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ORIGINAL PAPER

Synthesis of ABC miktoarm star block copolymers from a new heterotrifunctional initiator by combination of ATRP and ROP

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Abstract We described the obtention of well-defined ABC star block copolymers through the use of a new heterotrifunctional initiator. That way, well-defined PCL-arm–PS-arm–PLLA star block copolymers have been synthesized from a heterotrifunctional initiator bearing two hydroxyl groups able to initiate ROP of CL and LLA (using $Sn(Oct)_2$ as coinitiator) and a bromide function able to initiate ATRP of styrene.

Keywords Star block copolymer · Heteromultifunctional initiator · Coordinated anionic ring-opening polymerization · Atom transfer radical polymerization

Introduction

Miktoarm star block copolymers reveal interesting properties in the solid state, as well as in solution, due to their unique architectures. The synthesis of ABC type block copolymers can be accomplished according to three ways. The first one uses the selective step-by-step substitution reaction of the chlorine atoms in trichloromethylsilane with living polymer chains [1]. The second one is based on a macromonomer technique, in which non-homopolymerizable linking agent like

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1,1-diphenylethylene (DPE) groups at one chain end are incorporated at the block junction of a diblock copolymer [2–4]. The third procedure we have developed consists of two successive initiation steps on a "heterobifunctional macroinitiator", obtained by reaction of living polystyrene with a specific DPE derivative [5, 6].

The synthesis of block copolymers from monomers which polymerize by different mechanisms still remains difficult and constraining. For this purpose, the heteromultifunctional initiator route seems to be promising. The first heteromultifunctional initiator with four different initiating sites, called "universal initiator", has been developed by Sogah et al. [7]. Even if Sogah has used this initiator only for the synthesis of diblock and graft copolymers, it was a fruitful concept for the synthesis of miktoarm star block copolymers. So, few years later, ABC star block copolymers were directly obtained from heterotrifunctional initiators by Zhao et al. [8] and Tunca et al. [9]. These syntheses involved the coupling of three different polymerizations: ATRP, NMP and ROP in a sequential (three-step) process. PEO*n*–PS*m* miktoarm star block copolymers (with three or four arms) were obtained by Tsukruk et al. [10] using heteromultifunctional initiators partially protected. This implies the deprotection of the intermediate PS macroinitiator obtained after the first step (the styrene ATRP). These heterofunctional initiators can also be used in a simultaneous (one-step) process, it means that mixture of the initiator, the two or more monomers (eventually the co-initiators) leads directly to the expected block copolymer. This was reported for the synthesis of diblock and star block copolymers [7, 11, 12] and moreover in a control manner (control separately the size of each block) by our team [13].

In this paper, we describe for the first time the synthesis of well-defined PS-arm–PLLA-arm–PCL, starting from a new heterotrifunctional initiator, bearing one bromine for the ATRP of styrene and two hydroxyl groups, one being first protected, for the anionic coordinated ROP of CL and LLA.

Experimental part

Materials

Glycerol (99% puriss Riedel-de Haen), Iodine (purum p.a. >99.5%, Fluka), Acetone (Normapur analytical reagent), Tetrahydofuran (99+, extra pure, stabilized with BHT, Acros Organics), Dichloromethane (GPR Rectapur stabilized with 0.1% of ethanol VWR Prolabo), Triethylamine (Reagent Plus 99.5% Aldrich), Dowex 50Wx8-200 ion-exchange resin (Janssen Chimica), Pyridine (ACS For Analysis CARLO ERBA), Methanol (Chromasolv Sigma Aldrich) and Triphenylmethylchloride (98% Aldrich) were used as received. Tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, 96%, Alfa Aesar), 2,2′-bipyridyl (bipy, >98%, Fluka), 2-bromoisobutyrylbromide (98%, Aldrich), *p*-toluenesulfonic acid (98%, Aldrich), and vinyl acetate (>99%, Aldrich) were used without further purification. ε-caprolactone (CL, 99%, Aldrich) and styrene (99.5%, Fluka) were dried over CaH_2 and distilled under vacuum just before use. L-Lactide (LLA, 98%, Aldrich) was recrystallized from toluene, and then dried under vacuum (0.1 mmHg) at room temperature for 24 h. Toluene

(99.5%, Fluka) was distilled over CuCl/NaOH and over sodium, and dried over molecular sieves (3A°). Copper(I) bromide (98%, Aldrich) was purified according to a published procedure [14]. Novozyme 435 (kindly supplied to us by Novozymes, Germany) was dried under vacuum in a desiccator with phosphorous pentoxide (P_2O_5) as desiccant (0.1 mmHg, 24 h, room temperature).

