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From Jellyfish Macromolecular Architectures to Nanodoughnut Self-Assembly

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Introduction

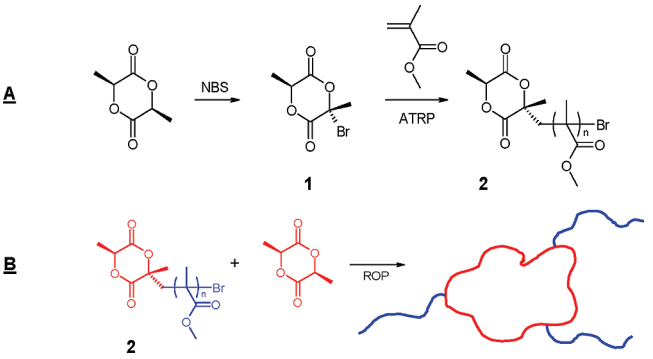
Because the macroscopic properties and potential applications of synthetic polymers directly depend on their molecular structure, the design of novel macromolecular architectures remains of prime importance.[1] In the field of nanotechnology, macrocyclic polyesters are very promising for the production of heterophasic materials with smaller size domains exhibiting distinct properties with respect to their linear counterparts.[2] While numerous methods have been explored for the preparation of these macrocyclics, a high dilution process is required leading to poor cyclization yields and competing reactions, involving tedious purifications to isolate pure macrocycles.[3] In comparison, *N*-heterocyclic carbenes (NHC) have been recently demonstrated to be potent transesterification agents able to catalyze the living ring-opening polymerization (ROP) of strained (di)lactones to macrocyclic polyesters in solution or in bulk.[4,5] Whatever the conditions, ROP is fast and generates well-defined macrocyclic structures of narrow polydispersity (PDI) and controlled molecular weight directly depending on the initial monomer-to-NHC ratio. Interestingly, tadpole-shaped polymers were also synthesized by cyclization of a linear precursor end-capped by reactive groups or by "grafting from" techniques initiated from preformed macrocyclic structures.[6]

Herein, we report a new process allowing the synthesis of "tadpole" to "jellyfish" structures based on a poly(L-lactide) macrocyclic inner-core grafted by poly(methyl methacrylate) chains (Scheme 1). Such tricky architectures are obtained by a two-step process. The first step relies on the atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) monomers from a brominated lactide (Scheme 1A) while the second one is gendered by the ring-opening copolymerization of the as-obtained macromonomer with L-lactide (LA) monomers using a 1,3-dimesitylimidazol-2-ylidene (IMes) *N*-heterocyclic carbene catalysis (Scheme 1B). The cyclic structure of the as-obtained products (*cyclic* PLA-*g*-PMMA) was attested by a combination of techniques (^{1}H NMR, MALDI−ToF, GPC, viscosity analysis) while their association in the solid state was briefly studied by atom force microscopy (AFM).

Results and Discussion

The key-step of this process relies on the synthesis of (3*R*,6*S*)-3-poly(methyl methacrylate)-3,6-dimethyl-1,4-dioxane-2,5-dione (**2**) macromonomer. Macromonomer **2** is obtained by atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) initiated from (3*R*,6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione (**1**) in the presence of CuBr/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) catalytic complex ($[Cu]_0/[HMTETA]_0 = 1$) (Scheme 1A).[7]

Scheme 1. (A) Synthesis of 1 and 2 from L-Lactide and (B) Copolymerization of LA and 2 Yielding Jellyfish Architectures



