Block Copolymer Synthesis by a Sequential Addition Strategy from the Organocatalytic Group Transfer Polymerization of Methyl Methacrylate to the Ring-Opening Polymerization of Lactide

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ABSTRACT: Sequential block copolymerization involving comonomers belonging to different classes, *e.g.*, a vinyl-type monomer and a heterocycle, is a challenging task in macromolecular chemistry, as corresponding propagating species do not interconvert easily from one to the other by crossover reactions. Here, it is first evidenced that 1-methoxy 2-methyl 1-trimethylsilyloxypropene (MTS), *i.e.,* a silyl ketene acetal (SKA)-containing initiator, can be used in presence of the P_4-*t*-Bu phosphazene organic base to control the ring-opening polymerization (ROP) of racemic lactide (*rac*-LA). The elementary reaction, which rapidly transforms SKA groups into propagating alkoxides, can be leveraged to directly synthesize well-defined poly(methyl methacrylate)-*b*-polylactide (PMMA-*b*-PLA) block copolymers. This is achieved using P_4-*t*-Bu as the single organic catalyst and MTS as the initiator for the group transfer polymerization (GTP) of methyl methacrylate (MMA), followed by the ROP of *rac*-LA. Both polymerization methods are implemented under selective and controlled/living conditions at room temperature in THF. This sequential addition strategy further expands the scope of organic catalysis of polymerizations for macromolecular engineering of block copolymers involving propagating species of disparate reactivity.

INTRODUCTION.

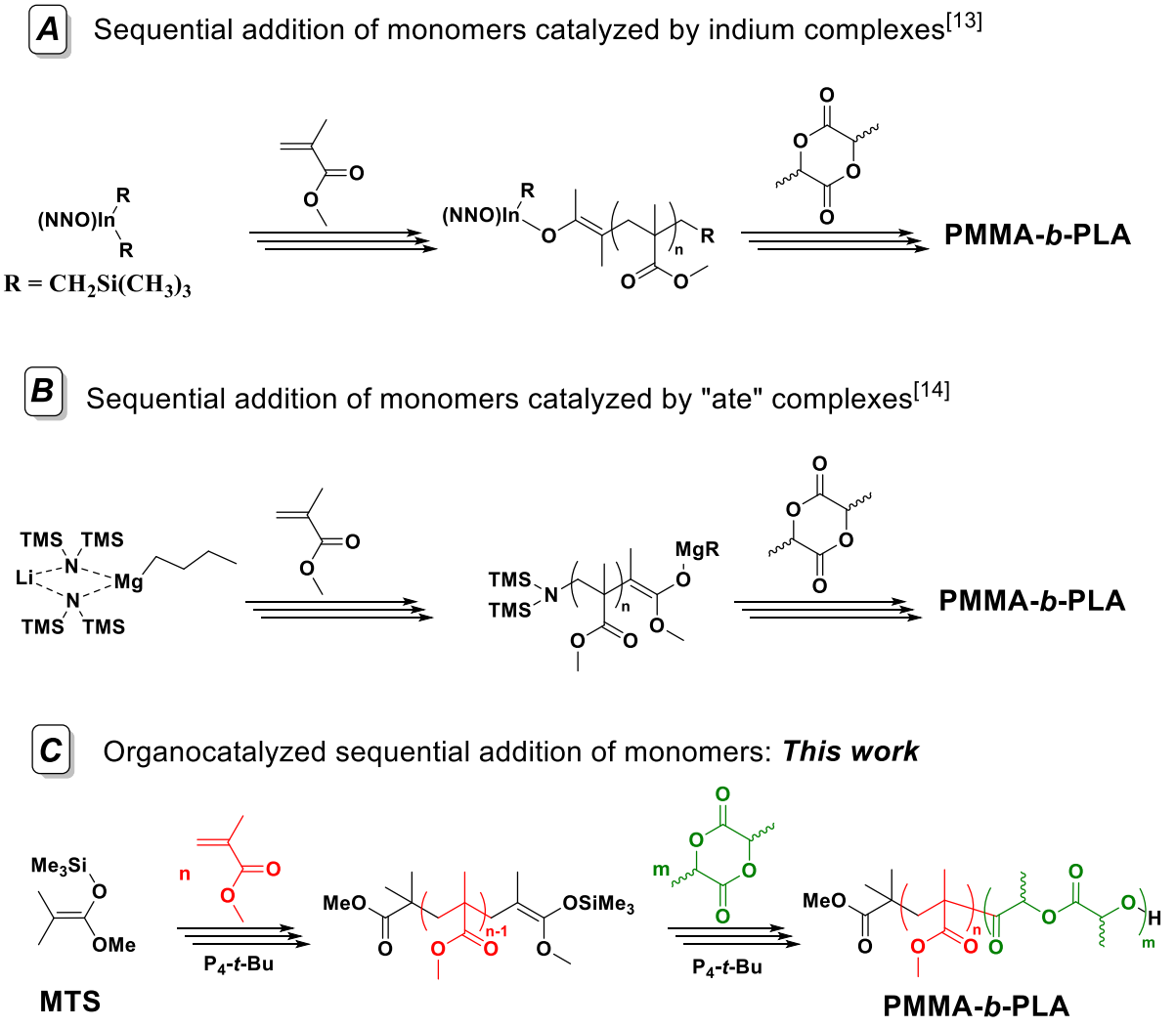
Methods of macromolecular chemistry are so mature that they now allow the preparation of nearly all sorts of block copolymers (BCPs), provided certain rules are fulfilled. In addition to the traditional i) sequential controlled/living polymerization (CLP), *i.e.,*