Measurements

Nuclear magnetic resonance (*^1H NMR*) spectra were recorded on a 400 MHz spectrometer (Brucker AC 400) using deuterated chloroform as a solvent.

Size exclusion chromatography (*SEC*) was carried out using a Waters 2690 liquid chromatograph equipped with three columns, Waters Styragel 5 μm, 10^4, 500 and 100 Å columns; injection and refractometer temperature, 35 °C; injection volume, 100 μL; solvent, THF at 1 mL/min, a refractive index detector (Waters 410). Size exclusion chromatography was calibrated with PS standards.

Syntheses

Heterotrifunctional initiator synthesis

*(2,2-dimethyl-[1,3]-dioxolan-4-yl) methanol (**1**)* Compound **1** was synthesized according to the following procedure: 7.5 g (81.44 mmol) of glycerol were dissolved in 300 mL of acetone into a 500 mL round bottom flask. A catalytic amount of iodine (0.75 g, 2.95 mmol) was added and the solution was stirred at room temperature for 5 days. The reaction mixture was concentrated under reduced pressure, dissolved in ethyl acetate and washed with sodium thiosulfate (10%) and NaCl and dried ($MgSO_4$). The organic phase was concentrated under reduced pressure to give colorless oil (9 g, 68.1 mmol, 84%).

^{1}H NMR ($CDCl_3$ 400 MHz) δ (ppm): 1.37 (*s*, 3H, CH_3), 1.44 (*s*, 3H, CH_3), 3.60 (*dd*, 1H, $^2J = 11.6$; $^3J = 5.2$, H_a–C(H_b–OH)), 3.74 (*dd*, 1H, $^2J = 11.6$; $^3J = 3.6$, H_b–C(H_a–OH)), 3.80 (*t*, 1H, $^3J = 7$, H_a–C(5)), 4.04 (*t*, 1H, $^3J = 7$, H_b–C(5)), 4.24 (*m*, 1H, H–C(4)).

*(2′,2′-Dimethyl-[1′,3′]dioxolan-4′-yl)-methyl-2-bromoisobutyrate = ((2′, 2′-dimethyl-[1′, 3′]-dioxolan-4′-yl)-methyl-2-bromo-2methylpropanoate)) (**2**)* A solution of **1** (9 g, 68.1 mmol) and triethylamine (10.41 mL, 74.9 mmol) in 150 mL of methylene chloride was cooled to 0 °C in an ice bath. Into this solution was added 2-bromoisobutyrylbromide (8.41 mL, 68.1 mmol) dropwise. The reaction was stirred at room temperature for 4 h. The salt was filtered off and the reaction mixture was washed sequentially with $NaHCO_3$ and NaCl. The CH_2Cl_2 organic phase was dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product was purified by CC (silica gel, AcOEt/petroleum ether 1:9) to give a yellow oil (17.66 g, 62.84 mmol, 92%,).

^{1}H NMR ($CDCl_3$ 400 MHz) δ (ppm): 1.37 (*s*, 3H, CH_3), 1.44 (*s*, 3H, CH_3), 1.94 (*s*, 6H, 2× CH_3–C(2)), 3.83 (*dd*, 1H, $^2J = 10$; $^3J = 7$, H_a–C(5′)), 4.09 (*dd*, 1H,

$^2J = 10$; $^3J = 7$, H_b–C(5′)), 4.22 (*m*, 2H, H_a and H_b–C(OCO)), 4.34 (*m*, 1H, H–C(4′)).

Glyceryl-2-bromoisobutyrate = (2,3-dihydroxypropyl-2-bromo-2-methylpropanoate) **(3)** To a round bottom flask was added **2** (17.66 g, 62.84 mmol) in 150 mL of THF/methanol (50/50 w/w) solvent mixture. 17.66 g of Dowex 50W4-50 ion H^+ exchange resin were then added and the reaction mixture was stirred at 50 °C for 48 h. After filtration and washings of the resin with methanol, the combined filtrates were concentrated under reduced pressure, dissolved in ethyl acetate and washed with $NaHCO_3$ and NaCl. The organic phase was dried over $MgSO_4$ and then concentrated under reduced pressure to give colorless oil (10.68 g, 44.3 mmol, 70%).

