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One-Pot Two-Step (First ROP, Then SET-LRP) Synthesis of Polycaprolactone-Polyacrylate Star Block Copolymers

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A one-pot, two-step method is applied to the controlled synthesis of poly-acrylate-*b*-(polycaprolactone)$_2$ three-arm AB$_2$-type star block polymers. First, ring-opening polymerization (ROP) of ε-caprolactone is carried out in toluene using either stannous octoate (Sn(Oct)$_2$) or diphenyl phosphate (DPP) as catalyst, and a multifunctional initiator featuring one bromoester and two alcohol groups. Then, single-electron transfer living radical polymerization (SET-LRP) of methyl acrylate and isobornyl acrylate is conducted in the same reaction vessel after sequential addition of its typical reactants, apart from the (PCL)$_2$-Br macroinitiator generated in the first step, in either toluene/toluene + phenol or toluene/dimethyl sulfoxide solvent systems. DPP (the ROP catalyst) from the first step is found to take part in an acid–base reaction with tris[2-(dimethylamino)ethyl]amine (the SET-LRP N-ligand) in the second part, but stoichiometry could be adjusted to avoid interference and keep the controlled nature of the polymerizations. Interestingly, the electrochemically active Sn(Oct)$_2$ ROP catalyst does not interfere with the SET-LRP process. Well-defined poly(methyl acrylate)-*b*-(polycaprolactone)$_2$ and poly(isobornyl acrylate)-*b*-(polycaprolactone)$_2$ are thus synthesized through a simple and cost-effective experimental procedure. The technique also applies to the synthesis of linear block copolymers.

1. Introduction

Many advances in materials science and engineering have used polymers to generate sophisticated structures at some point during the fabrication procedure. As part of the materials development process, polymer chemists are often requested to design and synthesize complex macromolecular structures with unique behavior. And they normally do it with great success by controlling chemical composition, functionality, and topography at different levels of sophistication through creative experimental approaches devised to almost seamlessly combine mechanistically distinct polymerization techniques and diverse monomers.[1]

Industry has always demanded easy access to the preparation of simple, yet important, linear, AB-type diblock copolymer architecture. The interest spans from the covalent linkage between two incompatible polymer chains in a mixture, which results in significantly distinct behaviors in the ordered and disordered state, and this can be a solution to many challenges related to interface science.[1–4] The answer to such a demand has never been closer than nowadays thanks to the advances in macromolecular design. Methods of synthesis of diblock copolymers have become straightforward to perform, environmentally friendly, cost-effective, and easy to scale up. Most of these achievements have their roots in the fact that radical-based chemistries turned to be less stringent to reagent purity, and appropriate to polymerize a vast array of monomers. Considering that the extensively exploited AB-type diblocks have attracted new interest from industry as polymer chemists offer suitable synthesis solutions, it is fair to say that "The old can be new again!"

In this context, single-electron transfer living radical polymerization (SET-LRP) has been highly regarded as a versatile and powerful tool for the construction of next-generation complex macromolecular architectures.[5–9] It can be performed for a large variety of functional monomer in several solvent systems, resulting in very fast polymerization, narrow molar mass distribution, and high end-group fidelity even at near quantitative conversion. The end-group can either be used to reinitiate the polymerization of another monomer through the same method, or be converted into an initiator of a different polymerization technique in order to produce copolymer of diverse architectures (linear blocks, stars, brushes, dendrimers, etc.).[5–7,9–11]

In most cases, however, the end product is obtained after successive reactions and purification steps.[1] Such is the case of polyester-*b*-poly(meth)acrylate diblock copolymers

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synthesized by ROP of cyclic esters and SET-LRP of acrylates and methacrylates.[12–17] Both of these techniques are well-known to date, and uniform macromolecules can be obtained without issues when performed separately. Albertsson's research group[12,14] used ROP of a-bromo-*g*-butyrolactone as a comonomer with ε-caprolactone or L-lactide to produce copolymers with pendant bromine groups. After isolation of the product, the halogen moiety was shown to function as grafting sites for SET-LRP of (meth)acrylate monomers, bridging the gap between ROP and SET-LRP. Other research groups undertook a different approach, starting by SET-LRP and then ROP, even though in all the cases purification of intermediates was necessary.[13,15–17] Fan et al.[15] synthesized a dendritic-like poly(*tert*-butyl acrylate) with a single focal hydroxyl group that was used to initiate the ROP of ε-caprolactone. Linear-dendritic-like poly(D or L-lactide)-*b*-poly(acrylic acid) amphiphilic polymers were obtained after hydrolysis. In the studies by Hao[16] and Zhai,[17] the strategy consisted first in the SET-LRP synthesis of a copolymer with pendant groups capable of initiating the ROP of a cyclic monomer to generate brush and graft copolymers.