consecutive addition of at least two monomers, other strategies can be implemented, namely, ii) coupling of two preformed polymer segments with antagonist end-groups, iii) switch from one to another polymerization mechanism, and iv) one-pot initiation from "double-headed" initiators.[1–5] The most straightforward synthetic route to BCPs remains the sequential addition of two chain polymerizable monomers, following the same CLP mechanism, method i). After the first monomer is consumed, active species (ionic, radical or organometallic) remain "alive" to initiate the polymerization of the second monomer.[1] Originally achieved with monomers such as styrene and dienes by an anionic route, such a strategy has been further applied to other CLP methods, including cationic, radical and organometallic routes. In many cases, however, it is essential to sequentially polymerize the two monomers in a certain order to access the targeted BCPs. The "golden rule" is to follow the scale of reactivity, starting by the polymerization of the monomer that forms the higher reactive propagating center and, then, polymerize the other monomer.[6,7] For instance, sequential anionic polymerization requires the following order of addition: dienes/styrene > methacrylates > acrylates > oxiranes ~ cyclic esters > siloxanes.

Synthesis of BCPs consisting of methyl methacrylate (MMA) and aliphatic ester units by sequential polymerization, as we envisage in this work, remains challenging. Yet, a proper catalyst design can offer relevant options to balance the reactivity of propagating species. Rare-earth-based metallic catalysts have thus enabled to achieve poly(alkyl (meth)acrylate)-*b*-polyester BCP by sequential vinyl addition polymerization of the acrylic monomer and ring-opening polymerization (ROP) of the heterocyclic monomer in this order.[8–20] In contrast, Mehrkhodavandi *et al.* employed neutral and cationic indium-based complexes to perform the sequential block copolymerization of racemic lactide (*rac*-LA) (or ε-caprolactone, ε-CL) and MMA in either order of monomer addition (**Scheme 1.a)**.[13] Very recently, Thomas *et al.* reported that the lithium magnesium "*ate*" complexes could trigger both the anionic polymerization of MMA and the ROP of LA, making possible the synthesis of PMMA-*b*-PLA copolymers in THF (**Scheme 1.b)**.[14] Alternatively, mechanism switch, *i.e.*, method iii), can be implemented to access BCPs based on aliphatic polyester and polyacrylate chains. This involves ROP of the lactone first, followed by chemical modification of hydroxyl end groups to switch the latter into initiating fragments for the controlled radical polymerization (CRP) of the (meth)acrylic monomer.[16] Resorting to bifunctional "double-headed" initiators, *i.e.*, method iv), for either the sequential or the concomitant CRP of the (meth)acrylate monomer and the ROP of the cyclic ester has also been reported.[12,20–22]

Organocatalysis has emerged in polymer chemistry 20 years back, as a powerful methodological approach to produce metal-free polymeric materials, with a potential use in biomedical and personal care applications, in microelectronics, or in food packaging.[23,24] Several classes of organic catalysts, including Brønsted/Lewis acids or bases and mono- or bicomponent bifunctional catalytic systems, have thus been developed, offering new options in polymer chemistry by an appropriate organocatalyst design.[24,25] For instance, some organic catalysts have enabled monomers of disparate reactivity, *e.g.*, cyclic esters and MMA, to be successfully incorporated in copolymer chains or be polymerized sequentially.[26–28] Zinck *et al.* thus used 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ^5,4λ^5-catenadi(phosphazene), P$_4$-*t*-Bu, to catalyze the sequential anionic-like polymerization of *ε*-decalactone and MMA, *i.e.*, involving a switch from alkoxides to enolate-type growing species. Resulting BCPs however characterized by a rather large dispersity (*Đ*= 1.94).[26] Much earlier work by Pispas, Zhang *et al.* in 2012 reported that the P$_4$-*t*-Bu base could enable the hybrid copolymerization of *ε*-CL and MMA, though not forming BCP in this case but supposedly statistical copolymers.[28] The sequential addition strategy we propose here involves the P$_4$-*t*-Bu organocatalyzed group transfer polymerization (GTP) of MMA first, followed by the ROP of *rac*-LA (**Scheme 1.c**).