^{1}H NMR ($CDCl_3$ 400 MHz) δ (ppm): 1.92 (*s*, 6H, 2× CH_3), 3.42 (br. *s*, 2H, 2xOH), 3.62 (*dd*, 1H, $^2J = 12$; $^3J = 5$, H_a–C(H_bOCO)), 3.72 (*dd*, 1H, $^2J = 12$; $^3J = 3$, H_b–C(H_aOCO)), 3.97 (*m*, 1H, H–C(OH)), 4.22 (*d*, 2H, $^3J = 5$, H_a and H_b–C(CHOH)).

[(3′-triphenylmethyl)-glyceryl]-2-bromoisobutyrate = ([2′-hydroxy-3′-(triphenylmethoxy)propyl]-2-bromo-2methylpropanoate): **(4)**

Compound **3** (10.68 g, 44.3 mmol), pyridine (7.85 mL, 97.46 mmol) and triphenylmethylchloride (24.7 g, 88.6 mmol) in 100 mL of dichloromethane were added into a round bottom flask and stirred at room temperature for 48 h. The solution was filtered off and the filtrate was washed with $NaHCO_3$ and NaCl. The combined organic phases were concentrated under reduced pressure and then purified by CC (silica gel, AcOEt/petroleum ether 1:9) and the desired compound **4** was obtained as a white solid (12.85 g, 26.61 mmol, 60%).

^{1}H NMR ($CDCl_3$ 400 MHz) δ (ppm): 1.82 (*s*, 6H, 2× CH_3), 2.40 (br. *s*, 1H, OH), 3.21 (*d*, 2H, $^3J = 5$, H_a and H_b–C(3′)), 4.05(*m*, 1H, H–C(2′)), 4.25 (*d*, 2H, $^3J = 5$, H_a and H_b–C(1′)), 7.18–7.21 (*m*, 3H, H arom), 7.24–7.28 (*m*, 6H, H arom), 7.38–7.40 (*m*, 6H, H arom).

Synthesis of the PCL arm

The polymerizations were carried out in a previously dried Schlenk tube equipped with a magnetic stirring bar under N_2. The tube was degassed three times by repeated vacuum/N_2 cycles. To 0.2 g (0.414×10^{-3} mol) of **4** previously dried under vacuum at room temperature were added 15 mL of dried toluene, 0.0134 mL (0.4×10^{-4} mol) of a solution of $Sn(Oct)_2$ in toluene and 2 mL (0.182 mol) of ε-caprolactone. The polymerization was allowed to proceed for 15 h at 110 °C. The reaction mixture was concentrated, and the polymer was precipitated into cold methanol, filtered, and dried to provide a white powder.

For the polymer $\mathbf{PCL_1}$, M_n (SEC) was 3,800, the PDI was 1.26 (after correction with the Mark–Houwink correction on a SEC instrument with THF as an eluent and with calibration at 35 °C using PS standards) and the yield was 82%.

Synthesis of the PS arm

To a Schlenk tube equipped with a magnetic stirring bar were added under N_2 0.015 g (0.105×10^{-3} mol) of CuBr, 0.58 mL (5×10^{-3} mol) of freshly distilled styrene and 0.033 g (0.21×10^{-3} mol) of bipy. The reaction mixture was degassed by three freeze–pump–thaw cycles and backfilled with N_2 and then the medium was stirred for half an hour at room temperature to allow the formation of a copper–ligand complex. 0.4 g (0.105×10^{-3} mol) of **PCL_1** in 0.25 mL of THF were then added and the polymerization was allowed to proceed at 110 °C for 9 h. The reaction medium was then passed through a column of Celite for the removal of the metal salts. The copolymer was precipitated from an excess of methanol, collected by filtration and then dried in vacuo to give a white powder.

For the copolymer **PCL_1–PS**, M_n (SEC) was 10,300 and the PDI was 1.23 (with THF as an eluent and with calibration at 35 °C using PS standards) and the yield was 100% for styrene.

Functionalization of the PCL arm

To a Schlenk tube equipped with a magnetic stirring bar were added under N_2 0.646 g (0.68×10^{-4} mol) of copolymer **PCL_1–PS**, 15 mL of anhydrous toluene, 0.187 mL (2×10^{-3} mol) of vinyl acetate and 0.065 g of novozyme previously dried under vacuum at room temperature. The medium was stirred at 30 °C for 15 h. The reaction medium was then filtered in order to eliminate the novozyme and concentrated. The copolymer was precipitated from an excess of methanol, collected by filtration and dried in vacuo to give a white powder.