Since bromination of L-lactide can form two diasteroeisomeric products ((3*R*,6*S*) and (3*S*,6*S*)), the exact stereochemistry of compound **1** ((3*R*,6*S*)) has been attested by ^{1}H NMR analysis taking into account the complete signal attribution referred by Hillmyer et al.[9] The polymerization of MMA via ATRP was performed in THF at 50 °C for a $[MMA]_0$ of 1.6 M and $[MMA]_0/[\mathbf{1}]_0$ of 200. For an easier end-group molecular characterization and to prevent inescapable transfer reactions, ATRP process was prematurely stopped to get PMMA chains (**2**) of low molar masses. Gel permeation chromatography (GPC) traces of the PMMAs proved monomodal and symmetric, and the polydispersity indices were less than 1.15 (Figure 1). While ^{1}H NMR analysis of **2** is inefficient to clearly identify PMMA end-groups (see Supporting Information, Figure S1), electrospray ionization mass spectrometry measurement (ESI−MS) unambiguously detects doubly and triply charged PMMA end-capped by bromide and lactide moieties at each extremity, respectively (Figure 2).

Doubly and triply charged most intensive signals agree perfectly well with the expected macromolecular structures and GPC data (M_n = 2,900 g·mol^{-1}). Remarkably neither bromination from LA nor MMA ATRP from **2** induces any modification of the lactide cyclic structure by concomitant ring-opening process.

Perfectly controlled macrocyclization of L-lactide (LA) was reported by Waymouth et al. using 1,3-dimesitylimidazol-2-ylidene (IMes) NHC. This kinetically controlled synthesis of cyclic polyesters occurred in THF to yield poly(L-lactide)s (PLAs) in 5−900 s.[4] In the present study, we suspected that the lactide

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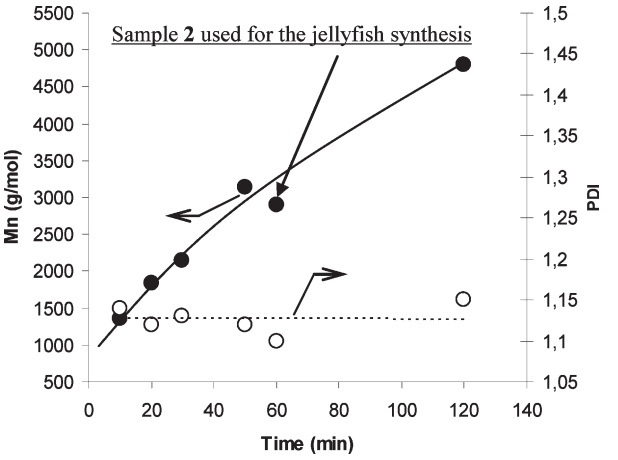


Figure 1. Experimental molecular weights (●) and polydispersity (○) evolutions of PMMA obtained by ATRP of MMA from (3*R*,6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione in the presence of CuBr/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) catalytic complex as determined by GPC ($[Cu]_0/[HMTETA]_0$ = 1; $[MMA]_0$ of 1.6 M and $[MMA]_0/[\mathbf{1}]_0$ of 200; solvent = THF; temperature = 50 °C).

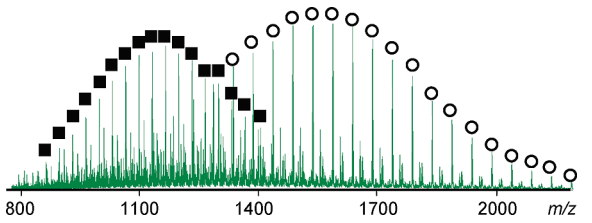
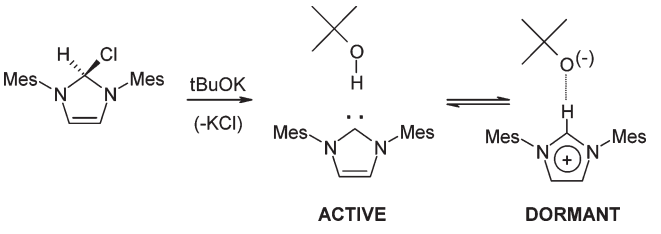


Figure 2. ESI mass spectrum of PMMA (**2**) doubly (○) and triply (■) charged (cationizing agents: Na^+ and K^+).

