-IR measurements. The typical ester carbonyl group band of the PLLA backbones could clearly be seen at 1756 cm^{-1} from the FT-IR spectra as shown in Figure 2 (a) and (b). The spectrum of the $(PLLA\text{-}alkyne)_4$ (Figure 2 (b)) showed a new peak at 3285 cm^{-1} due to the ≡CH stretch revealing the presence of alkyne groups at the polymer chain-ends after the functionalization reaction.

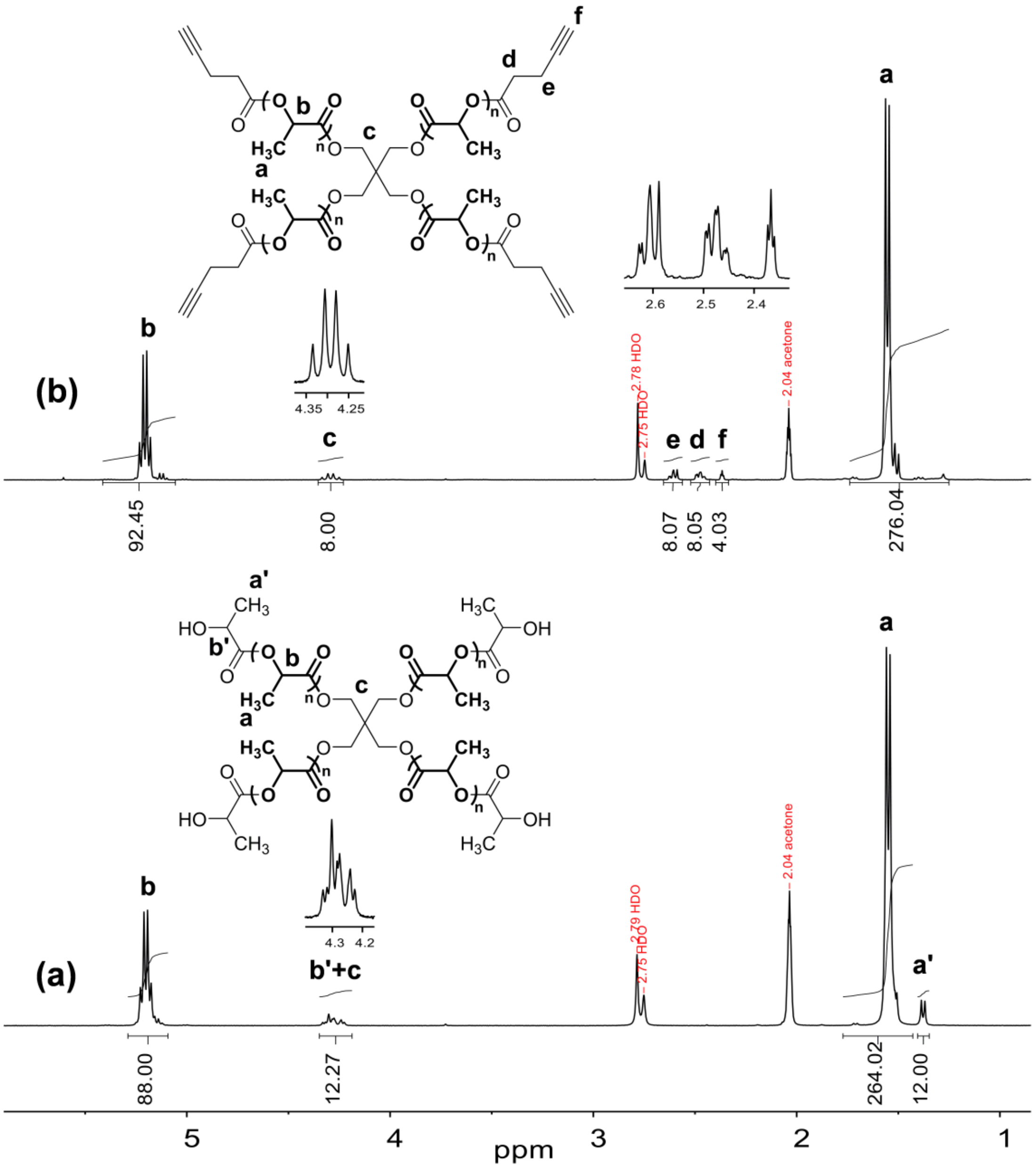


Figure 1. ^{1}H-NMR spectra of $(PLLA\text{-}OH)_4$ (a) and $(PLLA\text{-}alkyne)_4$ (b) in deuterated acetone.