Deprotection of the protected hydroxyl groups

To a round-bottom flask were added 0.64 g (0.67×10^{-4} mol) of previously functionalized copolymer **PCL_1–PS**, 0.051 g (0.27×10^{-3} mol) of para-toluene sulfonic acid in 10 mL of a mixture of THF/MeOH (v/v: 70/30). The medium was stirred at room temperature for 20 min. After evaporation of the solvent and extraction with a saturated solution of $NaHCO_3$ (pH 8), the copolymer was precipitated from an excess of methanol.

Synthesis of the PS-arm–PCL-arm–PLLA star block copolymer

To a Schlenk tube equipped with a magnetic stirring bar were added under N_2 0.365 g (0.38×10^{-4} mol) of functionalized and deprotected **PCL_1–PS**, 0.124 mL (3.8×10^{-6} mol) of a solution of $Sn(Oct)_2$ in toluene and 0.30 g (2.1×10^{-3} mol) of L-lactide. The polymerization was allowed to proceed for 15 h at 110 °C. The reaction mixture was concentrated, and the copolymer was precipitated into cold methanol, filtered, and dried to provide a white powder.

For the copolymer PCL_1–PS–$PLLA_1$, M_n (SEC) was 13,400, the PDI was 1.24 (with THF as an eluent and with calibration at 35 °C using PS standards) and the yield was 50% for LLA.

Results and discussion

Synthesis of the heterotrifunctional initiator

The preparation of the heterotrifunctional initiator was performed in four steps (see Scheme 1). This initiator was synthesized by protection as acetal of two hydroxyl groups of glycerol, esterification of the remaining hydroxyl function with 2-bromoisobutyrylbromide, deprotection of the acetal and selective protection of the primary hydroxyl group with triphenylmethylchloride.

After purification, the product was obtained in a sufficient purity for polymerizations, as shown by ^{1}H NMR analysis. This heterotrifunctional initiator contains one secondary alcohol used as initiating site for the living ROP of CL in the presence of stannous octoate as well as a tertiary bromide function for the ATRP of styrene. The third initiating function is, in a first time, protected, in order to avoid ROP from it.

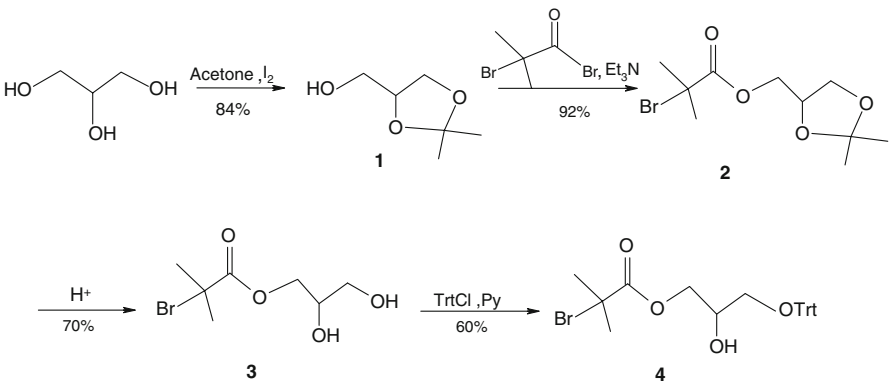
The synthetic strategy followed for the preparation of the ABC star block copolymers from this heterotrifunctional initiator is depicted in Scheme 2.