GTP has been reported in the 1980's as a living anionic-like polymerization of (meth)acrylic monomers being effective at room temperature.[29,30] GTP is an adaptation of the Mukaiyama-Michael reaction in macromolecular synthesis; it uses a silyl ketene acetal (SKA) as initiator and involves transfer of the trialkylsilyl group to the poly(meth)acrylate chain end.[31,32] In recent years, the scope of GTP has been expanded through the use of a variety of organic catalysts, such as *N*-heterocyclic carbenes (NHCs) or phosphazene bases, *e.g.*, P$_4$-*t*-Bu, or strong Bronsted acids (*e.g.*, bis(trifluoromethanesulfonyl)imide).[33–40] The synthetic approach to BCPs we develop in this work employs an organic catalyst to quantitatively switch enolate-type growing chain-ends of GTP-derived PMMAs to alkoxide chain ends of ROP-derived PLAs. Surprisingly, the synthesis of PMMA-*b*-PLA BCPs following an organocatalytic sequential block copolymerization pathway and involving propagating species of disparate reactivity, as we describe here, has never been reported.



Scheme 1. Catalysts employed to achieve of block copolymers based on PLA and PMMA by sequential polymerization.

RESULTS AND DISCUSSION.

The organocatalyzed GTP of MMA was carried out in THF at room temperature (RT), using 1-methoxy 2-methyl 1-trimethylsilyloxypropene (MTS)[41] as initiator (ESI, **Scheme S1**). Various organic catalysts were tested for these preliminary GTP experiments, namely, 1-tert-butyl-2,2,4,4,4-pentakis (dimethylamino)-2L5,4L5-catenadi(phosphazene) (P_2-*t*-Bu; pKa^{MeCN}= 21.4),[42] a thioimidate generated *in situ* by reaction between the phosphazene base P_4-*t*-Bu and the Takemoto aminothiourea (TU),[43,44] P_4-*t*-Bu used alone, as well as 1,3-di-*t*-butylimidazol-2-ylidene (NHC_{tBu}) and tetra-*n*-butylammonium bibenzoate (TBABB). The two first catalysts proved ineffective in initiating the GTP of MMA (**Table 1**, **run 1** and **2**). In contrast, P_4-*t*-Bu, NHC_{tBu} and TBABB enabled MMA polymerization to proceed under controlled conditions (**Table 1** and **S1** in ESI). The fastest reaction was observed using the strong P_4-*t*-Bu organic base (pKa^{MeCN}= 42.7),[42] achieving complete conversion in 60 minutes and a PMMA of low

dispersity (*Đ*= 1.07; **Table 1, run 3-6;** ESI, **Figure S1)**. These results are consistent with those reported by Kakuchi *et al.*[45] Both TBABB and NHC_{tBu} also allowed to reach full conversion of MMA, in 90 and 180 minutes, respectively, without any loss of reaction control (*Đ* < 1.15; ESI, **Table S1**, **run S1-S6**; **Figure S2-S3**). In particular, no UV signal was observed in the size exclusion chromatography (SEC) traces, at λ= 305 nm, a wavelength assignable to the absorbance of PMMA keto-ester chain ends resulting from a "*backbiting*" termination reaction.[46] This attested to the well-controlled GTP process utilizing TBABB, NHC_{tBu} and P_4-*t*-Bu as organic catalysts.

Table 1. MMA polymerization and ROP of *rac*-LA initiated by MTS in THF at room temperature.[a]

Run	Catalyst (C)	Monomer (M)	$[M]_0/[C]_0/[I]_0$	Time (min)	Conv. (%)[b]	$\overline{Mn}_{calcd}$ (kg/mol)[c]	$\overline{Mn}_{exp}$ (kg/mol)[d]	$Đ^d$
1	P_2-*t*-Bu	MMA	100:1:1	120	0	-	-	-
2	P_4-*t*-Bu/ TU	MMA	100:(0.1/1):1	300	0	-	-	-
3	P_4-*t*-Bu	MMA	50:0.01:1	45	≥99	5	5	1.16
4	P_4-*t*-Bu	MMA	100:0.01:1	60	96	9	8	1.11
5	P_4-*t*-Bu	MMA	150:0.01:1	60	97	15	16	1.07
6	P_4-*t*-Bu	MMA	200:0.01:1	90	95	19	18	1.07
7	P_4-*t*-Bu	*rac*-LA	50:1:1	240	≥99	7	5	1.26
8	P_4-*t*-Bu	*rac*-LA	100:1:1	300	96	14	12	1.20
9	P_4-*t*-Bu	*rac*-LA	150:1:1	300	91	20	18	1.22
10	P_4-*t*-Bu	*rac*-LA	200:1:1	340	95	27	24	1.18
11	TBABB	*rac*-LA	50:1:1	400	0	-	-	-
12	NHC_{tBU}	*rac*-LA	50:1:1	400	0	-	-	-

