이학석사 학위논문

Effect of the Molecular Weight on the Synthesis and Properties of the Discrete Molecular Weight Cyclic Polymer

분자량 분포가 없는 고리형 중합체의 합성과 성질에 대한 분자량의 영향

2023 년 2 월

서울대학교 대학원

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정지수의 이학석사 학위논문을 인준함

2023 년 2 월

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Abstract

Effect of the Molecular Weight on the Synthesis and Properties of the Discrete Molecular Weight Cyclic Polymer

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When the chain of cyclic polymer becomes long enough to dismiss the structural strain, only the conformation and composition of repeating units affect to the chemical properties of cyclic molecule. At this level, cyclic polymer has physical homogeneity from absence of chain ends. But in order to observe these unique properties of cyclic polymer, it is important to remove every linear impurity which can drastically affect the property of the material with only trace amount. Herein, we synthesized unimolecular cyclic polymer with the iterative exponential growth

mechanism and the intramolecular cyclization of end-functionalized polylactide. By using polymer backbone with extremely low dispersity, It is available to separate cyclic polymer from linear precursors with Prep-SEC since hydrodynamic volume of the polymer shrinks after cyclization. To improve the producibility of the cyclic polymer, cyclization condition is optimized by choosing the solvent, changing the injection rate, and controlling the injection concentration. By selecting copper sulfate and sodium ascorbate catalyst with DMSO solvent with high temperature and diluting the concentration at high molecular weight, cyclic polylactic acid producibility is increased. Based on these findings, we took a step closer to the practical application of cyclic polymers.

Keyword : cyclic polymer, dispersity, CuAAC reaction, optimization

Student Number : 2021-21486

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I. Introduction

Macrocyclic molecules like cyclodextrins and crown ethers were discovered more than a hundred years ago[1], but these molecules still remain interesting because of the unique chemical properties from the cavity which can accommodate guest molecules.[2-4] In case of cyclic polymers, the size of the ring is bigger and the chain is longer. As a result, this special chemical interaction from host-guest relationship disappears. Instead, cyclic structure relieves the ring strain as the chain becomes longer. And when it becomes long enough to dismiss the structural strain, only the conformation and composition of repeating units affect to the chemical properties of cyclic molecule. At this level, cyclic polymer has physical homogeneity from absence of chain ends.[5,6]

In contrast to linear and branched polymers, cyclic polymers have no chain ends and therefore feature a range of unexpected physical properties. For example, Kricheldorf et al. synthesized high molar mass cyclic polylactides by Ring-opening polymerization with simultaneous polycondensation mechanism with intermediate formation of linear chains having one Sn–O–CH end group and one mixed anhydride end group.[7] They also found characteristic properties of cyclic polymers such as smaller hydrodynamic volume, lower melt viscosities, and higher thermostabilities compared to the properties of their linear counterparts.[8]

Also, Grayson and his group synthesized cyclic polymers with click chemistry. to synthesize the polymer with it. The linear precursors were prepared via ring-opening polymerization from an azido-functionalized initiator, followed by end group modification to attach a terminal alkyne. Click coupling afforded the cyclic polymer in high yields and provided linear and cyclic poly(caprolactone) with

exactly identical molecular weight distributions and observed slower degradation profile compared with their linear counterparts.[9] They synthesized linear precursor through atom transfer radical polymerization on to investigate the confinement of bulk glass transition temperature on silica substrate and observed that glass transition temperature of cyclic polymer is invariant to substrate.[10] This group also demonstrated that cyclic block copolymers self-assemble into compact nanostructures, as illustrated by their reduced domain spacing when cast into thin films and their reduced micellar size in solution.[11]

Because of these unique properties, cyclic topology endows chances to become promising candidate for industrial applications.[12,13] There are many chemistries developed for the synthesis of cyclic polymers in the past decades. And two of the most popular and successful routes are the ring-closure and ring-expansion method. These approaches have their own advantages and limitations, as well as scope of applicability. For example, ring-closure strategies are compatible with various polymerization techniques and backbones, but they are only suitable for cyclizing polymers with molecular weight lower than 20k Da.12 In contrast, the ring-expansion strategy can be used for preparing much larger cyclic polymers around 1m Da. However, it is challenging to control the molecular weight and distribution of the obtained samples, and the backbone structure is limited.[14] No matter which strategy is chosen, because of ring opening or incomplete ring closure, it is impossible to be free of linear polymers as contaminants. The existence of linear impurity in trace amount can result in significant deviations to the measured physical properties of the cyclic polymer sample.[15] In order to dismiss the effect of impurities on cyclic polymers, many groups put tons of innovative endeavor.[16-18] As progress in the synthesis of high-purity cyclic samples enabled more reliable physical evaluations and a better understanding of the ramifications of the cyclic topology, it is important to remove the impurities from the cyclic polymer.[19-21]

Herein, we focused on synthesizing pristine cyclic polymer free of impurities by

utilizing unimolecular polymer precursor. To synthesize unimolecular polymer, iterative exponential growth method is applied. Iterative exponential growth is an alternative synthetic strategy wherein doubly protected molecules undergo cycles of orthogonal activations and couplings to yield macromolecules with length 2^n.[22] This approach to discrete polymers has merit on productivity because it requires smaller number of required steps compared to solid-phase synthesis.[23,24] Utilizing the molecular weight difference between reagents and coupled products, we adopted size-exclusion chromatography as a purification method for the discrete polymers. Preparative size-exclusion chromatography (Prep-SEC) could be performed for the preparation of high molecular-weight monodisperse polymers. We adopted polylactide oligomer as a unimolecular polymer for cyclization precursor. Starting from lactide, telechelic polymer with benzyl ester (-Bz) and *tert*-butyldimethylsilyl (-TBDMS) ether protecting group the exponentially grown polymer can be easily separated up to 32 monomer units by HPLC.[25,26] For cyclization, we adopted the pseudo-dilution conditions Copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction reported by Grayson group.[16] The crude mixture containing cyclic and linear polymers with same molecular weight can be separated by utilizing the difference in hydrodynamic volume. As the cyclic product has smaller hydrodynamic volume in solution due to the topological constraints on its conformation, it is possible to separate the product with Prep-SEC.[27]

II. Results and Discussion

Synthesis of linear PLA with desired molecular weight

We synthesized cyclic polymer with unimolecular polylactide (PLA) backbone by the iterative convergent method.[25] This type of linear precursor is worthy to prepare for high molecular-weight cyclic polymers and block copolymers as it is possible to decrease linear contaminants via intramolecular cyclization and Prep-SEC. Lactide having benzyl (Bz) ester and *tert*-butyldimethylsilyl (TBDMS) ether protecting groups (TBDMS-LA_2-Bz) was synthesized by ring opening with benzyl alcohol and hydroxy protection with TBDMSCl (Scheme 1a).[25]

And the linear chain doubles its length after one exponential growth cycle. This process is comprised of deprotection step and coupling step; Lactide unit with length n is A portion of LA_n is converted to HO-LA_n-Bz by selective deprotection of the silyl protecting group with $BF_3 \cdot Et_2O$ at room temperature. The other portion is subjected to hydrogenation with triethylsilane and Pd/C, which yields TBDMS-LA_n-COOH quantitatively (Scheme 1b). These linear polymers were characterized by ^1H and GPC, and MALDI-TOF mass spectrometry (Table 1). The yield for the coupling reaction is calculated through GPC and gradually decreased at longer chain length (Figure 7-12). Stoichiometric amounts of these coupling partners are converged with 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) and 4-dimethylamino pyridinium *p*-toluenesulfonate (DPTS) to afford TBDMS-LA_{2n}-Bz in high yield (Figure 7, 9, 11).

Yield of convergence step can be increased by using excess amount of HO-LA_n-Bz and excess benzyl ester protected reactant can be retrieved by flash column

chromatography. These recycled polymers have no difference in reactivity and purity is confirmed through ^{1}H NMR result (Figure 1).

To separate iterative grown product, JAIGEL 3HR, 2.5HR, 2HR columns are utilized. Product polymers with over 10k Da molecular weight are separated with 3 and 2.5 HR columns and others are separated with 2.5HR and 2HR columns. When each crude polymer 300mg is dissolved in 3mL of HPLC grade $CHCl_3$, a few cycles of chromatography separated most of the product from reactant. In case of TBDMS-LA_{192}-Bz, it is much harder to acquire the pristine product since molecular weight ratio and hydrodynamic volume difference is way much smaller (Table 2).

As it is hard to separate polymers with small molecular weight difference with prep-SEC, we utilized two types of half-activated PLA chain with same number of monomer units for backbone chain synthesis in previous works. But this time, we synthesized LA_{192} with TBDMS-LA_{64}-COOH and excess HO-LA_{128}-Bz and successfully separated pure product with prep-SEC. Also, during synthesis of linear backbone structure, it is confirmed that linear precursor with 192 and 256 repeating units can be separated through Prep-SEC with more than 20 circulations. (Figure 6).

Scheme 1. (a) Synthesis of telechelic di-lactide with protection groups from lactide (b) Synthesis of monodisperse oligomers and polymers by the iterative linear convergence of repeating units.

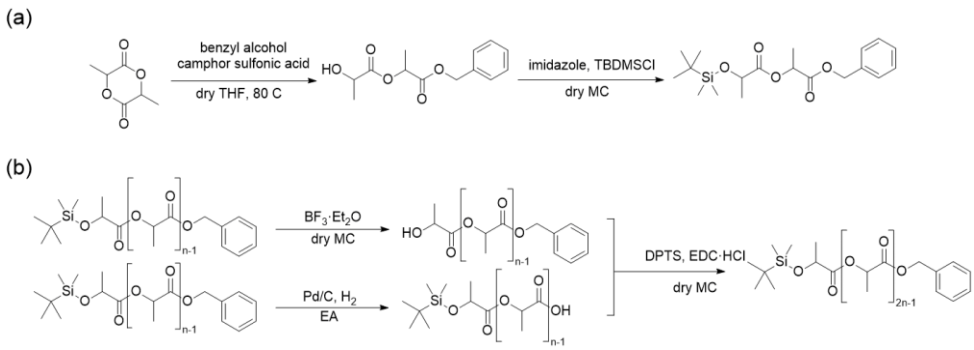


Table 1. Molecular weight analysis of discrete linear PLAs.