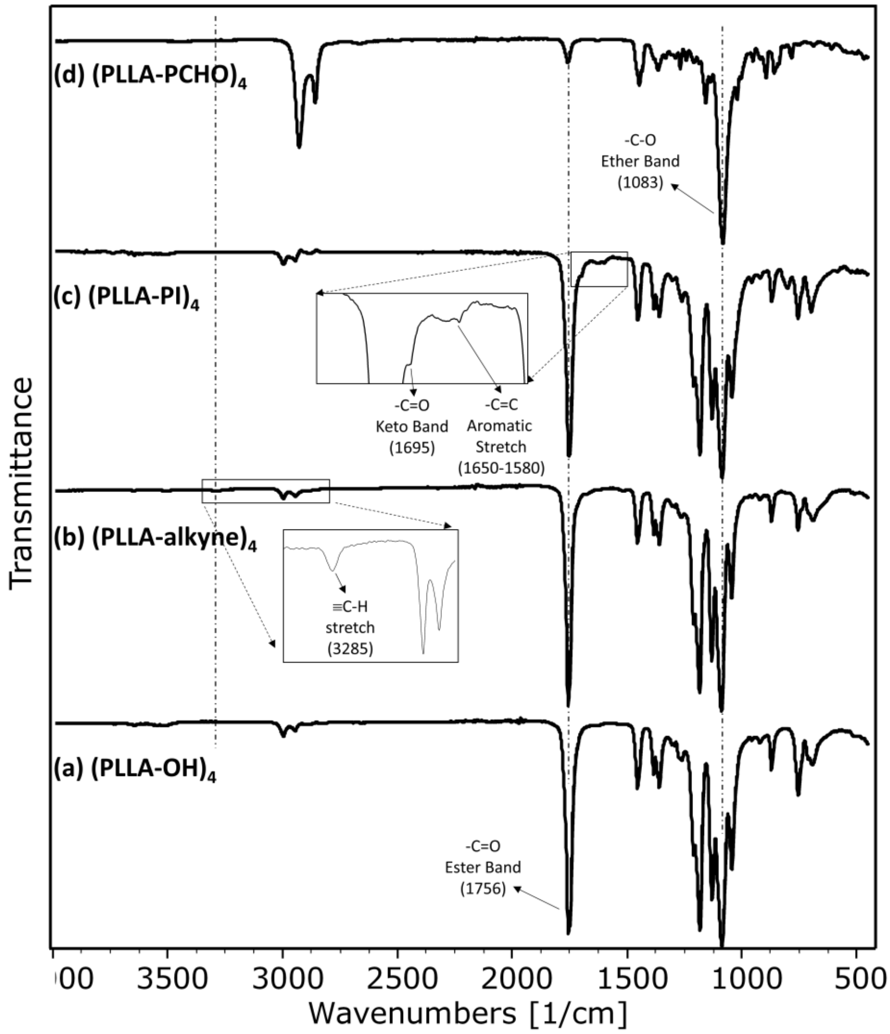


Figure 2. FT-IR spectra of $(PLLA-OH)_4$ (a), $(PLLA-alkyne)_4$ (b), $(PLLA-PI)_4$ (c), and $(PLLA-PCHO)_4$ (d).

Both $(PLLA-OH)_4$ and $(PLLA-alkyne)_4$ polymers showed unimodal and narrow GPC traces (Figure 3) indicating the controlled process of ROP of LLA and no occurrence of side reactions during the alkyne introduction.