Scheme 2. Equilibrium between Active IMes and Corresponding Dormant Hydrogen-Bonded Tertiary Alcohol Adduct



moiety anchored in α position of macromonomer **2** may suffer from inaccessibility during the macrocyclization process when directly initiated from the free isolated IMes. Rather than reducing the kinetics of the propagation by decreasing the initial (co)monomer concentration, the copolymerization of both LA and **2** was performed by *in situ* generation of IMes initiator in THF at room temperature. Since IMes is generated using potassium *tert*-butoxide (^{t}BuOK) from its corresponding chloride salt, the free NHC is generated together with an equimolar quantity of tertiary ^{t}BuOH and KCl salt. Being unable to initiate the ROP process, ^{t}BuOH is known to form hydrogen-bond with the free "active" carbene (Scheme 2) and might be suspected to lower the overall activity of the free IMes.[8]

The "active-dormant" equilibrium inducing a slower polymerization reaction has been attested for by carrying out the homopolymerization of LA in strictly identical conditions than those depicted in ref 4b and targeting a polymerization degree (DP) of 200 but generating *in situ* the IMes carbene without any isolation from the also generated tertiary alcohol ($[LA]_0$ = 0.6 M in THF, room temperature). After 90 s and 10 min, two separated LA ROP processes were independently quenched by dried carbon disulfide (CS_2) and precipitated in cold methanol. As highlighted in Figure S2, recorded conversions give credit to a reduced kinetics. Notably, this "active-dormant" NHC-mediated zwitterionic polymerization displays a good degree of control since the cyclic PLA obtained for example after 90 s were characterized by a low PDIs (1.3) and M_n(exp) in agreement with the expected M_n(th) (M_n(th) = 4320; M_n(exp) = 5200 g/mol).

Table 1. Molecular Characterizations Recorded during a Jellyfish Process in THF at Room Temperature ($[LA + 2]_0 \sim 0.7$M for a DP_{th} in lactide and in 2 of 40 and 3, respectively)

time (min)	convn(GPC) (%)[a]	M_n(GPC) (g mol^{-1})[a]	PDI[a]
8	26.0		
10	83.9	18 920	1.46
20	91.7	16 610	1.36
40	92.5	18 720	1.46

[a] As determined in THF at 35 °C.

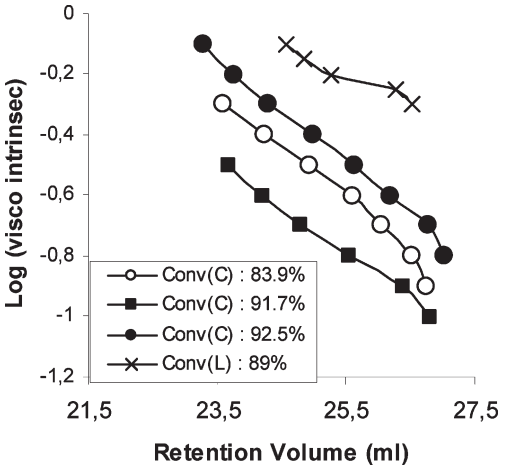


Figure 3. Plot of logarithm of intrinsic viscosity vs retention time (C, cyclic; L, linear PLA-*g*-PMMA).

The homopolymerization of **2** and accordingly the reactivity of the terminal lactide moiety has also been investigated. After 1 h, the medium was quenched by dried CS_2. The bimodal GPC reveals both the presence of remaining unreacted macromonomer and the expected jellyfish structure characterized by a M_n(exp) of 11 300 g·mol^{-1} in good agreement with the expected M_n(th) (9800 g·mol^{-1}). Undoubtedly this synthesis confirms that the cyclic lactide moiety is fixed at PMMA end-group and active in ROP from IMes carbene even if, compared to LA, its polymerization efficiency is lower.