Entry	MALDI-TOF		GPC		
	calculated ($[M+Na]^+$)	found ($[M+Na]^+$)	M_n (Da)	M_p (Da)	PDI
LA64	4854.49	4855.99	7209	7536	1.03
LA128	9469.46	9470.36	14112	14430	1.02
LA192	14081.49	14081.40	21304	21501	1.02
LA256	18693.52	18695.04	27730	28544	1.02

Figure 1. ^{1}H NMR result of retrieved HO-LA_{64}-Bz

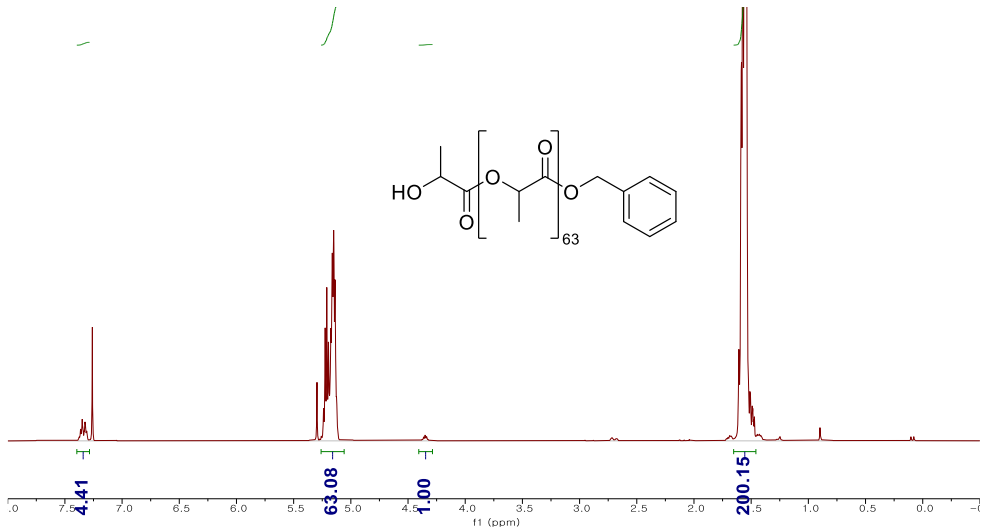


Table 2. Prep-SEC separation condition for linear polymers.

TBDMS-**LAn**-Bz	*MW* (g/mol)	Flow Rate (mL/min)	Concentration (mg/mL)	Injection volume (mL)	Required Cycles for Separation
LA64	4854.49	10	100	3.0	4
LA128	9469.46	10	100	3.0	5
LA192	14081.49	10	100	3.0	11*
LA256	18693.52	10	100	3.0	7

In case of LA_{192}, its is the required number of cycle for discrete 128 and 192 mer signal peaks.

End group modification and cyclization of PLA precursor

The hydroxy and carboxylic acid termini of LA_n were sequentially deprotected and converted to acetylene and azide groups, respectively. This resulted in Alk-LA_n-N_3 for an intramolecular click reaction catalyzed by copper sulfate and sodium ascorbate (Scheme 2). The product is purified by flash column chromatography and complete modification of end group is confirmed by ^{1}H NMR and MALDI-TOF. Distinctive peaks of Azido ethanol at 4.23 and 3.42 ppm shifts and 2.57 and 2.45 ppm shifts of 4-pentynoic acid are observed in ^{1}H NMR and azido group degradation signals can be detected with MALDI-TOF (Figure 8, 10, 12).

To prevent the formation of intermolecular click reaction product, we adopted the pseudo dilution conditions reported by Grayson and co-workers.[16] In this process excess amount of catalyst must be dissolved in batch to make the cyclization reaction as rapid as possible. Initially, we utilized THF as cyclization matrix and copper bromide and *N,N,N′,N″,N‴*-pentamethyldiethylenetriamine (PMDETA) catalyst. But even the moderate secondary amine catalysts can undermine the polylactide backbone structure, and degradation of the polymer chain is observed. So we changed click reaction catalyst to copper sulfate pentahydrate and sodium ascorbate known as Sharpless-Fokin catalyst.[28] Finn group reported that Cu(I) requires bidentate for ligand acceleration of the CuAAC click reaction. Kinetics measurements as a function of ligand-metal ratio and catalyst concentration were found to be consistent with an active Cu_2L formulation.[29]

After successful cyclization, GPC revealed the emergence of a novel peak corresponding to the chemical species with half the hydrodynamic volume (Figure 10-15). If internal strain is dismissed and the polymer is dissolved in the matrix pretty well enough to take random motion, hydrodynamic volume of one precursor becomes $n^{3/2}$ times when the length of chain increases n times and the

hydrodynamic volume of cyclic polymer is 1/2 of linear one with same molecular weight.[8, 30] And as the elution time difference of polymers with same composition in GPC is proportional to the logarithm of the hydrodynamic volume, our GPC results that cyclic polymers having 0.17 minute delayed elution time in average and that cyclic or linear polymer with half size eluted after 0.42 minutes (Table 3). The reason why the result does not comply to the theoretical value is that the volume of polymer itself can't be dismissed in oligomer level.

Scheme 2. Synthesis of unimolecular cyclic polymer with Cu(II)·5H_2O, sodium ascorbate catalyst

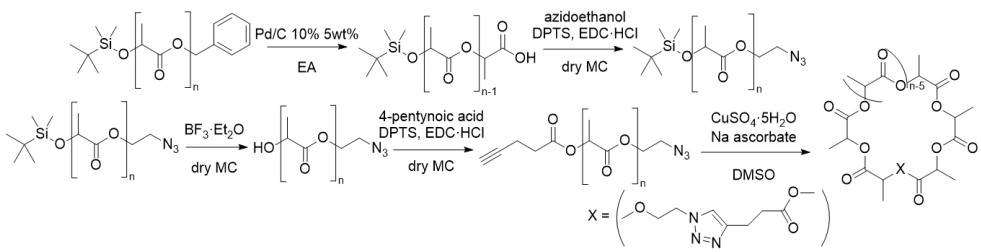


Table 3. GPC Elution time comparison of polymers with THF eluent.

Entry	GPC elution time	
	linear	cyclic
LA64	8.03	8.19
LA128	7.67	7.85
LA192	7.47	7.63
LA256	7.28	7.48

Optimization of CuAAC cyclization condition

The yield for the coupling reaction is calculated through GPC and gradually decreased with longer chain length (Figure 2). And more intermolecular product and inactive precursors are observed. It is majorly because of the decreased chance for intramolecular effective collision. As hydrodynamic volume of one precursor becomes $n^{3/2}$ times when the length of chain increases n times, we expected required time for CuAAC will become n^3 times. This is the main reason why ring-closure cyclic polymer synthesis is not suitable for cyclizing polymers with molecular weight lower than 20k.[14] But it is impossible to take other pathway since it is the only way to utilize unimolecular polymer for discrete backbone structure. We take effort on improving the yield and productivity of the product.

The first thing we changed is the type of the solvent. If the solvent is not good at solvating the precursor, the polymer chain would be entangled and the opportunity for the end group to participate in reaction would be decreased as there'd be less chances to be exposed to outside. Solvent less polar than DMF and DMSO (acetone, THF) can't dissolve copper sulfate and there's no cyclization reaction in acetonitrile. has chosen as a solvent for cyclization since it showed highest cyclization yield (Figure 3). Another merit from utilizing DMSO as a cyclization solvent is that it is possible to heat up reaction batch to higher temperature to accelerate the cyclization reaction.

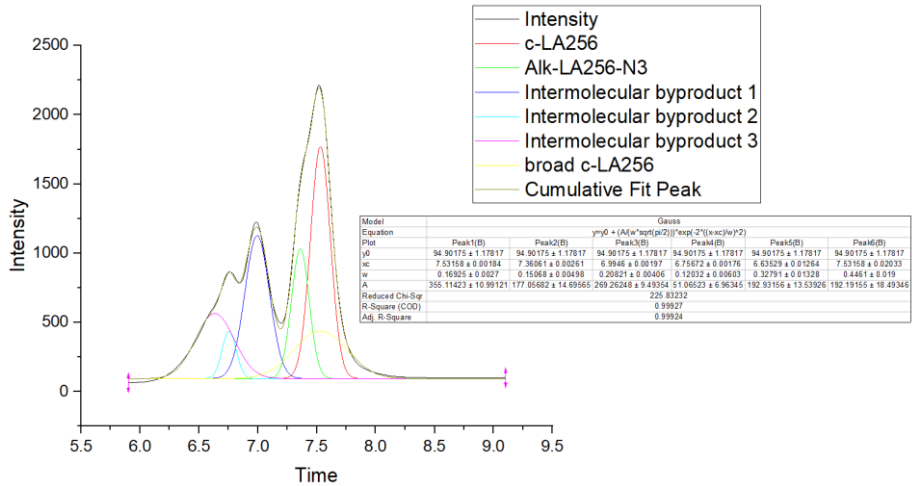
Also, to evade the intermolecular reaction, concentration and injection rate of the precursor for pseudo dilute condition is adjusted. Hypothesizing that the active polymer end group is located in random position of hydrodynamic volume, the effective concentration of polymer becomes $n^{-3/2}$ times when the polymer length increases n times. In this case, if same mass of the precursor is dissolved, then intramolecular reaction rate decreases n^{-3} times and intermolecular reaction rate

decreases n^{-2} times. In order to maintain the ratio of intra- and intermolecular reaction, dissolved mass of precursor per volume should be inversely proportional. In case of cyclization of precursor with more than 10k Da, deconvolution result of crude cyclization product showed considerable amount of intermolecular product (Figure 4 a-d). As the effect of intermolecular reaction from concentration can't be dismissed, we optimized cyclization reaction by making precursor concentration inversely proportional to molecular weight (Table 4).