Synthesis of the PCL precursors by anionic coordinated ROP

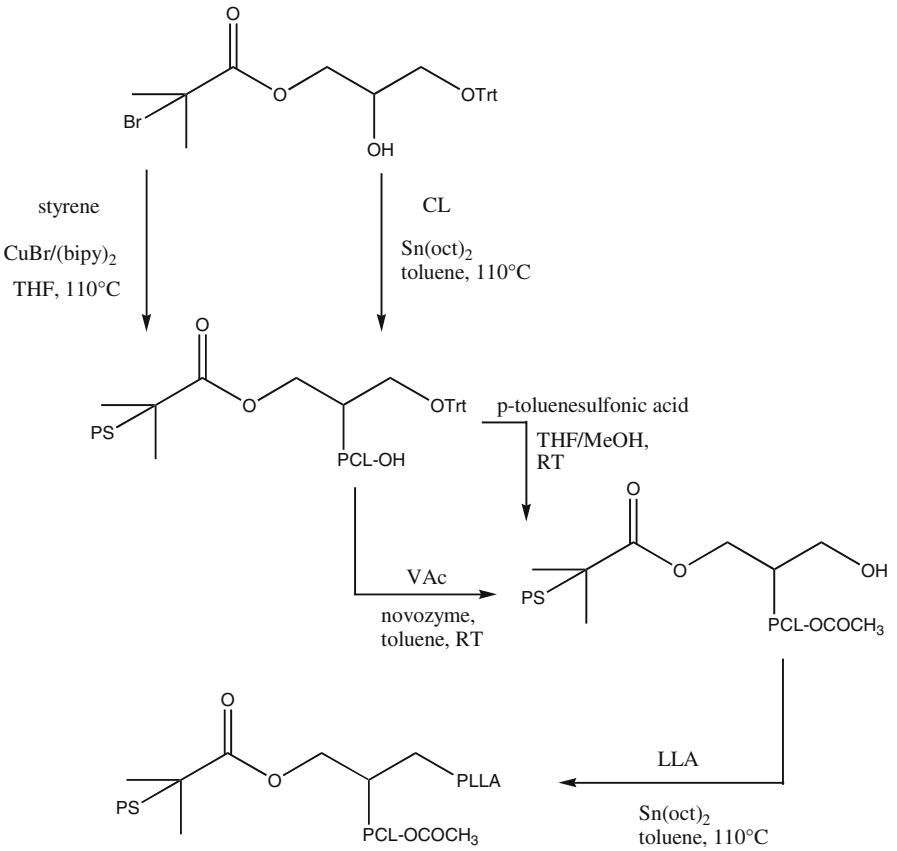
Polymerizations of CL to synthesize the macroinitiators, were realized in presence of $Sn(Oct)_2$ at 110 °C for 15 h, using a catalytic process [15].

Well-defined PCL macroinitiators with low polydispersity indices (PDIs) were obtained, as shown in Table 1.

The theoretical molecular weight (M_n expected) was calculated from the molar ratio of the monomer and the initiator. ^{1}H-NMR analyses were used to determine



Scheme 1 Synthesis of the heterotrifunctional initiator



Scheme 2 Synthetic strategy for the synthesis of ABC miktoarm star block copolymers from the heterotrifunctional initiator, coupling ROP and ATRP

Table 1 Characteristics of the different PCL macroinitiators synthesized

Macroinitiator	M_n expected	M_n (^{1}H NMR)	M_n (SEC)[a]	PDI
PCL_1	5,000	4,100	3,800	1.26
PCL_2	5,000	3,000	3,000	1.27
PCL_3	7,000	6,200	6,000	1.26
PCL_4	10,000	9,400	9,100	1.25

Reaction temperature is 110 °C for 15 h with $Sn(oct)_2$ as a co-initiator; [OH]/[metal] = 10; toluene

[a] $M_{n,SEC}$ using the Mark–Houwink parameters for PCL: $\alpha = 0.786$; $K = 14 \times 10^{-3}$ ml g^{-1} on a SEC instrument with THF as an eluent, at 35 °C and calibrated with PS standards $\alpha = 0.70$; $K = 14 \times 10^{-3}$ ml g^{-1}

the molecular average number DP_n (and therefore the molecular weight) of the PCL block by comparing the integral values of the PCL and the initiator characteristics resonance signals (I_2 and I_9 respectively) (Fig. 1).The experimental number average