[a][M]= 1 $mol.l^{-1}$. [b]Conversion of monomers determined by ^1H NMR in $CDCl_3$ using integrals of characteristic signals. [c]M_{ncalcd}= M_{MMA} (100.121 g mol^{-1}) x $([MMA]_0/[I]_0)$ x conversion + M_{MTS} (174.31 g mol^{-1}), in case of *rac*-LA (M_{LA} = 144.13). [d]Determined by SEC in THF using polystyrene standards and after applying a correction factor of 0.58 in case of *rac*-LA, as reported by Duda, Penczek *et al.*[47]

As we envisioned to achieve PMMA-*b*-PLA BCPs by a sequential organocatalytic pathway, the challenge was to fully convert SKA end-groups of GTP-derived PMMA chains into alkoxides characterizing growing PLA chains. This change in active species, from one block to the other, was first investigated using MTS serving as molecular model of GTP-derived PMMA growing chains. MTS was thus employed to initiate the ROP of *rac*-LA, in presence of either P_4-*t*-Bu, or NHC_{tBu} or TBABB as organic catalyst. ROP reactions were carried out in THF, under the same conditions to those implemented further for the synthesis of the PMMA-*b*-PLA BCPs. As summarized in **Table 1**, however, neither NHC_{tBu} nor TBABB could catalyze

the ROP of *rac*-LA under these conditions (**run 11** and **12**). In contrast, P4-*t*-Bu enabled to efficiently mediate the MTS-initiated ROP of *rac*-LA. The resulting PLAs were obtained in near quantitative yields, after a few hours of reaction. Experimental molar masses, as determined by SEC by applying a correction factor of 0.58,[47] agreed very well with theoretical values based on the [*rac*-LA]/[MTS] monomer-to-initiator ratio (**Table 1**). **Figure 1.a** shows the narrowly distributed SEC traces of PLAs of different molar masses ($Đ$ < 1.30). A typical ^{1}H NMR spectrum of a P4-*t*-Bu-catalyzed MTS-initiated PLA, obtained after workup, is displayed in **Figure 1.b**. In particular, one can note the presence of distinctive peaks around 1 ppm, attributed to the resonance of the non-magnetically equivalent methyl protons (a) adjacent to the ester group and arising from the MTS initiator, *i.e.*, in α-position of the PLA chains. Signals appearing at 1.57 ppm and 5.16 ppm can be assigned, respectively, to the methyl protons (b) and to the methine protons (c) of PLA. The relative integration of signals due to protons (a) and (c) allowed the molar mass of this PLA to be determined. A molar mass of 14000 g/mol was thus calculated, in agreement with the theoretical value and that delivered by SEC (**Table 1, run 8**). In addition, molar masses (M_n) were found to increase linearly with the monomer conversion, while the molar mass distribution remained fairly narrow ($Đ$ <1.2; ESI, **Figure S4**). All these results support that initiation of the ROP of *rac*-LA by MTS and catalyzed by P4-*t*-Bu is quantitative and fast relatively to the propagation step, the controlled character of the ROP process being proven, which has never been reported before, to the best of our knowledge.