The copolymerization of LA and **2** has then been investigated in THF ($[LA + 2]_0 \sim 0.7$M) at room temperature for a DP_{th} in lactide and in **2** of 40 and 3, respectively (macrocycle composed of 43 lactoyl units and 3 gangling PMMA chains, respectively in red and blue in Scheme 1B). The consumption of both comonomers was followed by GPC analysis from samples withdrawn after 8, 10, 20, and 40 min (Table 1). Interestingly the M_nGPC of 18920 recorded after 10 min (convn ~ 83.9%) drops down to 16 610 (convn ~ 91.7%) to finally reach up 18 720 g·mol^{-1} after 40 min (convn ~ 92.5%). Regarding the state of the art, this evolution tends to indicate a possible modification of the topology during the reaction.[10] Indeed, the incorporation of the macromonomer **2** into the cyclic PLA structure during the process (after 84% conversion) has an effect on the hydrodynamic radius of obtained jellyfish structures since their intrinsic viscosities evolution first decrease to finally move up after 92.5% conversion (Figure 3).

The cyclic structure of these products was determined by a combination of techniques, including NMR spectroscopy, matrix-assisted laser desorption/ionization time-of-flight (MALDI−ToF) mass spectrometry and comparisons of the solution properties of

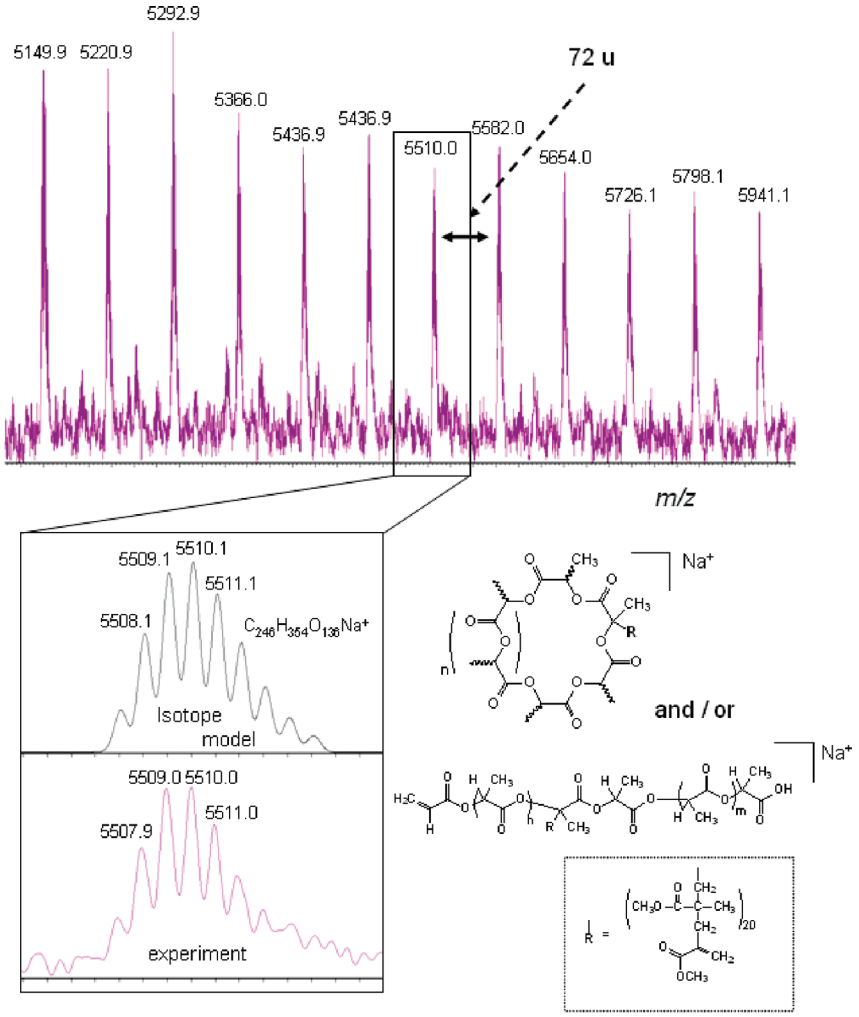


Figure 4. MALDI−Tof analysis of a *cyclic* PLA-*g*-PMMA (M_nGPC = 18 720). The zoomed region compares the experimental signal with an isotopic model (see main text).