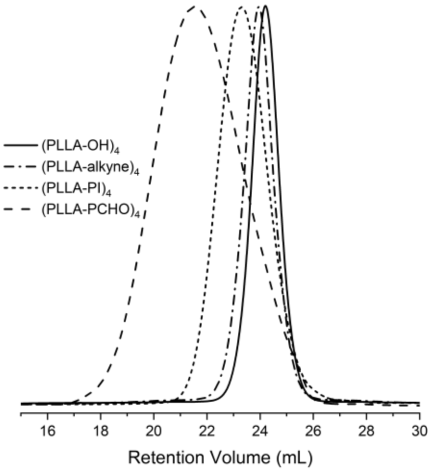
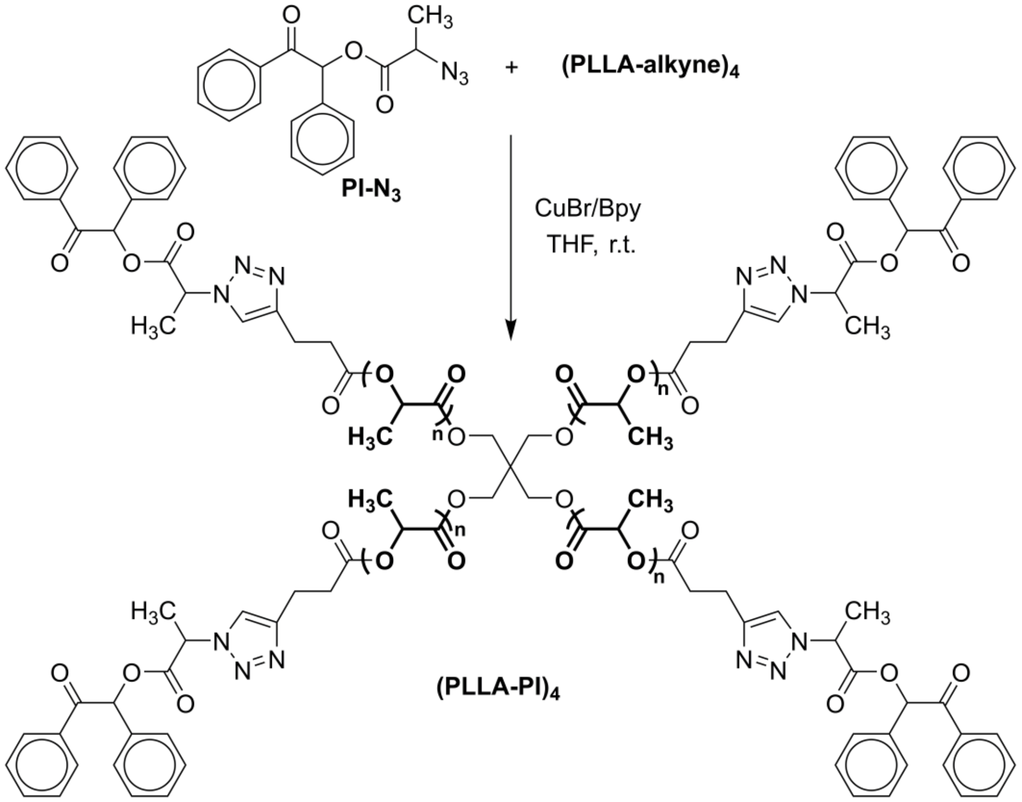


Figure 3. GPC traces $(PLLA-OH)_4$, $(PLLA-alkyne)_4$, $(PLLA-PI)_4$, and $(PLLA-PCHO)_4$.

Synthesis of the star-shaped telechelic macrophotoinitiator $(PLLA-PI)_4$

The "click chemistry", which is the Cu(I)-catalyzed dipolar cycloaddition reaction between an organic azide and a terminal alkyne, method was applied for the synthesis of the star-shaped telechelic macrophotoinitiator, $(PLLA-PI)_4$. For this aim, $PI-N_3$ and $(PLLA-alkyne)_4$ were used as the click couple molecules. The click reaction of these compounds in the presence of CuBr/2,2′-bipyridine catalyst system produced a tetra-arm star-shaped telechelic PLLA macrophotoinitiator with benzoin end-functional groups, $(PLLA\text{-}PI)_4$, (Scheme 2).



Scheme 2. Synthesis of the tetra-arm star-shaped telechelic poly(L-lactide) macrophotoinitiator with benzoin end-functional groups, $(PLLA\text{-}PI)_4$, by click reaction.

FT-IR, ^1H NMR, GPC, UV-Vis and Fluorescence analyses were used to characterize the structure of $(PLLA\text{-}PI)_4$ macrophotoinitiator. The appearance of typical absorption of the aromatic C=C double bond at 1650-1580 cm^{-1} and the disappearance of the ≡C–H stretching band at 3285 cm^{-1} in the FT-IR spectrum of the macrophotoinitiator as shown in Figure 2(c) indicates the completion of the click reaction quantitatively. Also, a new peak at 1695 cm^{-1} due to the C=O keto groups of the photoinitiator moieties appeared on the main ester peak as a sharp shoulder. ^1H-NMR measurements also support the formation of $(PLLA\text{-}PI)_4$ macrophotoinitiator.

Figure 4(a) shows that the repeating PLLA proton peaks (protons a and b) resonate exactly at the same chemical shift as the previous polymers, $(PLLA\text{-}OH)_4$ and $(PLLA\text{-}alkyne)_4$. Aromatic region shows the absorptions that belong to both aromatic protons of benzoin moieties and the only proton of triazole ring (proton f) at 8.10-7.30 ppm. Non-aromatic methine proton of benzoin moiety (proton i) also resonates in this downfield at 7.08 ppm due to the de-shielding effect of the highly electronegative adjacent atoms. The ^1H NMR molecular weight ($M_{n\ H\ NMR}$) of $(PLLA\text{-}PI)_4$ was calculated as 8312 g/mol by using the following equation;

$$M_{n\ H\ NMR} = 4 \times (DP_n \times M_m + 389.4) + M_I \quad \text{(Eq. 5)}$$

$$DP_n = I_{Poly}/I_{CH} \quad \text{(Eq. 6)}$$

where, $M_{n\ H\text{-}NMR}$ is the ^1H NMR molecular weight of macrophotoinitiator; DP_n is the polymerization degree of each polymer arm; M_m is the molecular weight of LLA monomer; 389.4 represents the molecular weight of the end-group of each PLLA arm; M_I is the molecular weight of initiator unit at the central group; I_{Poly} represents the integral value of the signals of two identical –C*H*– protons in PLLA backbone (b protons); I_{CH} represents the integral value of –C*H*– protons in benzoin unit (i protons), respectively.