Also, the other factor that can affect to the generation of intermolecular product; injection rate was on contemplation. If injection rate is too fast, precursor would be injected before the reaction is over. In this case, precursor remain constant concentration. And in this case, reaction rate constant for CuAAC click reaction is around 10–100 $M^{-1}s^{-1}$ with 20 μM Cu(I).[29] As the excess amount of catalyst facilitate the cyclization reaction, calculation result shows that one or two drops of precursor per minute with ~1μM concentration don't undermine dilute condition. Experiment result also showed no significant difference in generation of intermolecular product with molecular weight around 20k Da (Figure 4 c, e).

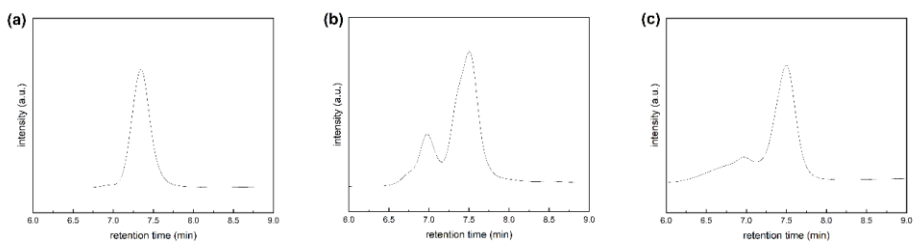
As separation of the product with Prep-SEC cannot be performed bulk compared with HPLC separation, yield loss at the final steps is critical to the productivity. It is important to reduce the steps after growing polymer length over 32-mer. synthesis. bulk synthesis. For this reason, processing end group modification before this stage seemed to be improve the productivity. We synthesized cyclic polymer with CuAAC click reaction and azido end group seems to be orthogonal to iterative growth process; deprotection and coupling reaction (Scheme 3). And the yield of the iterative polymer growth is calculated with GPC deconvolution (Figure 5). Though total yield of benzyl deprotection and azido ethanol esterification process is over than 90%, this process will be meaningful in case of cyclization of polymer with longer backbone chain.

Figure 2. deconvolution result of crude c-LA_{256}.



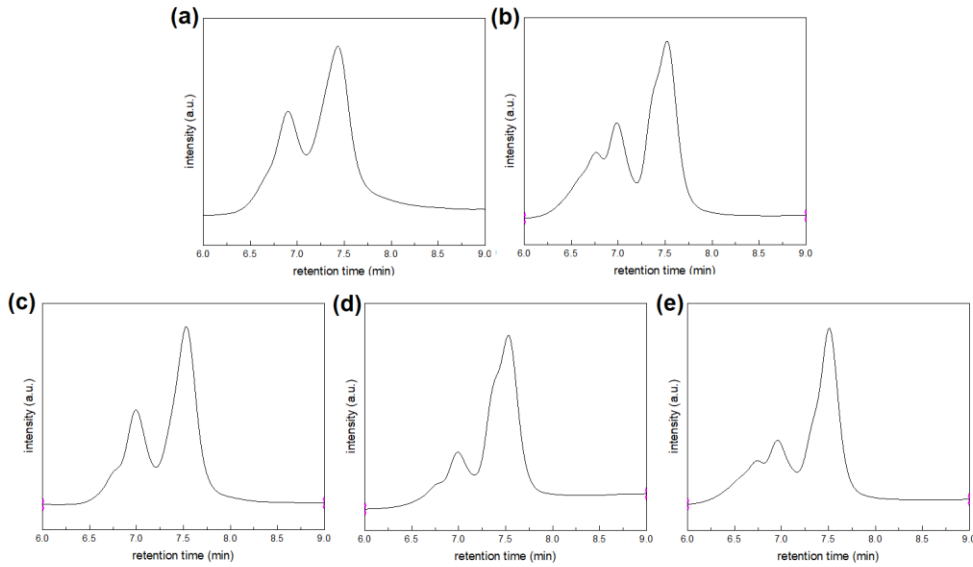
Model	Gauss					
Equation	y=y0 + (A/(w*sqrt(pi/2)))*exp(-2*((x-xc)/w)^2)					
Plot	Peak1(B)	Peak2(B)	Peak3(B)	Peak4(B)	Peak5(B)	Peak6(B)
y0	94.90175 ± 1.17817	94.90175 ± 1.17817	94.90175 ± 1.17817	94.90175 ± 1.17817	94.90175 ± 1.17817	94.90175 ± 1.17817
xc	7.53158 ± 0.00184	7.36061 ± 0.00261	6.9946 ± 0.00197	6.75672 ± 0.00176	6.63529 ± 0.01264	7.53158 ± 0.02033
w	0.16925 ± 0.0027	0.15068 ± 0.00498	0.20821 ± 0.00406	0.12032 ± 0.00603	0.32791 ± 0.01328	0.4461 ± 0.019
A	355.11423 ± 10.99121	177.05682 ± 14.69565	269.26248 ± 9.49354	51.06523 ± 6.96345	192.93156 ± 13.53926	192.19155 ± 18.49346
Reduced Chi-Sqr	225.83232					
R-Square (COD)	0.99927					
Adj. R-Square	0.99924					

Figure 3. GPC result of cyclization reaction of Alk-LA_{256}-N_3 in (a) acetonitrile (b) DMF (c) DMSO



Cyclic product is not observed in (a), and the cyclization yield is (b) 61.95% (c) 72.50%.

Figure 4. GPC result of Alk-LA_{256}-N_3 precursor with concentration and injection rate difference.



Concentration of injecting precursor is (a) 10 mg/mL (b) 5 mg/mL (c), (e) 2.5 mg/mL (d) 1 mg/mL and injection rate is 1 mL/hr except (e) with 0.25 mL/hr. Cyclization yield calculated by deconvolution of GPC result is (a) 50.62% (b) 54.92% (c) 57.93% (d) 60.39% (e) 58.54%

Scheme 3. Iterative growth mechanism with azido end group modification.

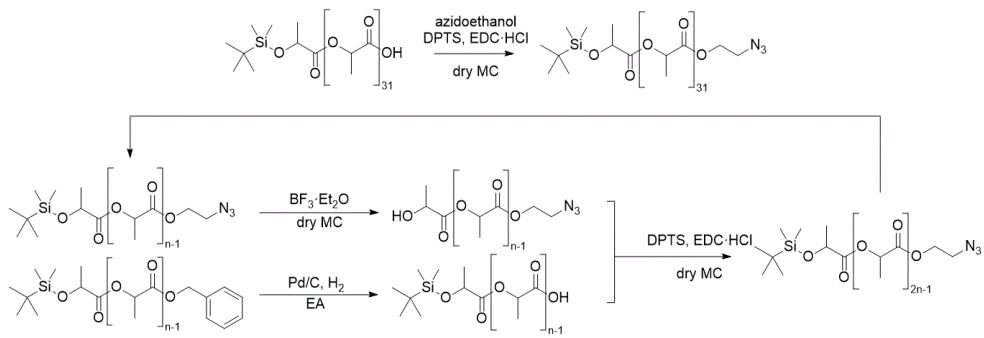
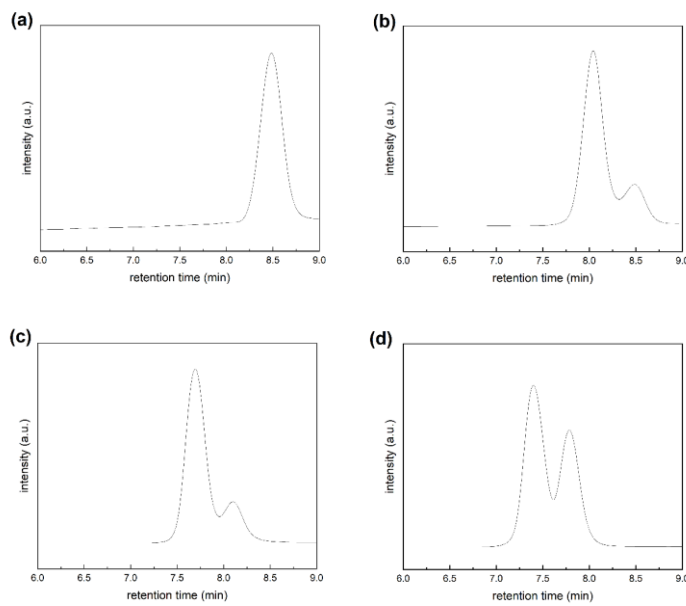


Figure 5. Iterative growth polymerization with azido end group modification of TBDMS-LA_{32}-Bz and GPC result of (a) TBDMS-LA_{32}-N_3 (b) crude TBDMS-LA_{64}-N_3 (c) crude TBDMS-LA_{128}-N_3 (d) crude TBDMS-LA_{256}-N_3



Coupling yield of iterative polymer growth with azido end group is calculated by deconvolution of GPC (b) 86.04% (c) 81.01% (d) 65.10%.

III. Conclusion

The effect of the molecular weight on the synthesis and properties of the discrete molecular weight cyclic polymer was investigated by using iteratively synthesized unimolecular polylactide with desired molecular weight. We isolated pure discrete cyclic PLAs composed of large numbers of repeating units without linear impurities by preparative SEC in a scalable manner in quantities and molecular weight. Different from theoretically expected result, it is confirmed that hydrodynamic volume of cyclic polymer is bigger than half of the linear polymer with discrete cyclic polylactide. Also, there's improvement in synthesizing cyclic polymer by optimizing the solvent, pseudo-dilute injection rate, and injection concentration. These polymers would be the model systems for the pioneer of the mechanical and chemical properties of synthetic macromolecules without statistical distribution and defects, which could lead to a new understanding of polymer properties and applications.