the cyclic polymers with linear congeners (molecular characterizations of *linear* PLA-*g*-PMMA available in the Supporting Information). As emphasized by Figure S3, no clear end-group was observed in the ^{1}H NMR spectrum while both MMA and LA structural unities were present. Additional evidence for the preparation of the expected jellyfish structure could arise from MS measurements. Unfortunately, upon electrospray ionization, the recorded spectrum (not shown) is too noisy to be analyzed given the fact that, for such a high mass polymer, the superposition of the different charge states for all oligomers leads to signals overlapping. In such a case, MALDI−MS analysis can be used to overcome the problem since MALDI is well-known to mainly afford single-charged ions. At this point of the discussion, it is worth first mentioning that our MALDI QToF instrument presents quite a limited mass range and is not dedicated to the measurement of such high mass polymers. Nevertheless, we submitted the polymer sample to MALDI analysis. As presented in Figure 4, a significant ion series is detected with a 72 u peak-to-peak mass difference. This value unambiguously confirms the presence of a lactic acid-based structure. A closer analysis of the exact mass and isotope pattern of the *m*/*z* 5510 signal reveals that the observed cations are likely to correspond to Na^+-cationized oligomers that incorporate lactic acid units and one gangling PMMA chain. This cation is however characterized by a HBr loss (from the dandling PMMA chains) which might be induced upon the high laser conditions required to obtain ions during the MALDI analysis or by a possible dehalogenation reaction induced by the free carbene during the propagation step.[11]

Whatever the origin of this HBr loss, the structure of the observed cations is not straightforward to propose. First of all, for the *m*/*z* 5510 cations, the measured composition is in keeping with a macrocyclic species incorporating 45 lactic acid units and one macromonomer **2**. Moreover, and as already observed in the literature upon MALDI analysis, cyclic PLA oligomers can undergo dissociation reactions that require an initial ring-opening reaction and subsequent 72 u losses.[4a,12] As a consequence, we can not neglect that the observed *m*/*z* 5510 ions originate from such a decomposition reaction leading to the structure presented in Figure 4. Again, the identification of those ions incorporating lactic acid and **2** fully confirms that copolymerization reaction was occurring.

As a key result and in perfect agreement with theory,[13] viscosity measurements using a light scattering detector coupled to a viscometer show that jellyfishes prepared in absence of alcohol have lower intrinsic viscosities than those prepared from alcohol initiators (Figure 3).

When a THF solution of *cyclic* PLA-*g*-PMMA is deposited on a freshly cleaved mica substrate and left to evaporate, individual nanoscale objects form, which can be visualized with atomic force microscopy or AFM (for a view over a large area, see Figure S4). Those objects appear as short cylinders (their width and height are 7 ± 1 nm and 8 ± 1 nm, respectively) presenting various topologies. Those cylinders can arrange to form 4-fold stars (Figure 5A), to wrap up to form "doughnuts" (Figure 5D) or other "intermediate" shapes (Figure 5, parts B and C). Those