The GPC chromatogram of $(PLLA\text{-}PI)_4$ (Figure 3) still shows a symmetrical and narrow peak just like those of $(PLLA\text{-}OH)_4$ and $(PLLA\text{-}alkyne)_4$ suggesting that the click reaction progressed without association of any side reaction or byproducts. GPC analysis also exhibited that the macrophotoinitiator has a quite low polydispersity (M_w/M_n) just like the previous polymers meaning no change occurred in the well-defined structure of polymeric chains during the click reaction and the reaction took place on the end groups as expected. Another important data obtained from GPC analysis is the molecular weight of the polymer ($M_{n\ exp}$) and this value is in good agreement with the molecular weights calculated by ^{1}H-NMR ($M_{n\ H\ NMR}$) and theoretically ($M_{n\ theo}$).

Since the star-shaped telechelic macrophotoinitiator bears photoreactive benzoin moieties at the end of each polymer chain, UV-Vis and Fluorescence measurements were also recorded to confirm the successful introduction of these chromophore groups to the chain ends. Figure 5 shows the comparison of UV-Vis absorption spectra of PI-N_3, and (PLLA-PI)$_4$. Both spectra are similar to each other with respect to displaying characteristic benzoyl chromophore absorptions between 300 and 400 nm. It should be noted that the previous polymers, (PLLA-OH)$_4$ or (PLLA-alkyne)$_4$, do not have absorptions in this region. As seen in Figure 6, a similar behavior was observed in comparison of fluorescence spectra of PI-N_3 and (PLLA-PI)$_4$. Both molecules showed emissions pertaining to the vibrational structure of the phenyl ketone chromophore. Judging from the data from various spectroscopic and analytical methods presented above, it is safe to claim that a successful and quantitative click reaction occurred yielding a tetra-arm star-shaped telechelic macrophotoinitiator with a photoreactive benzoin group at the end of each polymer arm, (PLLA-PI)$_4$.