IV. Experimental Section

Materials

rac-lactide (Alfa Aesar) was purified by recrystallization from MeOH/EtOAc mixture prior to use. *rac*-Lactic acid, ethyl lactate, benzyl chloride (99%), triethylamine (≥99%), imidazole (99%), tert-butyldimethylsilyl chloride (97%), boron trifluoride diethyl etherate, palladium on activated charcoal (10%) and 4-(dimethylamino)pyridine (DMAP) were purchased from Sigma Aldrich and used without further purification. 4- (N,N'-Dimethylamino)pyridium-4-toluenesulfonate (DPTS) was prepared by adding THF solution of DMAP (1 M, 100 mL) to THF solution of p-toluenesulfonic acid monohydrate (1 M, 100 mL) at room temperature and stirring. The precipitated product was filtered and dried under vacuum. 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) and 4-pentanoic acid were purchased from Tokyo Chemical Industry and used without purification. Dichloromethane (DCM), dimethyl sulfoxide (DMSO), and toluene were distilled over CaH_2 under N_2.

General Information

^{1}H NMR and ^{13}C NMR spectra were recorded by Varian 500 MHz and Agilent 400-MR DD2 Magnetic Resonance System using $CDCl_3$ as solvent. Gel permeation chromatography (GPC) was performed on an Agilent 1260 Infinity equipped with a PL gel 5 μm mixed D column and differential refractive index detectors. THF was used as an eluent with a flow rate of 0.3 mL min^{-1} at 35 °C. A polystyrene standard kit (Agilent Technologies) was used for calibration.

Mass spectra of linear and cyclic dPLAs were measured on a Bruker Ultraflex III TOF-TOF mass spectrometer equipped with a Nd:YAG laser (355 nm). The instrument was operated in linear and refractive positive ion modes. External calibration was conducted using the following peptides and proteins as reference: Bradykinin fragment 1-7 (757.3997 Da), Angiotensin II (1046.5423 Da), P14R (1533.8582 Da), ACTH fragment 18-39 (2465.1989 Da), Insulin oxidized B chain (3494.6513 Da), Insulin (5735 Da), Cytochrome c (12362 Da), Apomyoglobin (16952 Da), Aldolase (39212 Da) and Albumin (66430 Da)). The ion is $[M+H]^+$ ion. 2-(4-Hydroxyphenylazo)benzoic acid (HABA) and trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) were used as a matrix.

Synthesis of monodisperse polymer

(1) General procedure for deprotection of benzyl ester

The compound having benzyl ester protecting group was dissolved in EA under Ar. Palladium on activated carbon (10 wt% Pd/C) was added to the solution. After the suspension was purged with Ar for a few minutes, triethylsilane (5 equiv.) was added to the suspension. The reaction mixture was stirred for 4 hours at RT. After complete removal of benzyl group, the reaction mixture was filtered through celite cake to remove Pd/C. The filtrate was concentrated in vacuo and the crude was dissolved in DCM, prior to precipitation from cold hexane. Precipitated product was concentrated in vacuo.

(2) General procedure for deprotection of silyl ether

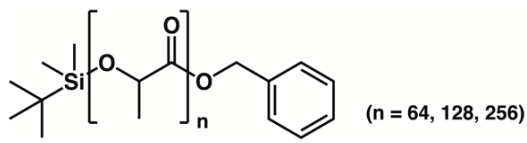
The compound having TBDMS ether protecting group was dissolved in dry DCM under Ar. $BF_3 \cdot Et_2O$ (4 equiv.) was added slowly to the solution at 0 °C. The reaction mixture was stirred for 4 hours at RT. After completion, the reaction was quenched with saturated $NaHCO_3$ and the mixture was washed with brine. The organic layer was dried over $MgSO_4$ and filtered, then concentrated in vacuo. The crude was purified by flash-column chromatography (Hexane/EA).

(3) General procedure for ester coupling reaction

The hydroxy group and carboxylic acid group containing compounds were dissolved in dry DCM under Ar. EDC·HCl (2 equiv.) and DPTS (0.3 equiv.) were added to the solution at 0 °C. The reaction mixture was stirred at RT. After 4 hours,

the reaction mixture was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash-column chromatography (Hexane/EA). The high molecular weight PLA polymers (repeating units ≥ 64) was purified by preparative size-exclusion chromatography (prep-SEC).

(4) Synthesis of PLA polymers via iterative convergent method



LA64. A white solid; ^{1}H NMR (500MHz, CDCl3): δ 7.40-7.30 (m, 5H, Ph-**H**), 5.27-4.98 (m, 65H, O-C**H**(CH_3)-C=O and Ph-C**H$_2$**-O), 4.38 (q, 1H, SiO-C**H**(CH_3)-C=O), 1.60-1.42 (m, 192H, C**H$_3$**-CH), 0.89 (s, 9H, (C**H$_3$**)$_3$C-Si), 0.09 (s, 3H, (CH_3)$_3$C-Si(C**H$_3$**)$_2$-O), 0.07 (s, 3H, (CH_3)$_3$C-Si(C**H$_3$**)$_2$-O) ppm; M_n and $Đ$ (GPC): 7208 Da and 1.02; MS (MALDI-TOF): m/z calcd for $C_{205}H_{278}O_{129}Si$ [**M**]: 4831.50; $C_{205}H_{278}O_{129}Si+Na^+$ [**M**+Na]$^+$: 4854.49; found 4855.99. Yield: 4.75g, 93%

LA128. A white solid; ^{1}H NMR (500MHz, CDCl3): δ 7.40-7.30 (m, 5H, Ph-**H**), 5.26-5.08 (m, 129H, O-C**H**(CH_3)-C=O and Ph-C**H$_2$**-O), 4.39 (q, 1H, SiO-C**H**(CH_3)-C=O), 1.64-1.42 (m, 384H, C**H$_3$**-CH), 0.91 (s, 9H, (C**H$_3$**)$_3$C-Si), 0.10 (s, 3H, (CH_3)$_3$C-Si(C**H$_3$**)$_2$-O), 0.08 (s, 3H, (CH_3)$_3$C-Si(C**H3**)$_2$-O) ppm; M_n and $Đ$ (GPC): 14112 Da and 1.02; MS (MALDI-TOF): molecular m/z calcd for $C_{397}H_{534}O_{257}Si$ [**M**]: 9446.47; $C_{397}H_{534}O_{257}Si+Na^+$ [**M**+Na]$^+$: 9469.46; found 9470.36. Yield: 3.99g ,86%

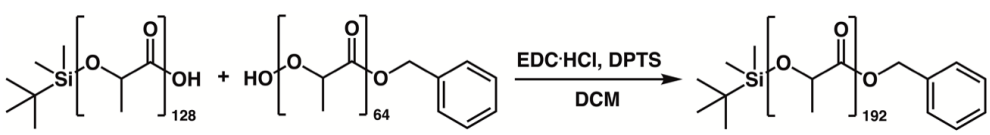
LA256. A white solid; ^{1}H NMR (500MHz, $CDCl_3$): δ 7.40-7.30 (m, 5H, Ph-**H**), 5.26-5.10 (m, 257H, O-C**H**(CH_3)-C=O and Ph-C**H$_2$**-O), 4.40 (q, J = 6.7Hz, 1H,

SiO-C**H**(CH_3)-C=O), 1.60-1.42 (m, 768H, C**H₃**-CH), 0.88 (s, 9H, (C**H₃**)$_3$C-Si), 0.11 (s, 3H, (CH_3)$_3$C-Si(C**H₃**)$_2$-O), 0.09 (s, 3H, (CH_3)$_3$C-Si(C**H₃**)$_2$-O) ppm; M_n and $Đ$ (GPC): 27730 Da and 1.02; MS (MALDI-TOF): molecular m/z calcd for $C_{781}H_{1046}O_{513}Si$ [**M**]: 18670.53; $C_{781}H_{1046}O_{513}Si+Na^+$ [**M**+Na]$^+$: 18693.52; found 18695.04. Yield: 2.78g, 72%

(6) Synthesis of PLA192 polymer via linear convergent method

TBDMS-PLA192-COOH and HO-PLA64-Bn were dissolved in dry DCM under argon. EDC·HCl (2 equiv.) and DPTS (0.3 equiv.) were added to the solution at 0 °C. The reaction mixture was stirred overnight at room temperature. The reaction mixture was washed with water and brine, and dried with $MgSO_4$. The product is filtered, and concentrated in vacuo. The crude product was purified by preparative size-exclusion chromatography (prep-SEC).

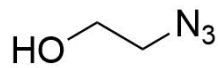
Scheme 4. Coupling reaction of LA_{192}.



LA192. A white solid; ^{1}H NMR (500MHz, $CDCl_3$): δ 7.40-7.30 (m, 5H, Ph-**H**), 5.26-5.10 (m, 193H, O-C**H**(CH_3)-C=O and Ph-C**H₂**-O), 4.40 (q, J = 6.7Hz, 1H, SiO-C**H**(CH_3)-C=O), 1.60-1.42 (m, 576H, C**H₃**-CH), 0.88 (s, 9H, (C**H₃**)$_3$C-Si), 0.11 (s, 3H, (CH_3)$_3$C-Si(C**H₃**)$_2$-O), 0.09 (s, 3H, (CH_3)$_3$C-Si(C**H₃**)$_2$-O) ppm; M_n and $Đ$ (GPC): 27730 Da and 1.02; MS (MALDI-TOF): molecular m/z calcd for $C_{589}H_{790}O_{385}Si$ [**M**]: 14059.50; $C_{589}H_{790}O_{385}Si+Na^+$ [**M**+Na]$^+$: 14081.49; found 14081.40. Yield: 2.78g, 79%

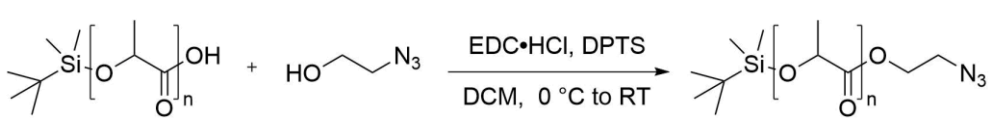
Synthesis of Cyclic PLAs

(1) Synthesis of 2-azidoethanol



A mixture of 2-bromoethanol (1 g, 8.00 mmol) and sodium azide (0.78 g, 12.00 mmol, 1.5 eq.) was dissolved in water (10 mL) and refluxed for two days. After cooled to room temperature, the solution was extracted with DCM. The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure, yielding the product as pale yellow oil (0.59 g, 6.77 mol, 84.67 %).; ^{1}H NMR (500MHz, $CDCl_3$): δ 3.75 (q, 2H, HO-C**H$_2$**-CH_2), 3.42 (t, 2H, CH_2-**CH_2**-N_3), 2.49 (s, 1H, **H**O-CH_2-CH_2) ppm; ^{13}C NMR (400MHz, $CDCl_3$): δ 61.4 (HO-**C**H_2-CH_2), 53.5 (CH_2-**C**H_2-N_3) ppm.