We felt inspired and challenged to simplifying the synthesis of polyacrylate-polycaprolactone copolymers in the quest for protocols that can accelerate industrial production of these materials. This paper describes a convenient, one-pot two-step method (first ROP, then SET-LRP) for the synthesis of polyacrylate-polycaprolactone three-arm AB_2 star block polymers, the approach also being suitable for the synthesis of linear AB diblocks by replacement of the initiator. We demonstrate for the first time that well-defined three-arm poly(isobornyl acrylate)-*b*-(polycaprolactone)$_2$ (PIBA-*b*-(PCL)$_2$), and poly(methyl acrylate)-*b*-(polycaprolactone)$_2$ (PMA-*b*-(PCL)$_2$) can be synthesized through the simple and cost-effective experimental procedure described herein. The effect of ROP catalysts (diphenyl phosphate and stannous octoate) on the SET-LRP process is also discussed.

2. Experimental Section

2.1. Materials

Methyl acrylate (MA, Aldrich, 99%, ≤100 ppm of monomethyl ether hydroquinone stabilizer) and isobornyl acrylate (IBA, Aldrich, 98.5%, 200 ppm of monomethyl ether hydroquinone stabilizer) were passed through a column of basic alumina to remove inhibitors prior to polymerization. ε-Caprolactone (CL, Aldrich, 97%) was distilled under reduced pressure over CaH_2 before use. Copper(0) wire (Aldrich, ≥99.9%, ⌀ = 1.0 mm) was activated with glacial acetic acid as described by Nguyen and Percec,[18] and used immediately. Tris[2-(dimethylamino) ethyl]amine (Me_6-TREN) was synthesized according to previous literature.[19] Diphenyl phosphate (DPP, 99%), stannous octoate (Sn(Oct)$_2$, ≈95%), solketal (Aldrich, 97%), dimethyl sulfoxide (DMSO, ≥99.5%), dimethylformamide (DMF, ≥99.8%), phenol (99%), diethyl ether, and toluene were of the highest purity available from Sigma-Aldrich, and used without any further purification.

2.2. Synthesis Procedures

2.2.1. 1-O-(2′-Bromo-2′-methylpropionoyl)-2,3-rac-glycerol ((OH)$_2$-SK-Br) ***(1)***

The title compound was prepared following a procedure previously described elsewhere.[20–22] First, the precursor compound 2,2-dimethyl-1,3-dioxolane-4-methoxy-(2′-bromo-2′-methylpropionoyl) (SK-Br) was synthesized as follows. SK (5 mL, 40.2 mmol), triethylamine (11.16 mL, 80 mmol), and tetrahydrofuran (THF) (50 mL) were loaded in a 100 mL round-bottomed flask equipped with a magnetic stirrer and cooled to 0 °C in an ice bath. 2-Bromo-2-methylpropionyl bromide (5 mL, 40.4 mmol) was added dropwise with a syringe. Next, the mixture was stirred for 45 min and allowed to reach room temperature. Then, the reaction mixture was stirred into an excess of cold water (100 mL) and extracted with diethyl ether (3 × 65 mL). The organic layer was washed subsequently with a saturated aqueous solution of sodium carbonate (3 × 60 mL), acidified water (pH = 4.0–4.5, 3 × 100 mL), and again the saturated solution of sodium carbonate (3 × 60 mL). The organic layer was dried over anhydrous sodium sulfate. Finally, the sodium sulfate was removed by filtration and the solvent was removed under reduced pressure using a rotary evaporator to give the title compound as a slightly yellowish oil. Yield = 85%. ^{1}H nuclear magnetic resonance (NMR) 400 MHz in $CDCl_3$ (δ, ppm): 4.35 (m, 1H), 4.23 (m, 2H), 4.09 (dd, 1H), 3.83 (dd, 1H), 1.95 (s, 6H), 1.45–1.37 (s, 6H).