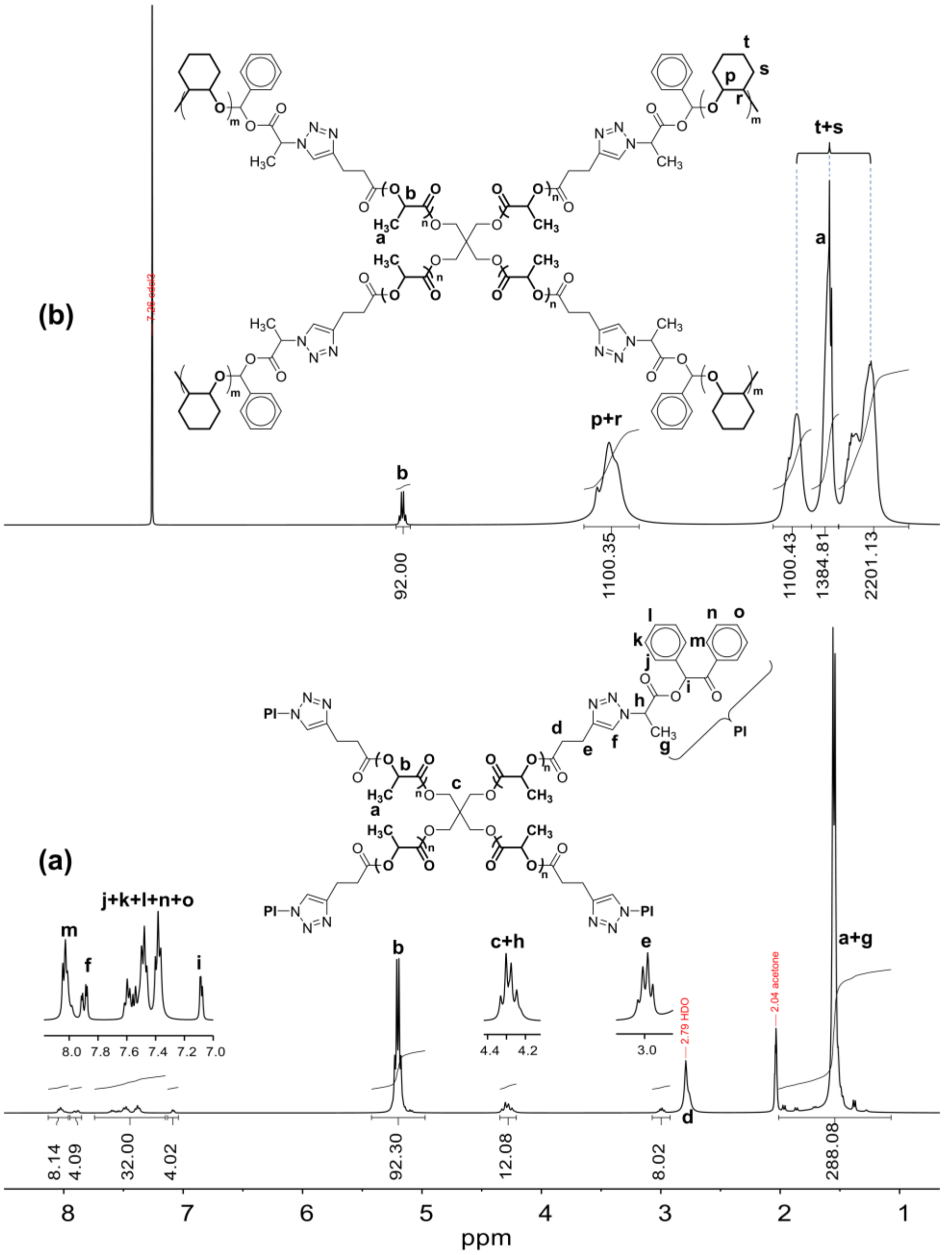


Figure 4. ^{1}H-NMR spectra of (PLLA-PI)$_4$ (a) and (PLLA-PCHO)$_4$ (b).

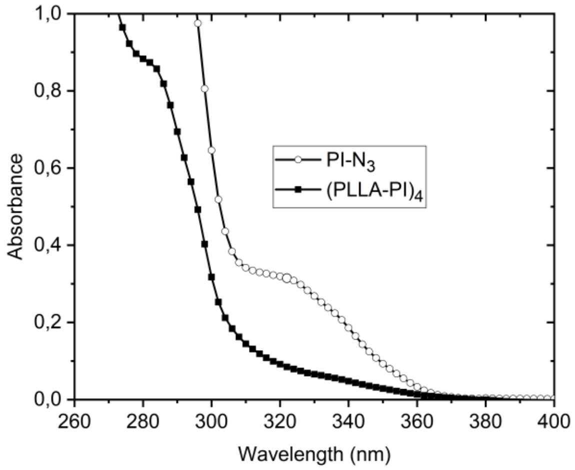


Figure 5. UV absorption spectra of PI-N$_3$ (1.12 x 10^{-3} mol L^{-1}), and (PLLA-PI)$_4$ (8.25 x 10^{-5} mol L^{-1}) in CH$_2$Cl$_2$.