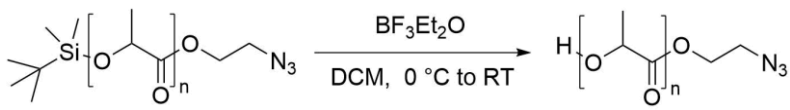
(2) Synthesis of TBDMS-**LAn**-N_3



TBDMS-**LAn**-COOH and 2-azidoethanol (3 eq.) were dissolved in dry DCM, and the reaction mixture was cooled to 0 °C in ice bath. To the solution, 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS, 0.3 eq.) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC•HCl, 2 eq.) were added, and the reaction mixture was stirred overnight at room temperature. After completion, the reaction mixture was washed with water and brine. The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The pure product was isolated via precipitation into cold diethyl ether. TBDMS-

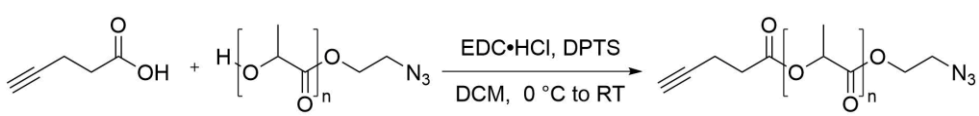
LAn-COOH was prepared by the debenzylation of **LAn** according to the described general procedure.

(3) Synthesis of HO-**LAn**-N_3



TBDMS-**LAn**-N_3 was dissolved in dry DCM under argon. The solution was cooled to 0 °C in ice bath, trifluoride diethyl etherate (BF_3•Et_2O, 4 eq.) was added slowly, and the reaction mixture was stirred at room temperature. After completion, saturated $NaHCO_3$ was poured into the mixture to quench the reaction, and the mixture was washed with brine. The organic layer was separated, dried with $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified via precipitation into cold diethyl ether.

(4) Synthesis of Alk-**LAn**-N_3



HO-**LAn**-N3 and 4-pentynoic acid (3 eq.) were dissolved in dry DCM, and the reaction mixture was cooled to 0 °C in ice bath. To the solution, 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS, 0.9 eq.) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC•HCl, 6 eq.) were added, and the reaction mixture was stirred overnight at room temperature. After completion, the reaction mixture was washed with water and brine. The organic

layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The pure product was isolated via precipitation into cold diethyl ether.

(5) Synthesis of ***c*-LAn** via click cyclization

Cu(II)SO_4 (30 eq.) and sodium ascorbate (36 eq.) were mixed with DMSO in a Schlenk tube, and the mixture was bubbled with argon for 15 min. To the degassed solution, the solution of Alk-**LAn**-N_3 in degassed DMSO was added via syringe pump at a certain feed rate at 60 °C. After complete addition, the mixture was stirred for an hour additionally. The crude product was filtered to remove copper salt and concentrated under reduced pressure. The pure product was isolated via preparative size-exclusion chromatography (prep-SEC). Conditions for cyclization of Alk-LAn-N_3 were described in Table 4.

Table 4. Experimental conditions for cyclization.

Alk-**LAn**-N_3	*MW* (g/mol)	Rate (mL/h)	Concentration (mM)	Solvent volume (mL)		Concentration (mM)	
				Syringe	Batch	Cu(II)SO_4	Asc acid
LA64	4779.20	1	1	20.92	2.1	300.0	360.0
LA128	9391.23	1	1	10.65	1.1	300.0	360.0
LA192	14003.19	1	0.7	10.20	0.71	300.0	360.0
LA256	18615.30	1	0.5	10.74	0.5	300.0	360.0

c-LA64. A white solid; ^{1}H NMR (500MHz, $CDCl_3$): δ 7.48 (s, 1H, N-C**H**-C), 5.26-5.10 (m, 64H, O-C**H**(CH_3)-C=O), 4.56 (t, 2H, O-C**H$_2$**-CH_2-N), 4.51 (t, 2H, O-CH_2-**CH$_2$**-N), 3.05 (t, 2H, C=O-**CH$_2$**-CH_2-C), 2.78 (t, 2H, C=O-CH_2-**CH$_2$**-C), 1.60-1.42

(m, 192H, C**H**$_3$-CH) ppm; M_n and $Đ$ (GPC): 5443 Da and 1.03; MS (MALDI-TOF): m/z calcd for $C_{199}H_{265}N_3O_{130}$+Na^+ [**M**+Na]$^+$: 4799.41; found 4801.0.

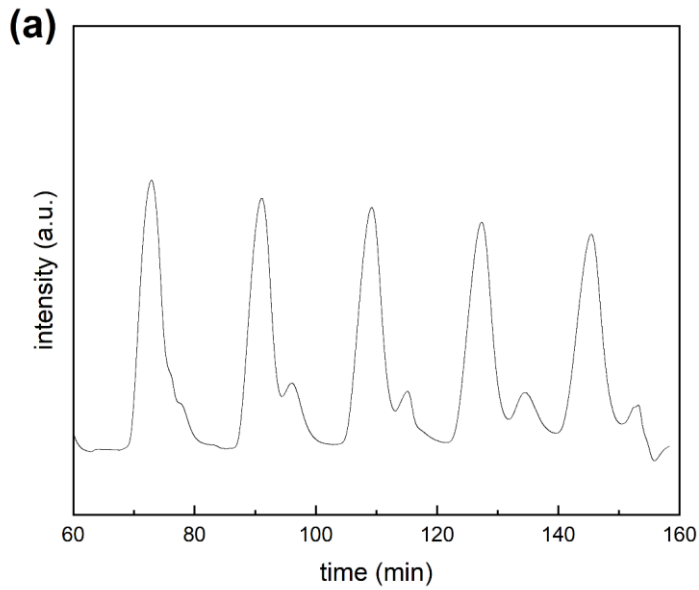
c-LA128. A white solid; ^{1}H NMR (500MHz, $CDCl_3$): δ 7.48 (s, 1H, N-C**H**-C), 5.26-5.10 (m, 128H, O-C**H**(CH_3)-C=O), 4.56 (t, 2H, O-C**H**$_2$-CH_2-N), 4.51 (t, 2H, O-CH_2-**C**H$_2$-N), 3.05 (t, 2H, C=O-**C**H$_2$-CH_2-C), 2.78 (t, 2H, C=O-CH_2-**C**H$_2$-C), 1.60-1.42 (m, 384H, C**H**$_3$-CH) ppm; M_n and $Đ$ (GPC): 11427 Da and 1.02; MS (MALDI-TOF): molecular m/z calcd for $C_{391}H_{521}N_3O_{258}$+Na^+ [**M**+Na]$^+$: 9414.22; found 9413.3.

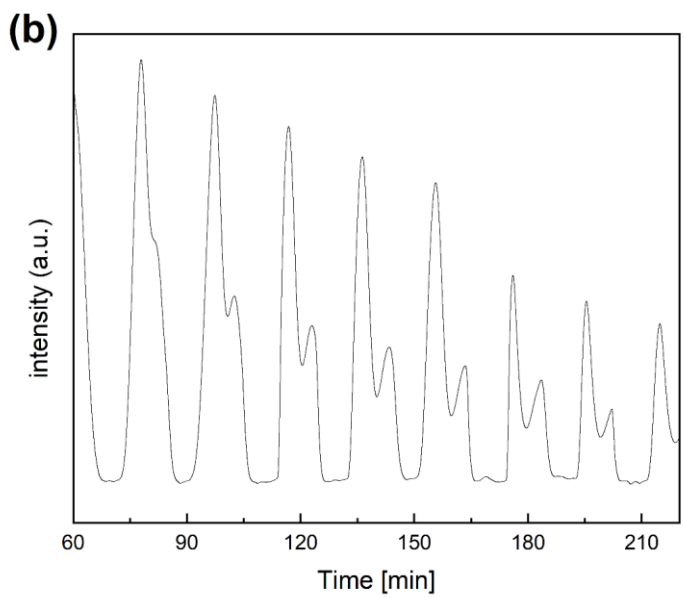
c-LA192. A white solid; ^{1}H NMR (500MHz, $CDCl_3$): δ 7.48 (s, 1H, N-C**H**-C), 5.26-5.10 (m, 512H, O-C**H**(CH_3)-C=O), 4.56 (t, 2H, O-C**H**$_2$-CH_2-N), 4.51 (t, 2H, O-CH_2-**C**H$_2$-N), 3.05 (t, 2H, C=O-**C**H$_2$-CH_2-C), 2.78 (t, 2H, C=O-CH_2-**C**H$_2$-C), 1.60-1.42 (m, 1536H, C**H**$_3$-CH) ppm; M_n and $Đ$ (GPC): 41764 Da and 1.03; MS (MALDI-TOF): molecular m/z calcd for $C_{583}H_{777}N_3O_{194}$+Na^+ [**M**+Na]$^+$: 14026.25; found 14029.71.