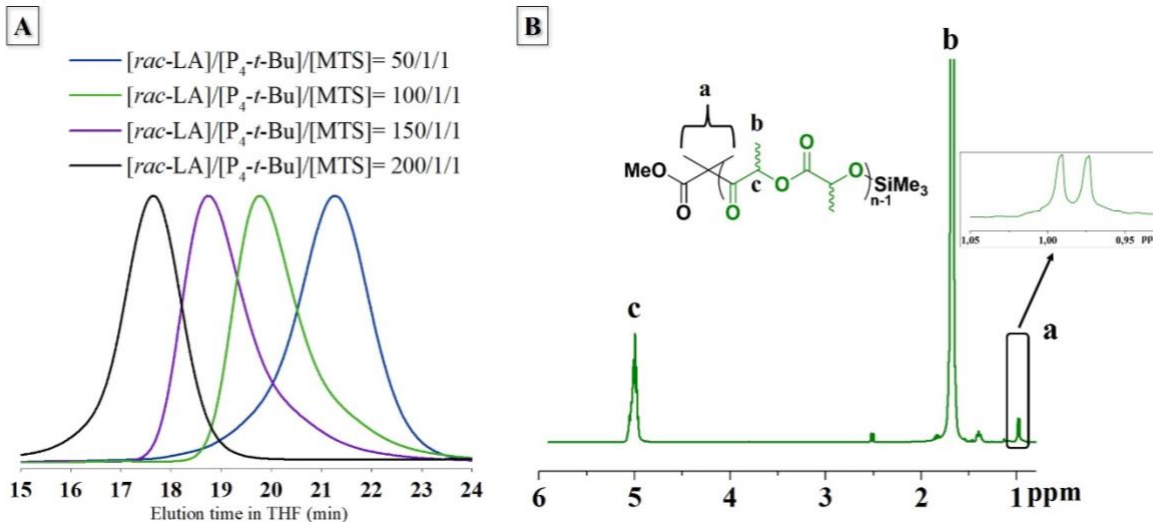
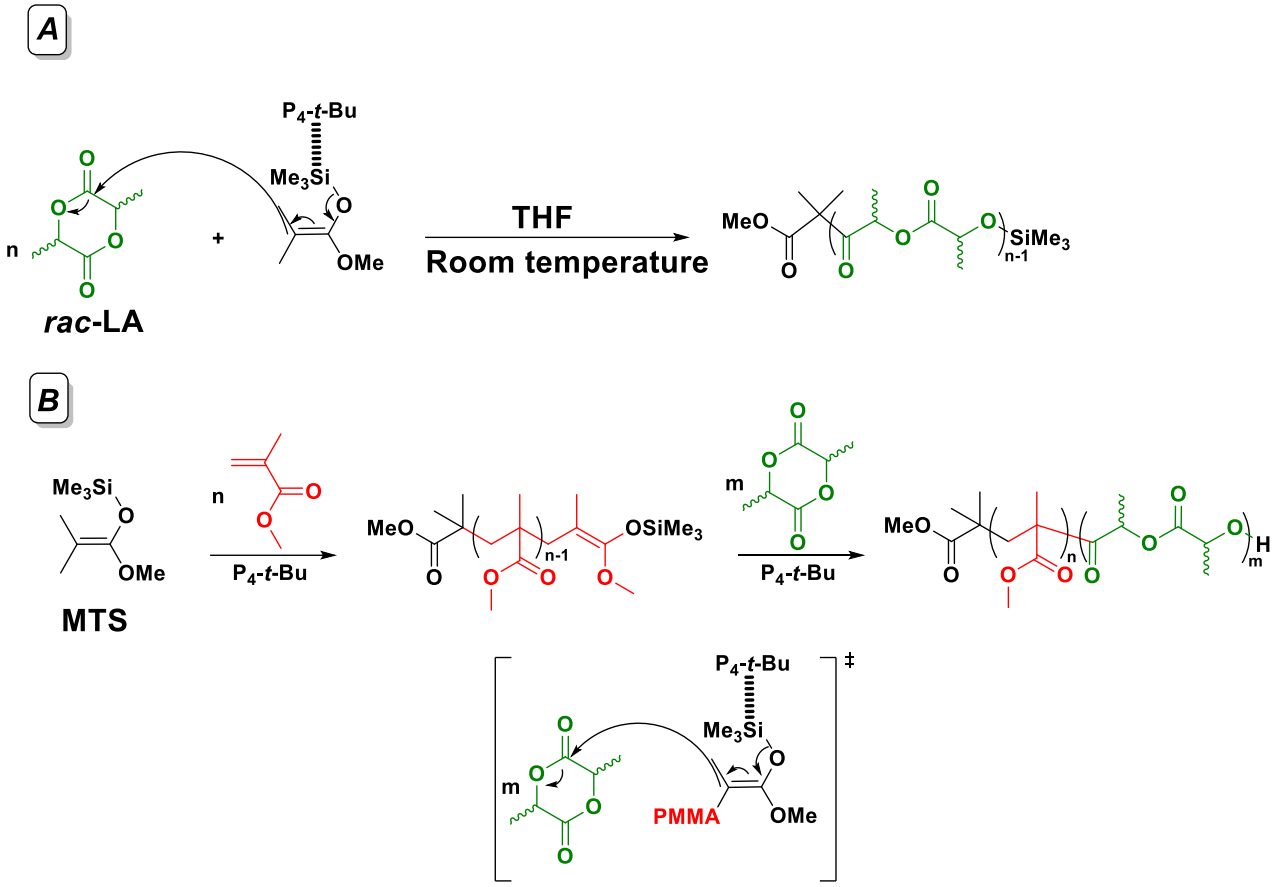


Figure 1. (A) SEC traces of PLA samples of different molar masses (**Table 1**, **run 7-10**) and (B) ^{1}H NMR spectrum of PLA sample initiated by MTS and catalyzed by P4-*t*-Bu (**Table 1**, **run 8**).