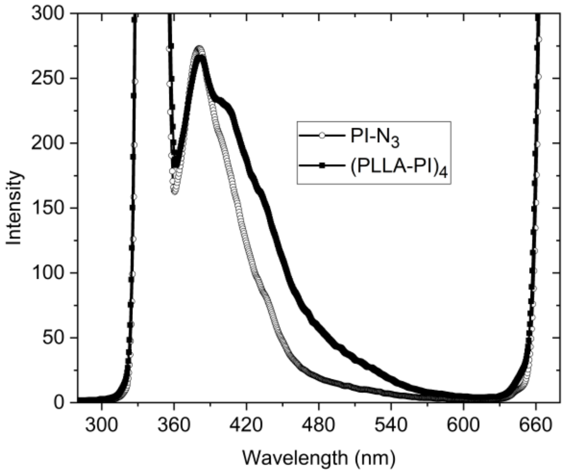


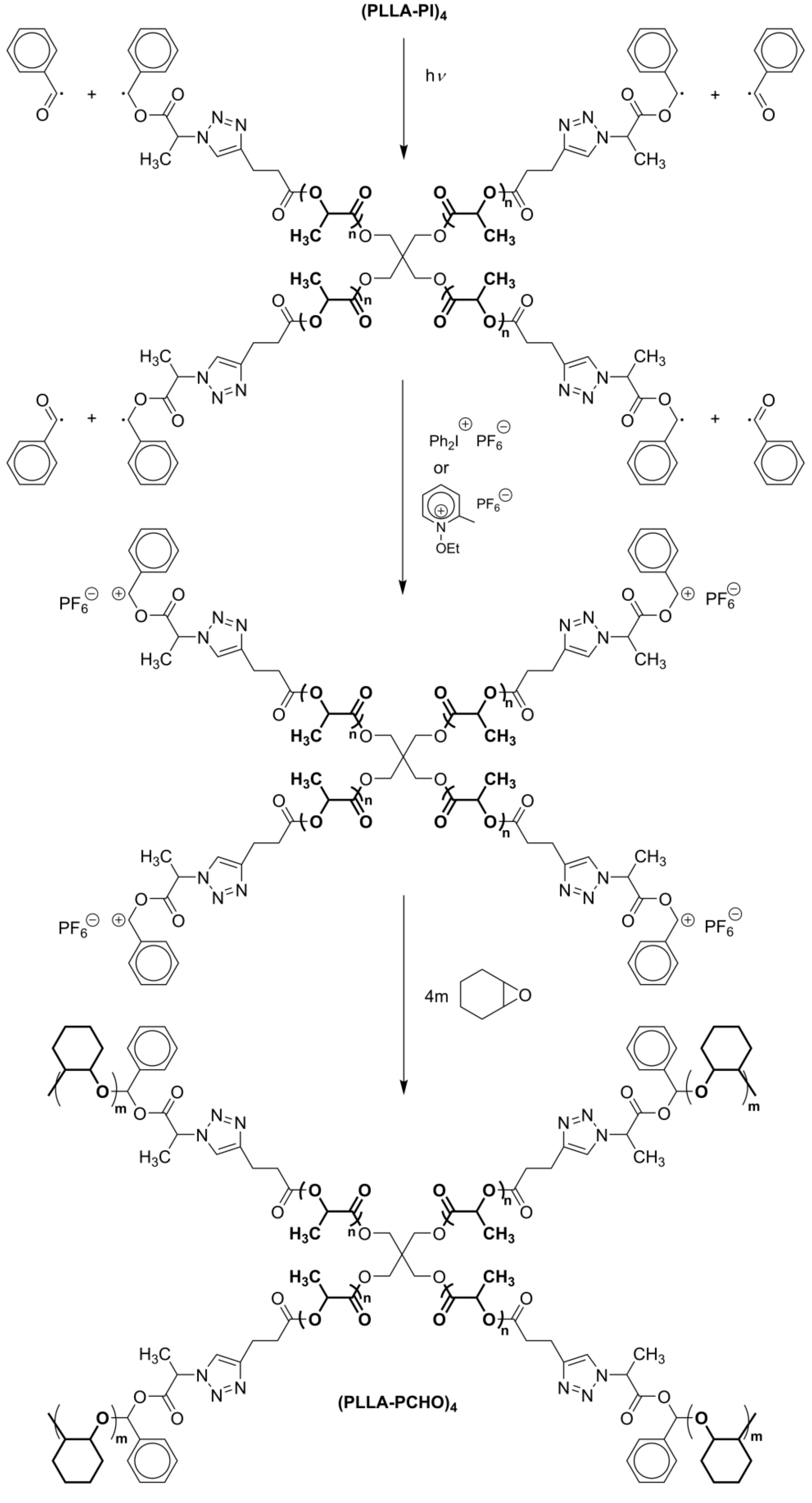
Figure 6. Fluorescence spectra of PI-N$_3$ (7.12 x 10^{-5} mol L^{-1}), and (PLLA-PI)$_4$ (7.93 x 10^{-5} mol L^{-1}) in CH$_2$Cl$_2$, λ_{exc} = 340 nm.

Synthesis of (AB)$_4$-type star block copolymer (PLLA-PCHO)$_4$

The synthesis of (AB)$_4$-type star block copolymer, or (PLLA-PCHO)$_4$ in short, has been conducted using (PLLA-PI)$_4$ as the macrophotoinitiator, cyclohexene oxide (CHO) as the monomer, and Ph$_2$I$^+$PF$_6^-$ or EMP$^+$PF$_6^-$ as the oxidizing agent in photoinduced free radical promoted cationic polymerization. UV irradiation of (PLLA-PI)$_4$ caused *α*-cleavage in photoreactive benzoin moieties generating benzoyl and alkoxybenzyl radicals connected to polymer chains in the initial step as described in Scheme 3. While the strong electron donor PLLA-bonded alkoxybenzyl radicals are oxidized by the onium salt (Ph$_2$I$^+$ or EMP$^+$) to give the corresponding carbocations, electron withdrawing benzoyl radicals cannot be oxidized. Thus, polymer attached alkoxy carbocations are able to react with CHO monomer to produce an (AB)$_4$-type star block copolymer consisting of PLLA as the A blocks and PCHO as the B blocks, whereas benzoyl radicals do not interfere the polymerization and can be easily removed from the reaction mixture during the work-up process. The control experiment done with all reagents except for the macrophotoinitiator resulted in no polymer formation even after 4 h of irradiation. This is yet another proof that the starting material, (PLLA-PI)$_4$, was successfully prepared considering that the photoinduced free radical promoted cationic polymerization only progresses in the presence of a proper photoinitiator group such as benzoin as the free radical source.