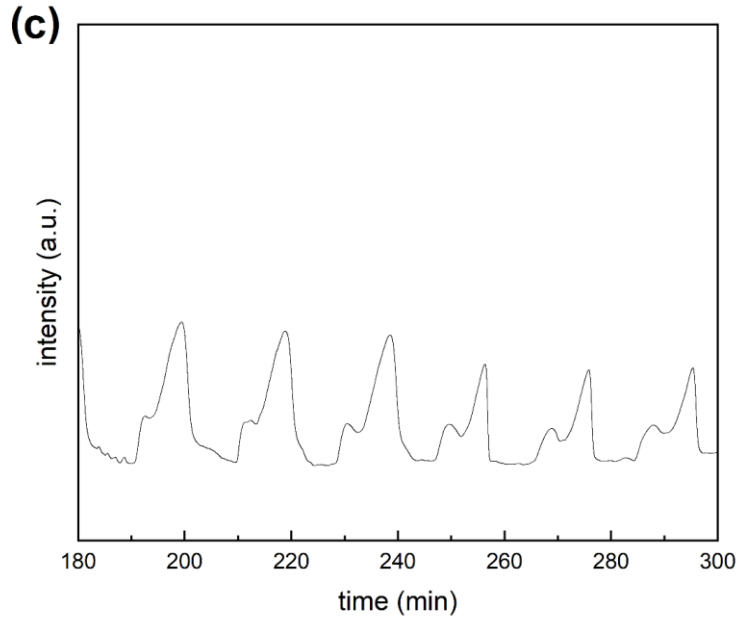
c-LA256. A white solid; ^{1}H NMR (500MHz, $CDCl_3$): δ 7.48 (s, 1H, N-C**H**-C), 5.26-5.10 (m, 256H, O-C**H**(CH_3)-C=O), 4.56 (t, 2H, O-C**H**$_2$-CH_2-N), 4.51 (t, 2H, O-CH_2-**C**H$_2$-N), 3.05 (t, 2H, C=O-**C**H$_2$-CH_2-C), 2.78 (t, 2H, C=O-CH_2-**C**H$_2$-C), 1.60-1.42 (m, 768H, C**H**$_3$-CH) ppm; M_n and $Đ$ (GPC): 21039 Da and 1.03; MS (MALDI-TOF): molecular m/z calcd for $C_{775}H_{1033}N_3O_{514}$+$Na^+$ [**M**+Na]$^+$: 18638.29; found 18641.66.

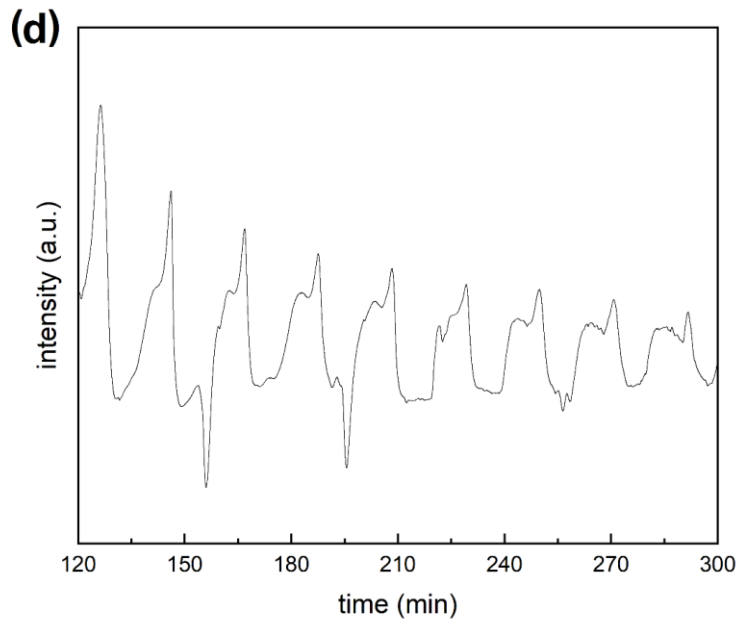
Prep-SEC separation of Cyclic PLAs

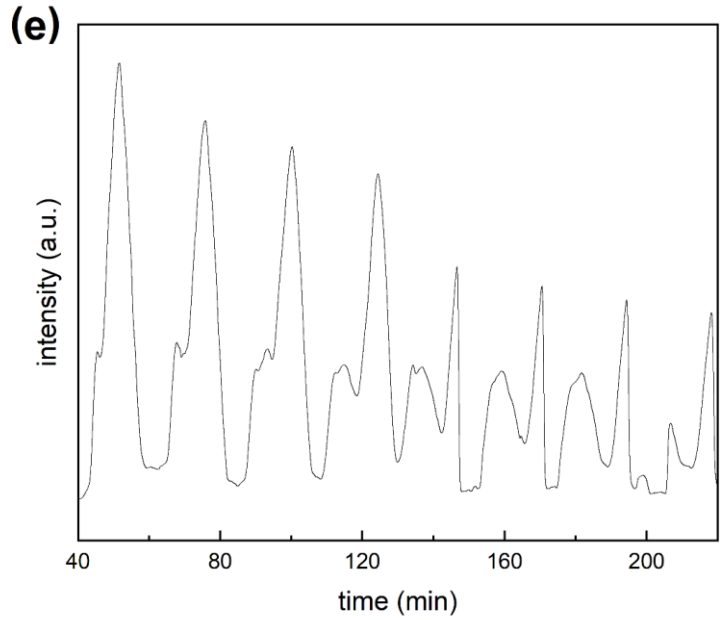
Figure 6. Prep-SEC separation of (a) TBDMS-LA_{128}-Bz (b) c-LA_{128} (c) TBDMS-LA_{192}-Bz (d) c-LA_{192} (e) TBDMS-LA_{256}-Bz (f) c-LA_{256}

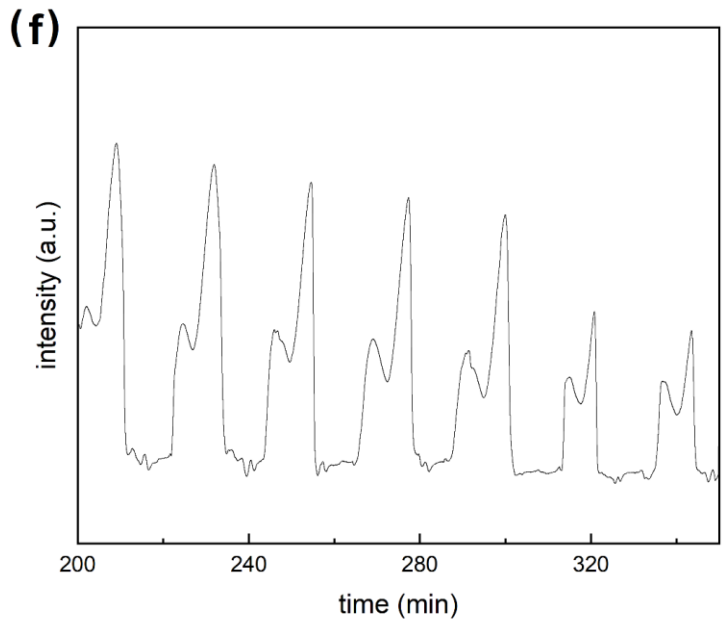





(c)
intensity (a.u.)
180
200
220
240
260
280
300
time (min)


(d)
intensity (a.u.)
120
150
180
210
240
270
300
time (min)





Prep-SEC condition is on table 2 and table 5.

Table 5. Prep-SEC separation condition for cyclic polymers

c-L**An**	*MW* (g/mol)	Flow Rate (mL/min)	Concentration (mg/mL)	Injection volume (mL)	Required Cycles for Separation
LA64	4779.20	10	50	2.0	9
LA128	9391.23	10	50	2.0	13
LA192	14003.19	10	50	2.0	~20
LA256	18615.30	10	50	2.0	~30

GPC and ^{1}H NMR result of monodisperse polymer

Figure 7. (a) GPC result of TBDMS-LA128-Bz (b) ^{1}H NMR result of TBDMS-LA128-Bz

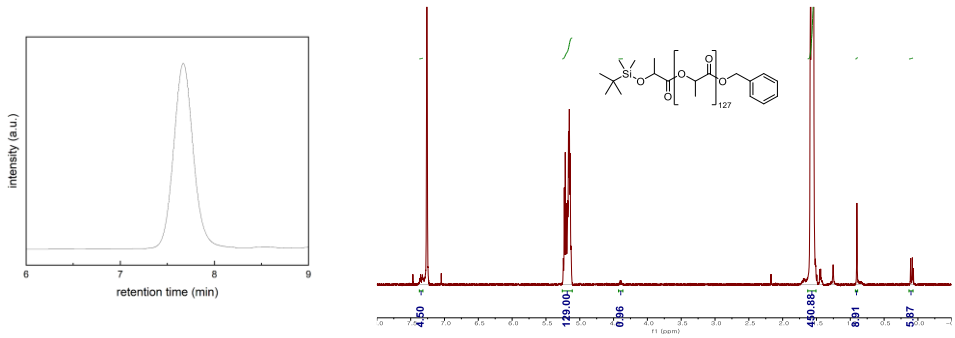


Figure 8. (a) GPC result of c-LA128 (b) ^{1}H NMR result of c-LA128

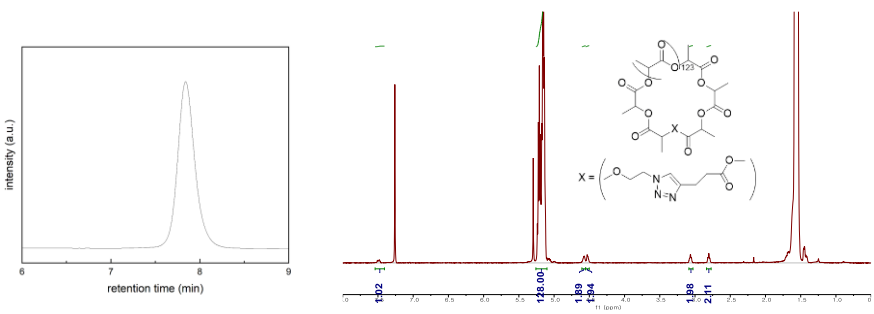


Figure 9. (a) GPC result of TBDMS-LA192-Bz (b) ^{1}H NMR result of TBDMS-LA192-Bz