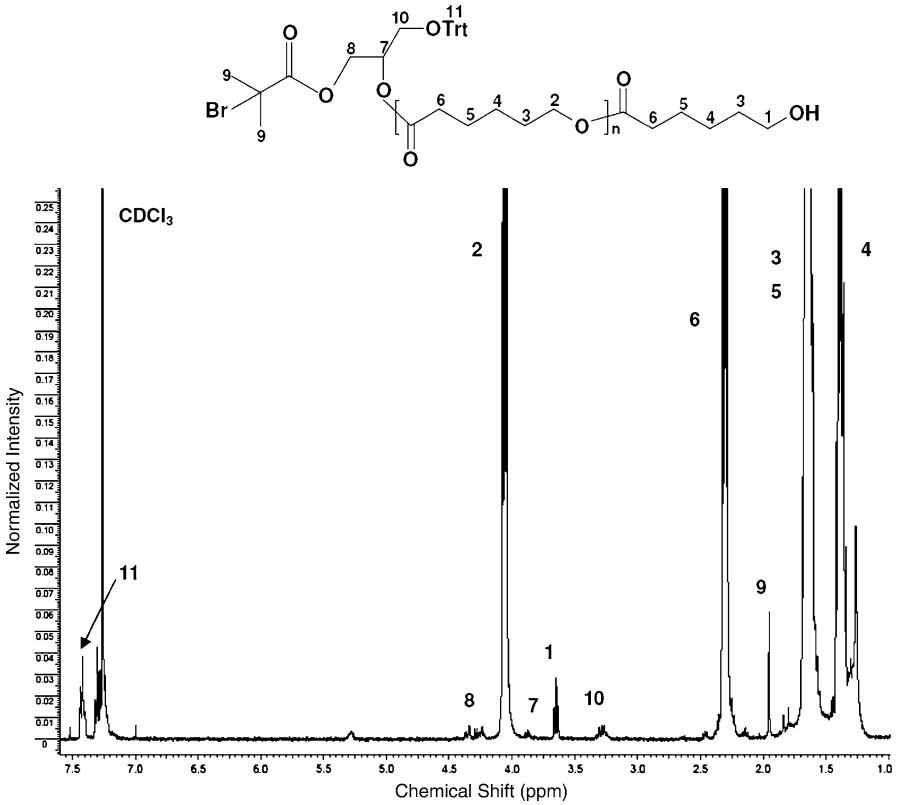


Fig. 1 ^{1}H NMR spectrum of PCL_1 macroinitiator

molecular weights determined from ^{1}H NMR are in good agreement with those calculated by SEC, using Mark–Houwink equation [15] (see also Table 1). Conversions determined by comparing the experimental and the expected molecular weights were found to be higher than 75% but not total in order to limit the back-bitting reactions occurring at the end of polymerization. The functionalization degrees (DF) determined from the characteristic resonance signals of the initiator (I_9) (Fig. 1) compared with those of polymer end (I_1) are equal to 100%, proving the total initiation from the initiator. These results showed that the polymerization of CL with **4** proceeded in a controlled manner with a high initiation efficiency.

These PCL macroinitiators were bearing a bromide group for the synthesis of the second arm by ATRP.

Synthesis of PS arm by ATRP from the PCL macroinitiators

Polymerizations of styrene, to synthesize the second arm, were realized in the presence of CuBr/2,2′-bipyridyl (bipy) at 110 °C. The main results are reported in Table 2.

Table 2 Characteristics of the PCL-b–PS

Diblock	Macroinitiator PCL		Second block PS		Diblock copolymer		
	M_n^a	M_n^b	M_n expected	M_n^b	M_n^c	M_n^b	PDI[c]
PCL_1–PS	3,800	4,100	5,000	5,700	10,300	9,800	1.23
PCL_2–PS	3,000	3,000	5,000	5,200	9,970	8,200	1.19
PCL_3–PS	6,000	6,200	5,000	4,900	12,300	11,100	1.19
PCL_4–PS	9,100	9,400	9,000	8,500	18,100	17,900	1.16

Reaction temperature is 110 °C for 9 h. PCL/CuBr/bipy: 1/1/2 in THF

[a] $M_{n,SEC}$ using the Mark–Houwink parameters for PCL: $\alpha = 0.786$; $K = 14 \times 10^{-3}$ ml g^{-1} on a SEC instrument with THF as an eluent, at 35 °C and calibrated with PS standards $\alpha = 0.70$; $K = 14 \times 10^{-3}$ ml g^{-1}

[b] Determined by ^{1}H NMR

[c] Determined by SEC using a PS calibration curve

^{1}H NMR analyses were used to determine the molecular average number DP_n (and therefore the molecular weight) of the PS block by comparing the integral values of the PCL and PS characteristics resonance signals (I_1 and I_8 respectively) (Fig. 2). The M_n values of the PS block obtained by 1H NMR are in good agreement with the M_n expected ones. Whatever macroinitiator was used, the obtained diblock copolymers were well-defined, with narrow polydispersity indices ($1.19 < PDI < 1.23$). The disappearance of the macroinitiator peak in the SEC chromatograms showed the total initiation from the macroinitiator. A ^{1}H NMR spectrum of a PCL-b–PS block copolymer is given in Fig. 2.

Besides, additional experiments have proved that PCL-b–PS diblock copolymers could be obtained in a controlled manner either by polymerizing the CL first (as presented here), or by polymerizing the styrene first (not presented here).