^{1}H NMR spectrum of the star block copolymer, (PLLA-PCHO)$_4$, is shown in Figure 4 (b). The typical signals of the −OC*H* group protons in the PCHO blocks (proton p and r) appeared at 3.70-3.15 ppm. The other repeating proton signals of PCHO blocks resonate at upfield region between 2.06 and 1.04 ppm and assigned properly in Figure 4 (b). There is not a significant chemical shift observed for the repeating units of PLLA block compared to the previous polymer as expected. The degree of polymerization (DP_n) for each PCHO blocks was found as 138, by comparing the integral ratio of –C*H*– protons (b) of PLLA backbone to those of –OC*H*C*H*O– protons (p+r) of PCHO backbone.

The successful photoinduced free radical promoted cationic polymerization processes and the formation of star block copolymer (PLLA-PCHO)$_4$ were also supported by FT-IR measurements (Figure 2(d)). A very intense band at 1083 cm^{-1}, which is even surpassing the intensity of the characteristic band of carbonyl peak of PLLA blocks at 1756 cm^{-1}, appeared due to the repeating etheric band of PCHO blocks. This is an expected phenomenon considering that PCHO segment has many more repeating units compared to PLLA segment based on the calculations from ^{1}H-NMR and GPC data.



Scheme 3. Synthesis of the $(AB)_4$-type star block copolymer $(PLLA\text{-}PCHO)_4$ by photoinitiated free radical promoted cationic polymerization.

The unimodal and relatively broader GPC peak of $(PLLA\text{-}PCHO)_4$ compared to those of the well-defined pre-polymers is a typical result observed for the uncontrolled polymerizations. GPC curve of the $(PLLA\text{-}PCHO)_4$ shows no peak attributed to the starting macrophotoinitiator (Figure 3), indicating completely depletion of the macrophotoinitiator used during the photopolymerization process.

Thermal analyses of polymers

Thermogravimetric and differential thermal analyses (TG/DTA) of $(PLLA\text{-}OH)_4$, $(PLLA\text{-}alkyne)_4$, $(PLLA\text{-}PI)_4$, and $(PLLA\text{-}PCHO)_4$ were carried out under N_2 atmosphere. The DTA analyses of the polymers are shown in Figure 7.

While $(PLLA\text{-}OH)_4$, $(PLLA\text{-}alkyne)_4$, and $(PLLA\text{-}PCHO)_4$ have displayed two endothermic peaks, $(PLLA\text{-}PI)_4$ has shown three endothermic peaks. The glass transition temperatures (T_g) were observed as endothermic peaks at 62.45 °C for $(PLLA\text{-}OH)_4$, 68.17 °C for $(PLLA\text{-}alkyne)_4$, 62.55 and 84.54 °C for $(PLLA\text{-}PI)_4$, and 62.22 °C for $(PLLA\text{-}PCHO)_4$. The other main endothermic peaks at 128.87 °C, 127.44 °C, 113.43 °C, and 178.80 °C indicate the melting temperature (T_m) of $(PLLA\text{-}OH)_4$, $(PLLA\text{-}alkyne)_4$, $(PLLA\text{-}PI)_4$, and $(PLLA\text{-}PCHO)_4$, respectively. In addition, the exothermic peak observed at 99.25 °C represents the crystallization temperature (T_c) of the $(PLLA\text{-}PI)_4$ while ($(PLLA\text{-}OH)_4$, $(PLLA\text{-}alkyne)_4$, and $(PLLA\text{-}PCHO)_4$ displayed no crystallization temperatures most probably owing to the groups linked to the PLLA chains. The T_gs and T_ms found for the polymers synthesized in this study are the typical temperatures of PLLA based polymers and are consistent with the literature. The higher T_m observed for $(PLLA\text{-}PCHO)_4$ in comparison with the other homo type polymers is probably attributed to the conformation and construction of star block copolymer.

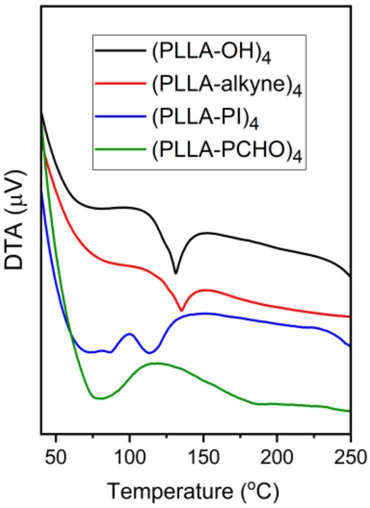


Figure 7. DTA traces of the synthesized polymers.