Initiation by MTS using P4-*t*-Bu thus implies the quantitative conversion of the masked enolate-type species, *i.e.*, in the form of SKAs, into dormant silylated ethers generating alkoxide species during the growth of PLA chains. The supposed mechanism of this key elementary step is shown in **Scheme 2.a.** This new option prompted us to further investigate BCP synthesis, involving GTP of MMA and ROP of *rac*-LA, in this order, using the same P4-*t*-Bu organic catalyst (**Scheme 2.b**). Corresponding results are summarized in **Table 2**.



Scheme 2.(A) Homopolymerization of *rac*-LA initiated by MTS. (B) PMMA-*b*-PLA synthesis and the transformation of the GTP active site into a ROP active site *via* activation by the phosphazene base P4-*t*-Bu.

Table 2. Sequential group transfer polymerization of MMA and ring-opening-polymerization of *rac*-LA initiated by MTS in THF using P4-*t*-Bu as organic catalyst.[a]

Run	Polymer	$[M]_0/[C]_0/[I]_0$	Time (min)	Conv (%)[b]	$\overline{Mn}_{calcd}$ (kg/mol)[c]	$\overline{Mn}_{exp}$ (kg/mol)[d]	$\overline{Mn}_{NMR}$ (kg/mol)[e]	$Đ^d$
1	PMMA	50:0.01:1	45	≥99	5	4	-	1.12
	PMMA-*b*-PLA	50:1:1	320[f]	97	12	9	10	1.30
2	PMMA	50:0.01:1	45	≥99	5	4	-	1.10
	PMMA-*b*-PLA	100:1:1	340[f]	96	19	17	19	1.15
3	PMMA	50:0.01:1	45	≥99	5	4	-	1.12
	PMMA-*b*-PLA	150:1:1	340[f]	93	25	23	23	1.13
4	PMMA	50:0.01:1	45	≥99	5	4	-	1.14
	PMMA-*b*-PLA	200:1:1	340[f]	87	30	28	27	1.09
5	PMMA	100:0.01:1	60	≥99	10	9	-	1.09
	PMMA-*b*-PLA	100:1:1	400[f]	94	24	21	21	1.11
6	PMMA	100:0.01:1	60	≥99	10	10	-	1.09
	PMMA-*b*-PLA	150:1:1	400[f]	96	29	27	28	1.14
7	PMMA	100:0.01:1	60	≥99	10	10	-	1.07
	PMMA-*b*-PLA	200:1:1	400[f]	89	35	32	32	1.14
8[g]	PMMA	100:0.01:1	60	≥99	10	10	-	1.08
	PMMA-*b*-PLA	100:1:1	400[f]	85	22	19	18	1.12

[a][M]= 1 mol.l^{-1}. [b]Conversion of monomers determined by ^{1}H NMR in $CDCl_3$ using integrals of characteristic signals.[c]$M_{ncalcd.}$= M_{MMA} (100.121 g.mol^{-1}) x ($[MMA]_0/[I]_0$) x conversion + M_{MTS} (174.31 g.mol^{-1}), in case of copolymers, $M_{rac\text{-}LA}$ (144.13 g.mol^{-1}) x ($[rac\text{-}LA]_0/[I]_0$) x conversion is added to the formula. [d]Determined by SEC in THF using polystyrene standards for the parent PMMA's; in case of the BCPs: M_{nSEC} = ($M_{n,SECraw\ data}$ × 0.58 × composition of PLA) + ($M_{nSECraw\ data}$ × composition of PMMA);[20] $M_{n,SECraw\ data}$= raw molar mass determined by SEC without the use of correction factor. [e]Determined by ^{1}H NMR giving the molar composition of the PMMA-*b*-PLA BCP and knowing the molar mass of the parent PMMA. [f]Cumulated time. [g]Polymerization performed at 0 °C. ***N.B.*** Molar mass of PMMA homopolymer was not determined by NMR as MTS signals overlapped those of the polymer.