Functionalization of the PCL arm

The protection of the hydroxyl group located at the end of the PCL chain was realized using vinyl acetate. This protection was necessary to avoid initiation of the further ROP of L-lactide from the PCL block. ^{1}H NMR analyses of the protected macroinitiators showed the total disappearance of the CH_2–OH terminal group, meaning that the functionalizations were total. No degradation of the copolymers was observed, the SEC spectra of the polymers before and after functionalization being identical.

Hydrolysis of the triphenylmethyle group

The triphenylmethyle group was eliminated in acidic conditions, using *p*-toluene-sulfonic acid. ^{1}H NMR analyses of the new copolymers macroinitiators obtained showed the total disappearance of the phenyl peaks (7.4 ppm) characteristics of the protector group, meaning that the deprotection was total, the end of the PCL arm

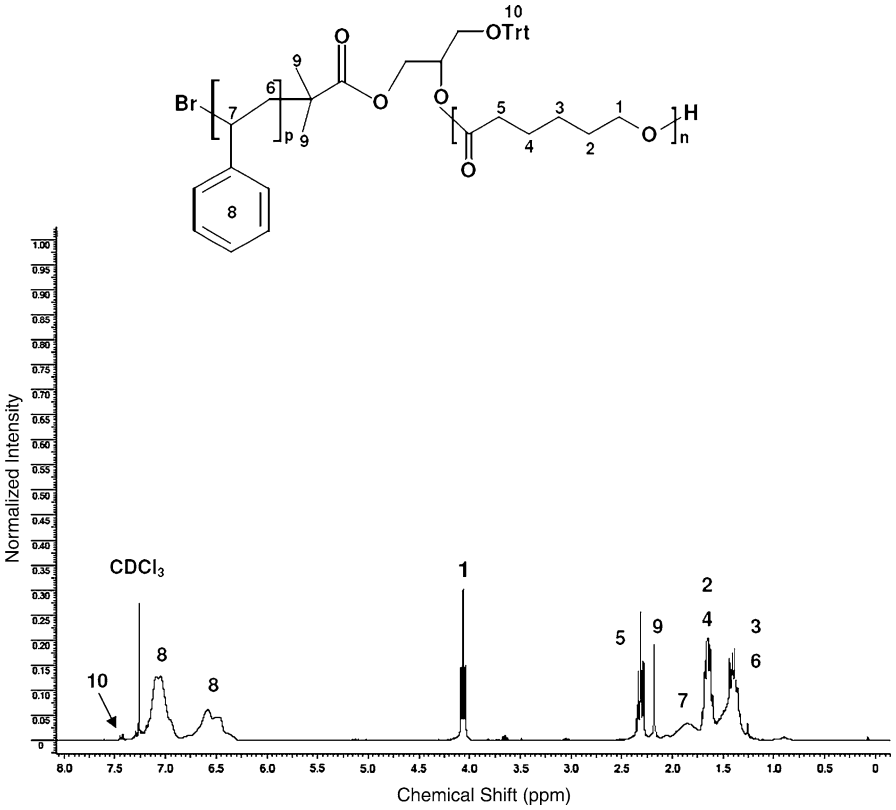


Fig. 2 ^{1}H NMR spectrum of a PCL_1-b–PS diblock copolymer

being unchanged. No degradation of the polymer was observed as proved by SEC analyses.

The copolymers macroinitiators obtained possessed one hydroxyl function, which was used to initiate a further ring opening polymerization.

Synthesis of PCL-arm–PS-arm–PLLA star block copolymers

The PCL-b–PS macroinitiators have been used to initiate the coordinated ROP of LLA in presence of stannous octoate (at 110 °C), using a catalytic process. The characteristics of the star copolymers obtained are reported in Table 3.

^{1}H NMR analyses were used to determine the molecular average number DP_n (and therefore the molecular weight) of the PLLA block by comparing the integral values of the PCL and PLLA characteristics resonance signals (I_1 and I_9 respectively) (Fig. 3). PCL-arm–PS-arm–PLLA star block copolymers having narrow polydispersity indices ($1.14 < PDI < 1.24$) have been synthesized. A ^{1}H NMR spectrum of one of the star block copolymer is given in Fig. 3.