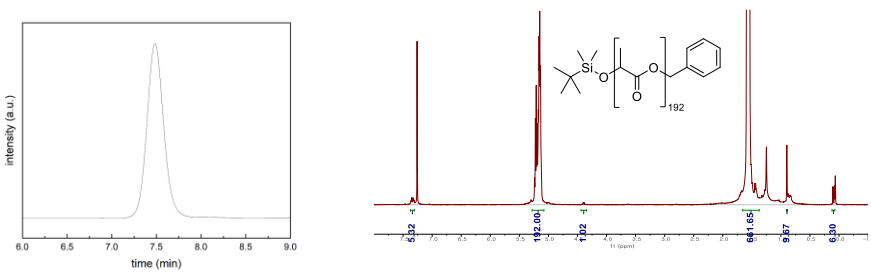


Figure 10. (a) GPC result of c-LA192 (b) ^{1}H NMR result of c-LA192

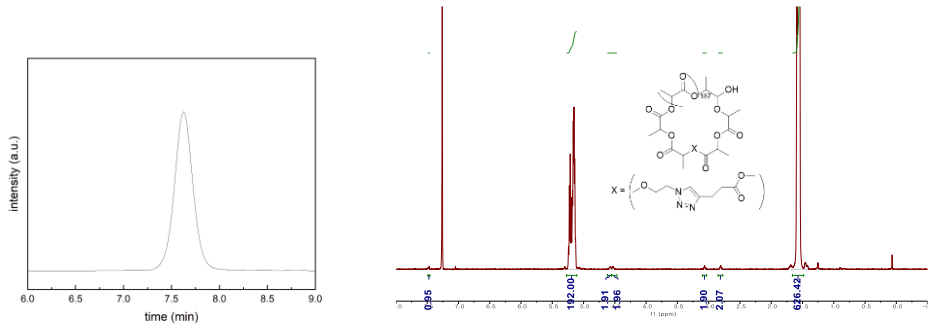


Figure 11. (a) GPC result of TBDMS-LA256-Bz (b) ^{1}H NMR result of TBDMS-LA256-Bz

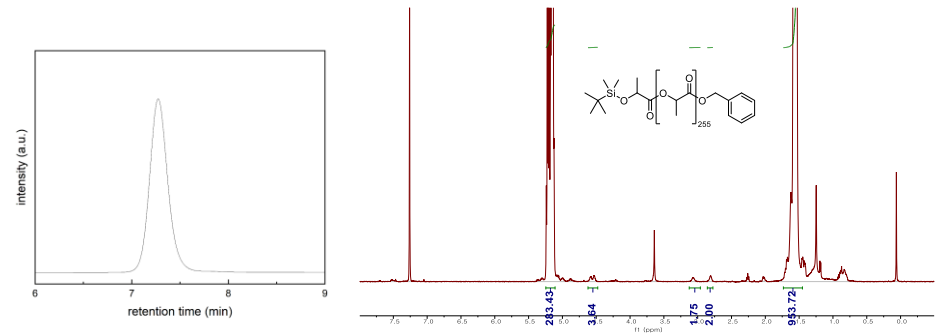
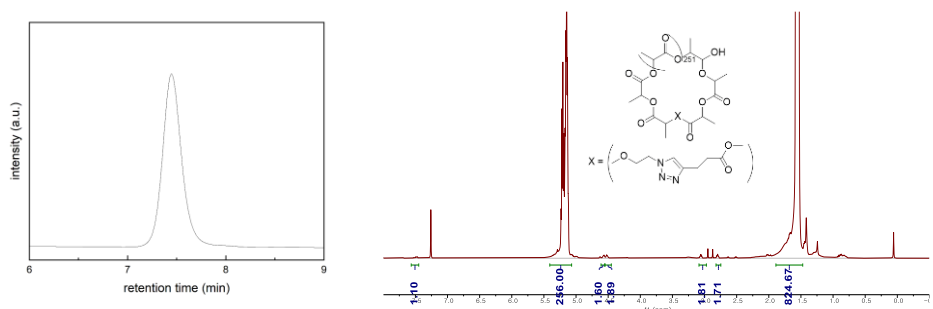


Figure 12. (a) GPC result of c-LA256 (b) ^{1}H NMR result of c-LA256



MALDI-TOF Mass Spectra of Linear PLAs

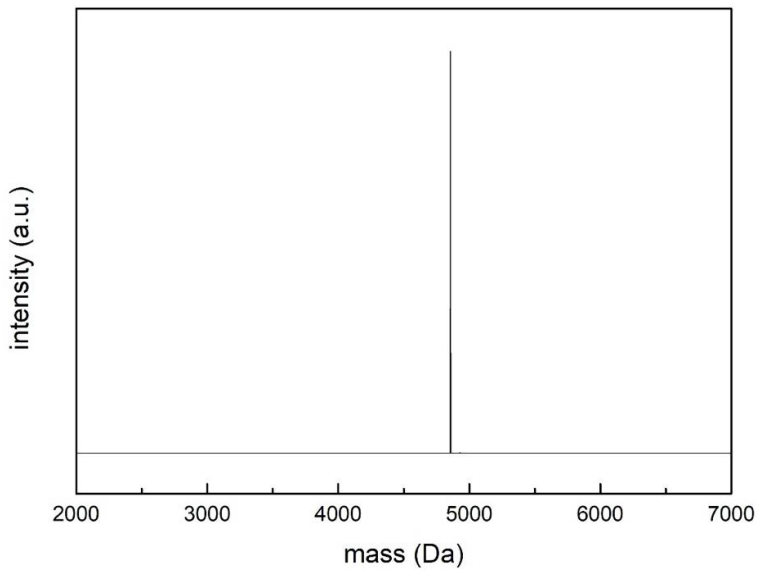
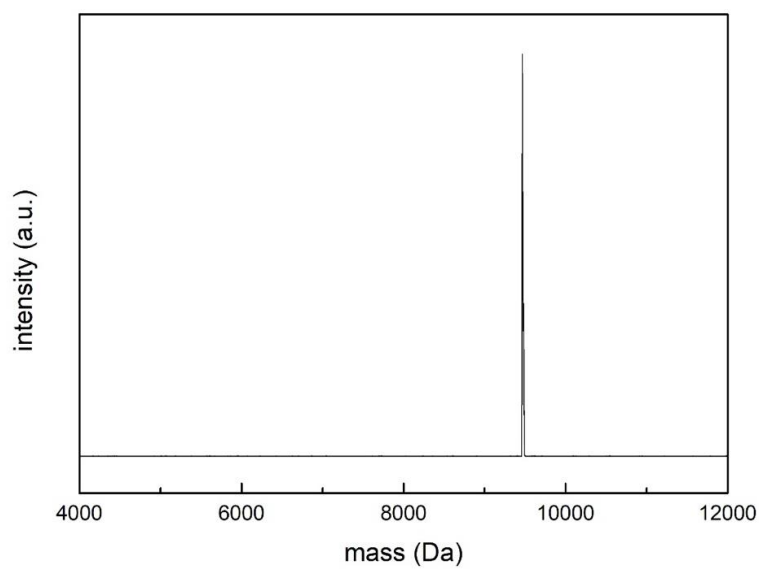
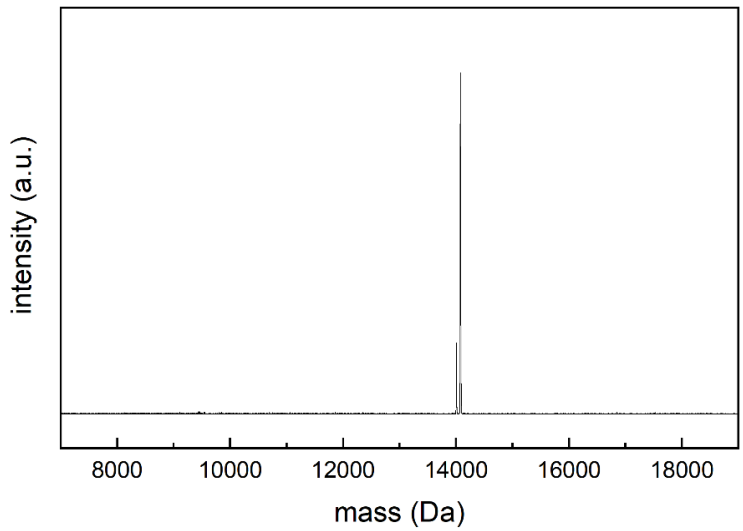


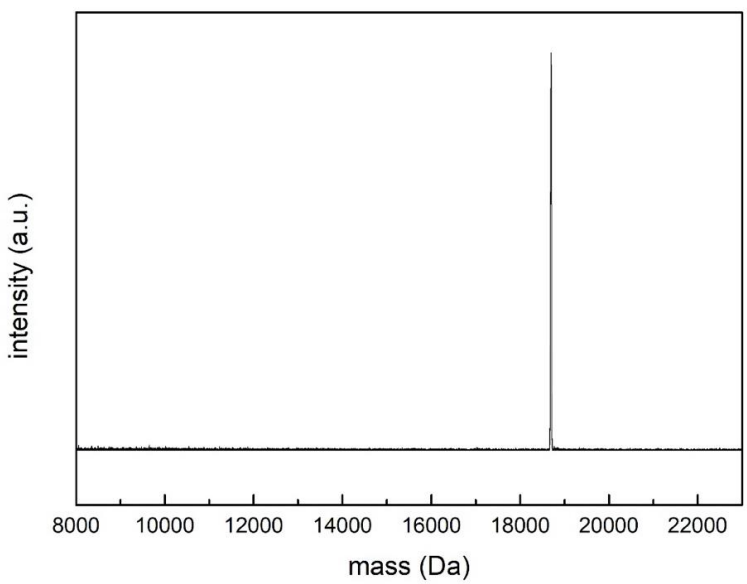
Figure 13. (a) MALDI-TOF mass spectrum of **LA64**. m/z calcd for $C_{205}H_{278}O_{129}Si+Na^+$ [**M**+Na]$^+$: 4854.49; found 4855.99.