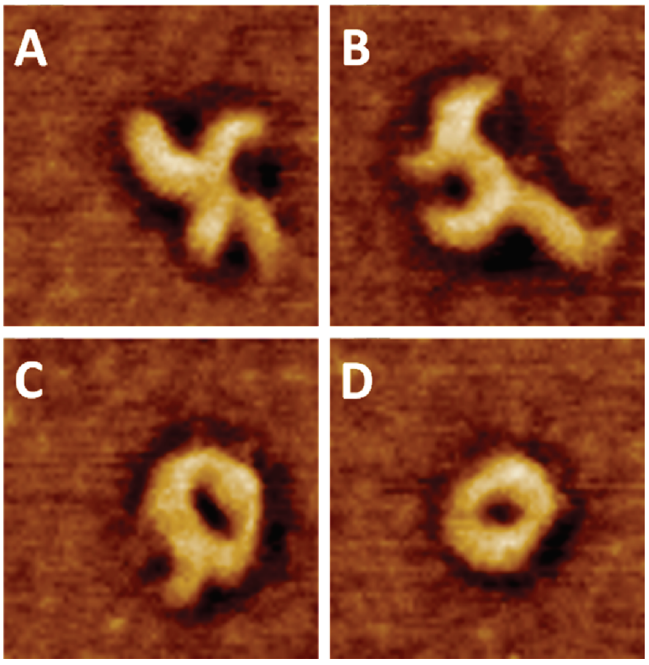


Figure 5. AFM phase images illustrating different observed solid state topologies from polymer **2**. The scale size is 100 nm.

objects are not single macrocycles; they are most probably made of molecules self-assembling with their PLA rings interacting in a cofacial manner. The diameter of the cylinders is consistent with a fully extended cycle of roughly 35 PLA units (surrounded by PMMA segments). Indeed, based on a rough modeling of a fully extended cyclic PLA (excluding the presence of PMMA chains),[14] it has been estimated that each lactide unit contributes to 4.8 Å of the total circumference of the cycle. The diameter of such a macrocycle, constituted by 35 to 40 LA units, would then amount to *ca.* 53 to 61 Å, respectively. This value is consistent with the experimental width and height measured from the AFM pictures.

In conclusion, multifunctionalized macrocycles named jellyfish structures have been obtained by a two-step polymerization process. While gangling PMMA branches have been obtained by a controlled ATRP process from selectively brominated lactide, the as-obtained LA−PMMA has been copolymerized with LA by ROP using IMes carbene. Upon deposition from solution, these jellyfish structures tend to self-assemble in solution by cofacial arrangement creating merged cylinder assemblies in dry state. By extrapolation to hydrophilic (meth)acrylate monomers, amphiphilic jellyfish structures, potentially useful in drug targeting applications, might be expected to be obtained.

Experimental Part

Materials. L-Lactide (GALACTIC, Belgium) was recrystallized from dried toluene and stored in a glovebox under dry nitrogen atmosphere before use. *N*-Bromosuccinimide (Janssen, 99%) was recrystallized from water before use (Yield ∼ 65%). Methyl methacrylate (MMA, Acros-Organics, 99%) was passed through a column of basic alumina to remove the stabilizer, bubbled with nitrogen, and stored under slight nitrogen overpressure. Copper(I) bromide (CuBr, Aldrich, 98%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Aldrich, 97%) and 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (IMesCl, StremChemicals, >95%) were used without any purification. THF and toluene solvents were dried using a MBraun Solvent Purification System (model MB-SPS 800) equipped with alumina drying columns.