Addition of 1 equivalent of P4-*t*-Bu compared to MTS after the formation of the PMMA block allowed conducting the ROP reaction with reasonable kinetics (**Table 2**, **run 5** *vs.* ESI, **Table S1**, **run S7-S8**). Both MMA and *rac*-LA were fully consumed by the GTP and the ROP reaction, respectively. Crossover from GTP of MMA to ROP of *rac*-LA proved highly effective. This is illustrated by the SEC trace of all compounds collected after 5 hours of reaction, showing a clear shift to the higher molar masses (*e.g.* M_n= 19000 g.mol^{-1}; $Đ$= 1.12, **Table 2**, **run 8**), compared with the SEC trace of the GTP-derived PMMA macroinitiator (**Figure 2**). Experimental molar masses of the resulting compounds, denoted as $\overline{Mn}_{exp}$ in Table 2, were determined by SEC using both the correction factor of PLA and the composition of

each block, *i.e.* $M_{n,SEC}$ = ($M_{nSECraw\ data}$ × 0.58 × composition of PLA) + ($M_{nSECraw\ data}$ × composition of PMMA).[20] A good agreement between observed molar masses and expected ones was noticed after applying the correction factor.

A typical ^{1}H NMR spectrum of a PMMA-*b*-PLA BCP is shown in **Figure 3**. The composition in each monomer unit was thus determined from the relative integrations of characteristic signals at 5.16 ppm and at 0.84-1.18 ppm (Me) for PLA and PMMA blocks, respectively. Knowing the molar mass of the PMMA precursor, the M_n value of the PMMA-*b*-PLA BCPs could be estimated ($\overline{Mn}_{NMR}$, Table 2). For instance, a $\overline{Mn}_{NMR}$ value of 21844 g.mol^{-1} was calculated, corresponding to a molar mass of 9830 and 12014 g.mol^{-1} for the PMMA and PLA block, respectively (**Table 2**, **run 5**).

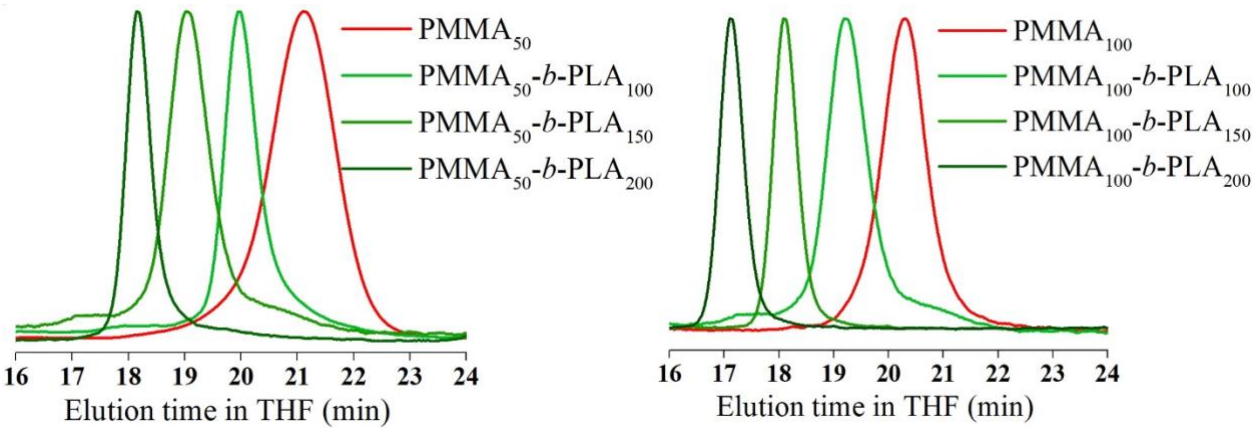


Figure 2. SEC traces of the GTP-derived PMMA's (**red line**) and of PMMA-*b*-PLA BCPs (**green lines**); **Table 2**, **run 2** and **5**.

Analysis by homonuclear decoupled ^{1}H NMR spectroscopy showed that the PLA block of all BCPs was atactic. For instance, the probability of formation of LA meso dyads, P_m,[48] was found equal to 0.58 (**Table 1, run 5)**. Simple analysis by ^{1}H NMR allowed evaluating the tacticity of the PMMA block, considering the relative ratios of the peaks at 1.18 1.02 and 0.84 ppm (**Figure 3**). These peaks are due to the resonance of the methyl groups of MMA monomer units corresponding to the isotactic (mm), atactic (mr) and syndiotactic (rr) triads, respectively. In a general manner, the room temperature P_4-*t*-Bu-catalyzed GTP produced PMMA's with a slight syndiotactic predominance (~60 %), with a low rate of isotactic triads (<5 %) in THF as solvent (**Figure 3**). Block copolymerization carried out at 0 °C slightly improved the tacticity of the PLA block, as a P_m value of 0.66 was obtained (**Table 2**, **run 8**; **Figure 3**). Analysis of the homopolymers by DSC show a T_g value of 41 and 112 °C for PLA and PMMA, respectively (ESI, **Figure S5-S6**). Owing to their atactic character, BCPs proved amorphous in all cases and a single glass transition temperature (T_g) value around 50 °C was detected by DSC (ESI**, Figure**

S7-S8), which was ascribed to the PLA block only, suggesting a fairly good compatibility between the two blocks, at least in the range of molar masses targeted, a result which is consistent with previous reports.[13,14,49] However, a slight signal observed at 92 °C might be ascribed to the T_g of PMMA segments (**Figure S8**).