Table 3 Characteristics of the miktoarm star block copolymers

Star block copolymer	PCL	PS	PLLA		Star block copolymer		
	M_n[a]	M_n[a]	M_n expected	M_n[a]	M_n[b]	M_n[a]	PDI
PCL_1–PS–$PLLA_1$	4,100	5,700	3,000	1,500	13,400	11,300	1.24
PCL_1–PS–$PLLA_2$	4,100	5,700	6,500	6,700	17,000	16,500	1.15
PCL_2–PS–$PLLA_1$	3,000	5,200	3,500	1,400	10,500	9,600	1.14
PCL_2–PS–$PLLA_2$	3,000	5,200	6,400	4,700	13,900	12,900	1.14

Reaction temperature is 110 °C for 15 h with $Sn(oct)_2$ as a co-initiator; [OH]/[metal] = 10; toluene

[a] Determined by ^{1}H NMR

[b] Determined by SEC using a PS calibration curve

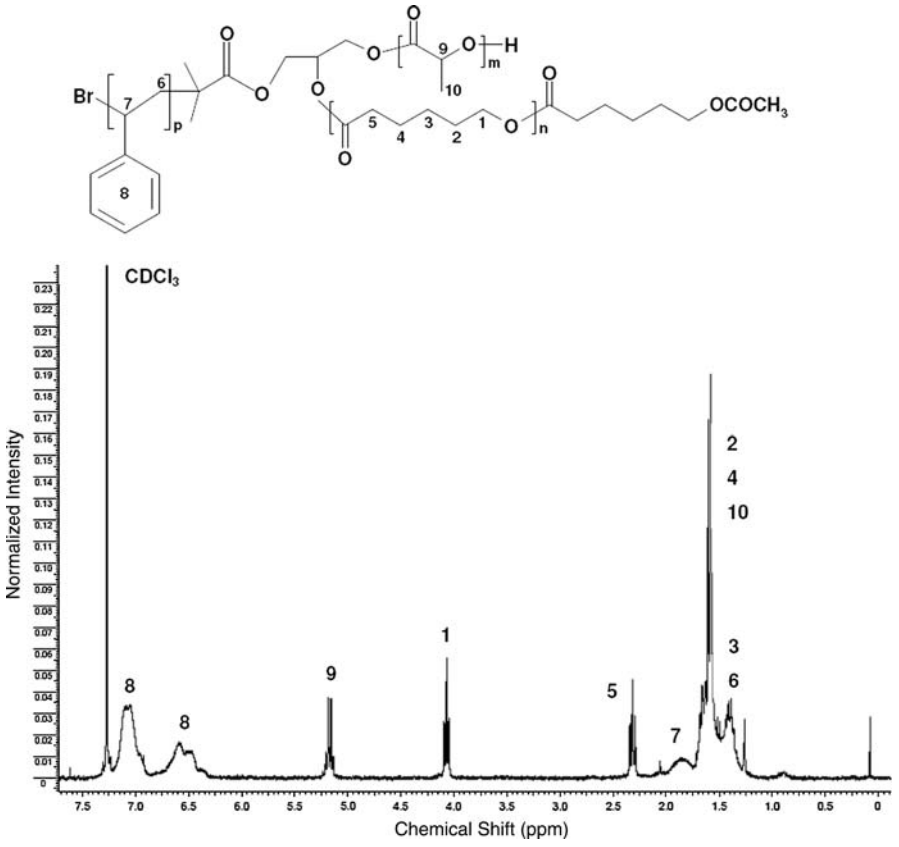


Fig. 3 ^{1}H NMR spectrum of a PCL-arm–PS-arm–PLLA star block copolymer

The absence of PCL-b–PS residual peak on the SEC spectra of the star block copolymers showed the total initiation from the diblock macroinitiators. The absence of hydrodynamic volume contraction (characteristic of a star structure)

when we compare the molecular weights determined by SEC and those determined by ^{1}H NMR can be attributed to an overestimation of the SEC values obtained using a PS calibration curve for PCL and PLLA (for example, M_n of PCL after correction using the Mark–Houwink coefficients is 1/3 times weaker than before). We have already reported the same behaviour for PS_2–PCL and PS_2–PCL_2 star block copolymers [16, 17].

Conclusion

A new heterotrifunctional initiator was synthesized and successfully used in the preparation of miktoarm star block copolymers via a combination of two ROP and one ATRP in a sequential process. The synthetic route implies first the ROP of CL using $Sn(oct)_2$ as catalyst followed by the ATRP of styrene or inversely. The hydroxyl group located at the end of the PCL arm has to be protected before deprotection of the second hydroxyl function and polymerization from it. Using this way, well-defined PCL-arm–PS-arm–PLLA star block copolymers have been synthesized. Extension to anionic polymerization of ethylene oxide from the second OH is now under investigation.

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