Characterizations. ^{1}H NMR spectra were recorded using a Bruker AMX-300 apparatus at room temperature in $CDCl_3$ (30 mg/0.6 mL). The molecular mass measurements as well as the end-groups determinations were performed on a Waters QToF2 mass spectrometer equipped with an orthogonal electrospray (ESI) source (Z-spray) operated in positive ion mode. LA-PMMA **2** was dissolved in acetonitrile in order to approximately achieve 10^{-4} M concentrations, as estimated from the molar mass determined by GPC analysis. The solution was infused into the ESI source at a rate of 5 μL.min^{-1} with a Harvard syringe pump. Typical ESI conditions were as follows: capillary voltage, 3.1 kV; cone voltage, 80 V; source temperature, 80 °C; desolvation temperature, 120 °C. Dry nitrogen was used as the ESI gas. The quadrupole was set to pass ions from 100 to 3000 Th and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass-analyzed with a 1 s integration time. Data were acquired in continuum mode until acceptable averaged data were obtained. MALDI mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 J/m^2 delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analysis were performed in the reflectron mode at a resolution of about 10 000. The matrix (trans-2-[3-(4-tertbutylphenyl)-2-methylprop-2-enylidene] malononitrile) was prepared as 10 mg/mL solution in acetone. The matrix solutions (1 μL) were applied to a stainless steel target and air-dried. Polymer samples were dissolved in dichloromethane to obtain 1 mg/mL solutions. 1 μL aliquots of these solutions were applied onto the target area already bearing the matrix crystals, and then air-dried. Finally, 1 μL of a solution of NaI (2 mg/mL in acetonitrile: water (1:1)) was applied onto the target plate. For the recording of the single-stage MALDI−MS spectra, the quadrupole (rf-only mode) was set to pass ions from 1000 to 7000 Th, and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time. Data were acquired in continuum mode until acceptable averaged data were obtained.

Tapping-mode atomic force microscopy was performed with a Nanoscope V microscope from Veeco (operating in air at room temperature). Microfabricated silicon cantilevers were used with a spring constant of ∼ 40 N·m^{-1}. The working frequency (around 300 kHz) was chosen slightly below the resonance frequency. Images of different areas of the samples were collected with 2048 pixels in each direction. The Nanoscope v7.20 image processing software was used for image analysis. Size exclusion chromatography (SEC/GPC) was performed in THF at 35 °C using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 1 mL/min), a triple detector: refractive index (ERMA 7517), capillary viscometry and light scattering RALS (Viscotek T-60) (Polymer Laboratories GPC-RI/CV/RALS), an automatic injector (Polymer Laboratories GPC-RI/UV) and four columns: a PL gel 10 μm guard column and three PL gel Mixed-B 10 μm columns. PMMA standards were used for calibration (*even if such standards are useful for the determination of absolute molecular weight of LA−PMMA, they only allow the determination of relative molecular weights for all other samples such as linear or cyclic PLA-g-PMMA*).

Synthesis of (3*R*,6*S*)-3-Bromo-3,6-dimethyl-1,4-dioxane-2,5-dione (1). The monomer **1** has been synthesized according the experimental procedure of Harwood et al.[15]

To a 100 mL three-neck flask were added L-lactide (5.0 g, 35 mmol), benzene (25 mL), and *N*-bromosuccimide (6.8 g, 38 mmol). The mixture was brought to reflux under mechanical stirring. Benzoyl peroxide (0.17 g, 0.7 mmol) in benzene (4 mL) was added to the reaction dropwise through a dropping funnel in 20 min. After 2.5 h, the reaction mixture was cooled down to room temperature, and the solid was filtered off (∼3.5 g). The filtrate was evaporated to dryness and pale yellow solid was formed. The solid was dissolved in dichloromethane (40 mL), and the solution was washed with saturated sodium bisulfite solution three times and saturated NaCl solution once. The organic layer was dried over $MgSO_4$, and the solution was

Table 2. GPC Analyses for Cyclic PLA-*g*-PMMA

time (min)	M_n(GPC) (g/mol)	PDI	convn(GPC) (%)
8			26.0
10	18 920	1.46	83.9
20	16 610	1.36	91.7
40	18 720	1.46	92.5

evaporated to dryness. The orange solid was recrystallized from ethyl acetate and hexanes to give 2.96 g of white crystal. Yield: 38%. ^{1}H NMR ($CDCl_3$): 5.48 (q, J = 6.9 Hz, 1H), 2.32 (s, 3H), 1.72 (d, J = 6.9 Hz, 3H).