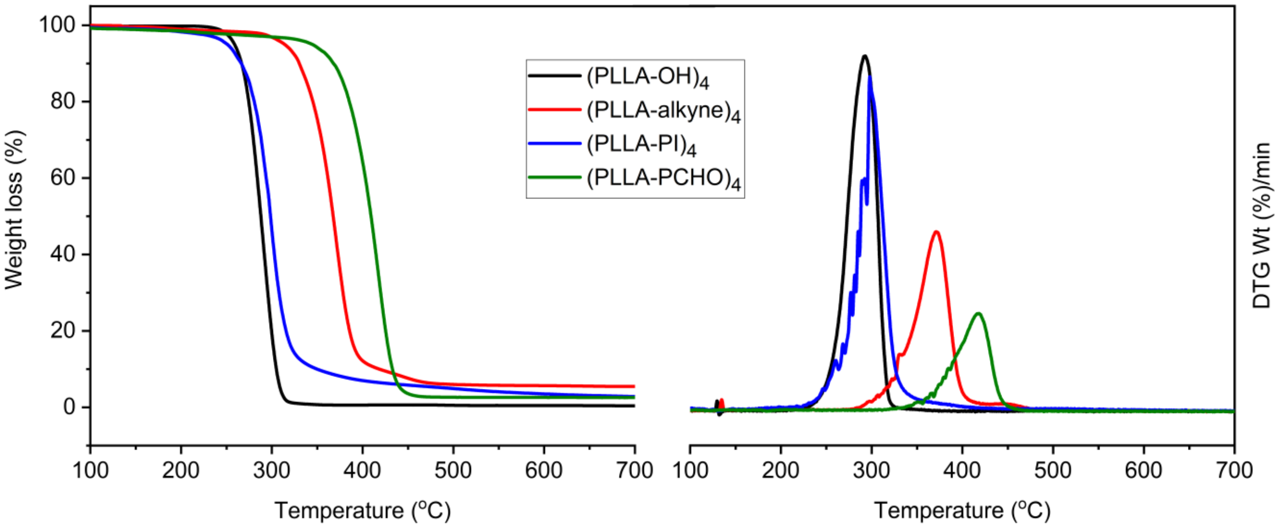


Figure 8. TG and DTG profiles of the synthesized polymers.

The thermogravimetric (TG) curves and derivative (DTG) curve of the polymers are shown in Figure 8. The onset decomposition temperatures of the $(PLLA\text{-}OH)_4$, $(PLLA\text{-}alkyne)_4$, $(PLLA\text{-}PI)_4$, and $(PLLA\text{-}PCHO)_4$ were found as 227 °C, 274 °C, 225 °C, and 377 °C, respectively. The onset decomposition temperatures and degradation rates of homo-type PLLAs are lower than those of star-type block copolymer, indicating higher thermal stability of $(PLLA\text{-}PCHO)_4$ polymer. It is well- known that non-crystalline PCHO is a thermally stable polymer with a decomposition temperature over 400 °C. It seems introducing this durable block into the structure of the polymer has enhanced its thermal stability judging from its boosted decomposition temperature in comparison with the prepolymers (24). Figure 8 shows that terminal alkyne groups also contribute to the thermal stability of the polymer positively compared to other homopolymers, (PLLA-OH)$_4$ and (PLLA-PI)$_4$. As seen from the figure, while (PLLA-OH)$_4$ has shown one maximum decomposition rate at 290 °C, (PLLA-alkyne)$_4$ and (PLLA-PI)$_4$ have shown three maximum decomposition rates at 324 °C, 362 °C, 436 °C and 258 °C, 290 °C, 300 °C, respectively. The obtained star block copolymer has displayed two maximum decomposition rates at 357 °C and 408 °C.

CONCLUSION

The combination of a controlled polymerization technique with click chemistry is a very versatile method to prepare custom-tailored copolymers with well-defined structures and desired functionalities. We have used this approach to synthesize a novel tetra-arm star-shaped telechelic macrophotoinitiator of poly(L-lactide) with photoreactive benzoin groups at the end of each polymer arm by combining ROP and click chemistry. These photofunctional benzoin groups at the end of each PLLA block served as a means to introduce a new polymer block of cyclohexene oxide to each arm to create an (AB)$_4$-type star block copolymer by photoinduced free radical promoted cationic polymerization. Structural elucidations of the intermediate and final polymers confirmed the all the compounds were successfully synthesized. Thermal behaviors of the polymers indicated that the star block copolymer, (PLLA-PCHO)$_4$, is more stable than the prepolymers. All data and results are in good agreement with each other. As a conclusion, this approach can be used to prepare star-type block copolymers with monomers having different nature and polymerizing with different mechanisms.

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