(b) MALDI-TOF mass spectrum of **LA128.** molecular m/z calcd for $C_{397}H_{534}O_{257}Si+Na^+$ [**M**+Na]$^+$: 9469.46; found 9470.36.



(c) MALDI-TOF mass spectrum of **LA192**. molecular m/z calcd for $C_{781}H_{1046}O_{513}Si+Na^+$ [**M**+Na]$^+$: 14081.49; found 14081.40.



(d) MALDI-TOF mass spectrum of **LA256**. molecular m/z calcd for $C_{781}H_{1046}O_{513}Si+Na^+$ [**M**+Na]$^+$: 18693.52; found 18695.04

MALDI-TOF Mass Spectra of Cyclic PLAs

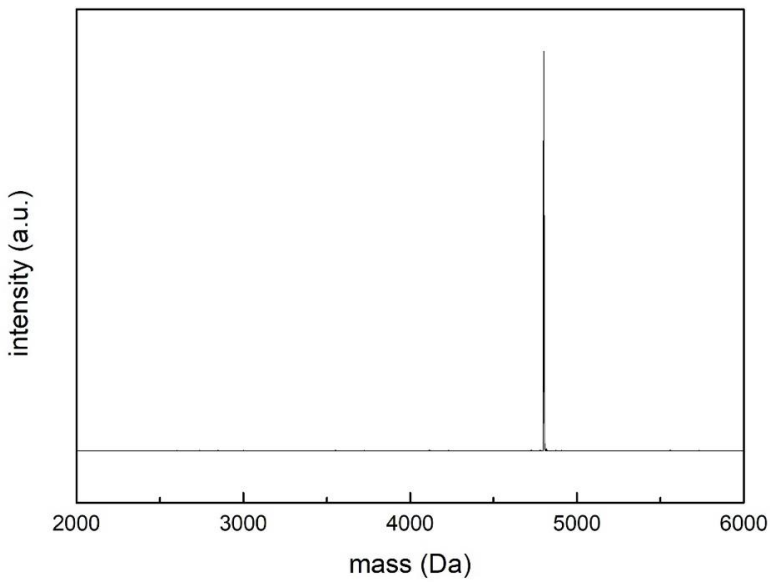
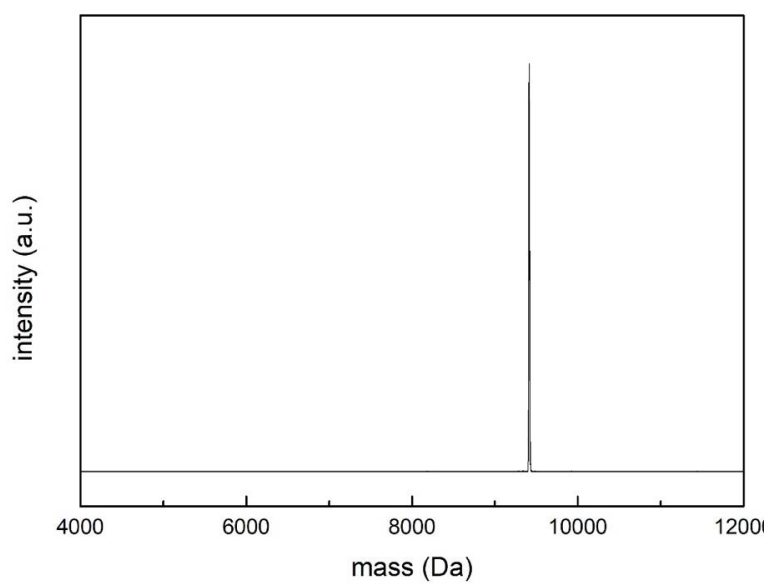
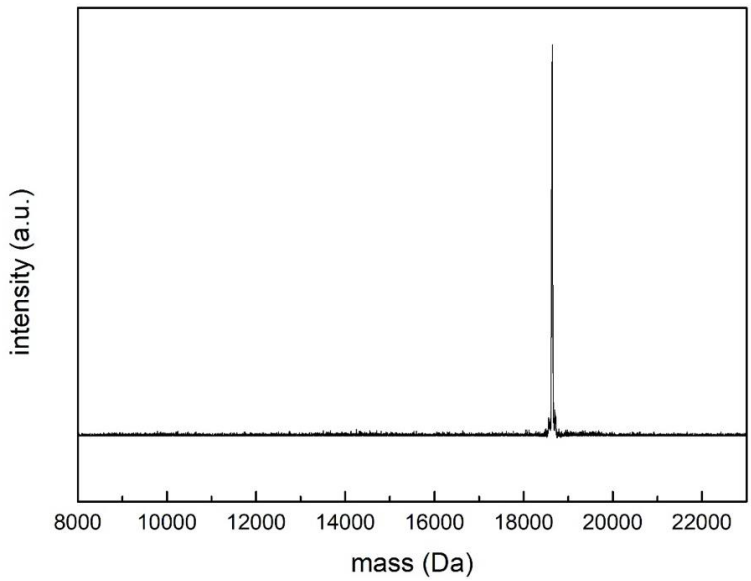


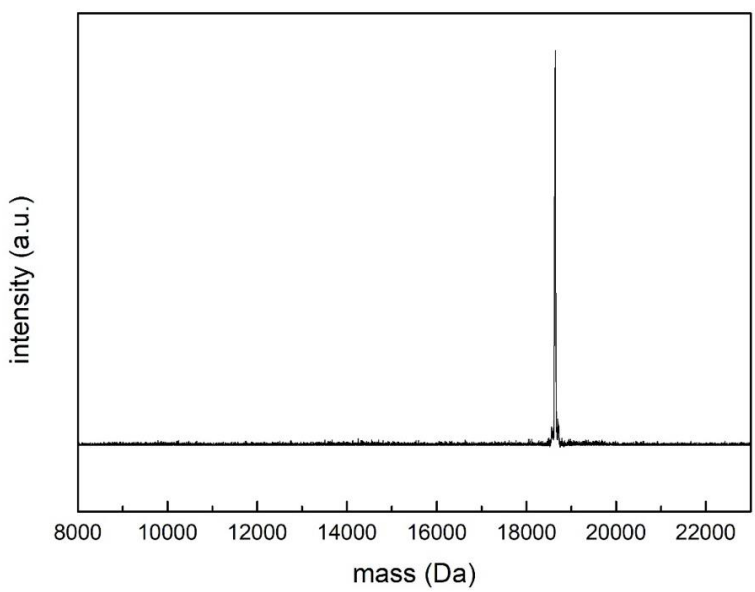
Figure 14. (a) MALDI-TOF mass spectrum of c-**LA64**. m/z calcd for $C_{199}H_{265}N_3O_{130}$+Na^+ [**M**+Na]$^+$: 4799.41; found 4801.02.



(b) MALDI-TOF mass spectrum of c-**LA128**. molecular m/z calcd for $C_{391}H_{521}N_3O_{258}$+Na^+ [**M**+Na]$^+$: 9414.22; found 9413.29.



(c) MALDI-TOF mass spectrum of c-**LA192**. molecular m/z calcd for $C_{583}H_{777}N_3O_{194}$+Na^+ [**M**+Na]$^+$: 14026.25; found 14029.71.



(d) MALDI-TOF mass spectrum of c-**LA256**. molecular m/z calcd for $C_{775}H_{1033}N_3O_{514}$+$Na^+$ [**M**+Na]$^+$: 18638.29; found 18641.66.

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국문 초록

분자량 분포가 없는 고리형 중합체의 합성과 성질에 대한 분자량의 영향

고리형 중합체 사슬의 길이를 충분히 늘려 구조에 따른 힘을 무시할 수 있게 되면, 반복 단위의 형태와 구성만이 고리형 분자의 화학적 특성에 영향을 미치게 되는데, 이때 고리형 고분자는 사슬의 말단이 존재하지 않기 때문에 구조상 모든 부분이 동일하여 균질한 화학적 특성을 갖게 된다. 그러나 고리형 고분자의 이러한 고유한 특성을 관찰하기 위해서는 물성에 큰 영향을 미칠 수 있는 선형의 미량 불순물을 모두 제거하는 것이 중요하다. 이때 반복 과정을 거쳐 기하급수적으로 성장하는 고분자 구조의 말단에 작용기를 달아 이 분자가 해당 분자 내부에서 고리 형태로 결합을 형성하게 하여 단분자 고리형 폴리머를 합성했다. 분자량의 분산이 극히 낮은 단일 화학종 고분자를 뼈대로 사용함으로써 고리형태를 갖춘 고분자의 유체역학적 부피가 감소하였을 때 이 부피 차이를 이용하여 선형 전구체에서 고리형 폴리머를 분리하였다. 이후 고리형 고분자의 생산성을 향상시키기 위해 용매 선택, 주입 속도 변경, 주입 농도 조절 등을 통해 고리화 조건을 최적화하였으며, 각각의 요인이 영향을 미치는 정도와 그 원인을 파악하여 고리형 고분자의 생산성을 높였다. 이를 바탕으로 유용한 성질을 가진 고리형 고분자의 실제 적용에 한발 다가갔다.

주요어 : 고리형 고분자, 분자량 분포, 클릭 반응, 생산성 최적화

학 번 : 2021-21486