Synthesis of (3*R*,6*S*)-3-Poly(methyl methacrylate)-3,6-dimethyl-1,4-dioxane-2,5-dione (2). A dry flask was charged with CuBr (27.0 mg, 0.18 mmol), HMTETA (43.4 mg, 0.32 mmol) and a magnetic stirrer. The flask was fitted with a rubber septum and degassed with three successive freeze−pump−thaw cycles. A second flask was charged with **1** (42 mg, 0.18 mmol), THF (20 mL), and MMA (4 mL, 40 mmol). The flask was fitted with a rubber septum and degassed under N_2 flow for a few minutes. This mixture was then transferred into the first flask and the polymerization was carried out under stirring at 50 °C. Sample withdrawals were performed at time intervals to determine both M_n(exp) and associated PDIs (See Figure 1). After 2 h, the polymerization is stopped by fast cooling in liquid nitrogen. The copolymer was recovered by precipitation in 7-fold excess of cold methanol, filtrated and dried up to constant weight. Copper catalyst was removed by filtration of a PMMA/THF solution through an alumina gel column. Yield: 12% (DP_{th} = 24; M_n(th) = 2620). GPC analysis: M_n = 4800, PDI = 1.15 (f = efficiency factor = M_n(th)/M_n(exp) = 0.55). ^{1}H NMR: See Figure S1.

Synthesis of Jellyfish Poly(L-lactide)-*graft*-poly(methyl methacrylate) (*Cyclic* PLA-*g*-PMMA). In a previously flamed and nitrogen purged round-bottom flask are dried 134 mg of **2** (M_n = 2900, $n = 4.6 \times 10^{-5}$ mol) by three azeotropic distillations from dried THF before addition of 200 mg of L-LA (n = 1.4 mmol) and solubilization in 0.6 mL of THF. In a second flask, 12 mg of IMesCl ($n = 3.53 \times 10^{-5}$ mol) and 4 mg of tBuOK ($n = 3.53\ 10^{-5}$ mol) are dried under vacuum for 1 h at 35 °C. After drying treatment, 1 mL of dried THF is added and the crude mixture (let under agitation for 10 min) is injected via a previously flamed and nitrogen flushed capillary to the first round-bottom flask. Sample withdrawals were performed at time intervals to determine conversions, M_n(exp) and associated PDIs . ^{1}H NMR: See Figure S3(top). GPC analyses are given in Table 2.

Synthesis of Linear Poly(L-lactide)-*graft*-poly(methyl methacrylate) (*Linear* PLA-*g*-PMMA). In a previously flamed and nitrogen purged round-bottom flask, 134 mg of **2** (M_n = 2900, $n = 4.6 \times 10^{-5}$ mol) are dried by three azeotropic distillations from dried THF before addition of 200 mg of L-LA (n = 1.4 mmol) and solubilization in 0.6 mL of THF. In a second flask, 12 mg of IMesCl ($n = 3.53\ 10^{-5}$ mol) and 4 mg of tBuOK ($n = 3.53 \times 10^{-5}$ mol) are dried under vacuum for 1 h at 35 °C. After the drying treatment, 3.8 mg of dried benzylic alcohol (3.5×10^{-5} mol) and 1 mL of dried THF are added and the crude mixture (put under agitation for 10 min) is injected via a previously flamed and nitrogen flushed capillary to the first round-bottom flask. Sample withdrawals were performed at 10 min intervals to determine conversions, M_n(exp) and associated PDIs. Since a high increase in viscosity, the polymerization has been stopped after 20 min by addition of dried CS_2 and precipitated in cold methanol. ^{1}H NMR: See Figure S3(bottom). GPC analyses are given in Table 3.

Table 3. GPC Analyses for Linear PLA-*g*-PMMA

time (min)	M_n(GPC) (g/mol)	PDI	convn(GPC) (%)
10	11 000	1.34	81.3
20	13 400	1.41	89.0

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Supporting Information Available: Figures showing NMR spectra, a plot of concentration ratios vs time, and Tapping Mode AFM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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