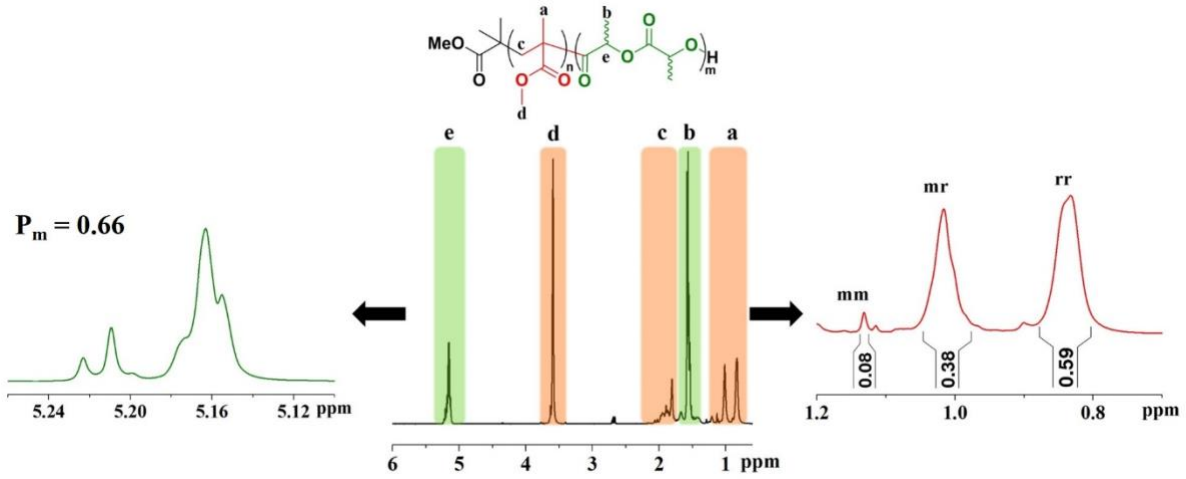


Figure 3. ^{1}H NMR spectrum of a PMMA-*b*-PLA copolymer in $CDCl_3$; at the **left** enlarging of the methine area of the PLA block after homonuclear decoupling; at the **right** enlarging of the lateral methyl area of the PMMA block.

CONCLUSION.

A single organic catalyst, namely, the strong P_4-*t*-Bu Brønsted organic base, allows conducting the group transfer polymerization of methyl methacrylate (MMA), followed by the ring-opening polymerization of racemic lactide (*rac*-LA) by a successive addition of the two monomers. This sequential addition strategy can be readily achieved at room temperature in THF as solvent, using 1-methoxy 2-methyl 1-trimethylsilyloxypropene (MTS) as initiator. We provide clear evidence that silyl ketene acetal moieties serving here as dormant enolates can be rapidly and quantitatively transformed into growing alkoxides, as the ROP of *rac*-LA initiated by MTS shows a controlled/living character and a high chain end fidelity. This elementary reaction can be leveraged to directly access block copolymers based on PMMA and PLA by an organocatalytic pathway. Highly efficient crossover from one block to the other is demonstrated through the selective synthesis of structurally well-defined PMMA-*b*-PLA block copolymers of varied molar masses and compositions. Future work will focus, in the one hand, on MTS-initiated organocatalyzed ROP of other cyclic monomers and, on the other hand, on the synthesis and investigations of the physical properties of a variety of block copolymers following this sequential addition strategy.

ASSOCIATED CONTENT

Supporting information

Experimental procedures for synthesis and characterization including NMR spectra and SEC traces.

AUTHOR INFORMATION CONTENT

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The P4-*t*-Bu Brønsted organic base is here employed to directly switch from the group transfer polymerization of methyl methacrylate to the ring-opening polymerization of lactide, allowing an easy access to well-defined PMMA-*b*-PLA block copolymers by an organocatalytic pathway.

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Block Copolymer Synthesis by a Sequential Addition Strategy from the Organocatalytic Group Transfer Polymerization of Methyl Methacrylate to the Ring-Opening Polymerization of Lactide