The title compound was then obtained after opening the protecting group of SK. SK-Br (3 g, 10.6 mmol) and 4-methoxyphenol (0.132 g, 1.06 mmol) were added to in 40 mL of a glacial acetic acid:water 1:3 v/v mixture and stirred for 45 min at 80 °C. The solution was allowed to cool to room temperature before addition of diethyl ether. The organic layer was extracted and dried over anhydrous sodium sulfate. Finally, the sodium sulfate was removed by filtration and the solvent was removed under reduced pressure using a rotary evaporator. The crude solid was re-crystallized from toluene to give a white powder. Yield = 75%. ^{1}H NMR 400 MHz in $CDCl_3$ (δ, ppm): 4.26 (m, 2H), 4.00 (m, 1H), 3.74 (m, 1H), 3.66 (m, 1H), 3.02 (d, 1H), 2.65 (t, 1H), 1.95 (s, 6H).

2.2.2. One-Pot Two-Step Synthesis of Polycaprolactone-Polyacrylate Star Block Copolymers ***(7)***

A typical reaction procedure is given below for a three-arm PIBA-*b*-(PCL)$_2$, three-arm AB_2 type, star block copolymer. The same protocol also applies for MA monomer or monohydroxy initiators that lead to linear AB block copolymers.

The bifunctional (OH)$_2$-SK-Br initiator **(1)** (43 mg, 0.180 mmol), ε-CL monomer **(2)** (1.03 g, 9 mmol) and dry toluene (1 mL) as solvent were placed in a dry 25 mL Schlenk flask. The tube was closed, subjected to three freeze-pump-thaw cycles, and subsequently backfilled with nitrogen gas. The ROP catalyst DPP **(3)** (45.0 mg, 0.180 mmol) or Sn(Oct)$_2$ **(4)** (36.5 mg, 0.09 mmol) was then added under gentle nitrogen flow and the flask was closed and immediately immersed in an oil bath at

50 °C (for DPP) or 115 °C (for $Sn(Oct)_2$) to start the first step of the polymerization, unless otherwise indicated. Samples were taken periodically with an airtight degassed syringe for conversion, molar mass, and polydispersity analysis. The polymerization was stopped after a given time by cooling down to room temperature, opening the flask to air.

Reactants for the second reaction step were then added to the same flask. Toluene (2 mL), phenol as an additive to enhance the rate of SET-LRP (340 mg, 3.61 mmol), Me_6TREN ligand (41.6 mg, 0.180 mmol), IBA (3.75 g, 18 mmol) were charged into the Schlenk flask in the mentioned order. The mixture was immersed in an ice bath and purged gently with a stream of nitrogen gas for 20 min. Under a gentle stream of nitrogen gas through flask, the latter was immersed in an oil bath at 30 °C, and an activated copper(0) wire (⌀ = 1.0 mm, length = 12.5 cm) wrapped around a magnetic stirrer was then added to the reaction vessel. NMR and gel permeation chromatography (GPC) were used, respectively, to monitor monomer conversion and to obtain molar mass information. Polymerization was stopped by the addition of THF and bubbling with air for 2 min. The final product was obtained after precipitation in cold methanol and vacuum drying.

2.2.3. UV–Vis Disproportionation Experiment

A solution of Me_6-TREN (11.3 mg, 0.049 mmol) in 3.0 mL of toluene/DMSO 1/1 v/v was placed in a 10 mm square quartz cell containing varying amounts of DPP catalyst (1, 4, and 10 eq. in relation to Me_6-TREN, see Section 3). The mixture was immersed in an ice bath and purged gently with a stream of nitrogen gas for 20 min. Then, CuBr (7.0 mg, 0.049 mmol) was added to the solution under a slow stream of nitrogen gas through the top of the cuvette. UV–vis spectra were recorded immediately.

2.3. Physical Methods and Techniques

2.3.1. NMR

^{1}H NMR 400 MHz spectra were acquired using an Avance DPX 400 spectrometer with $CDCl_3$ as the solvent.

2.3.2. GPC

Number-average molar mass (M_n) and polydispersity index (M_w/M_n) values were determined by GPC in THF at a flow rate of 1.0 mL min^{-1} using SKgel H_{XL} guard and TSKgel G3000H_{XL} columns thermostated at 40 °C on a Shimadzu apparatus equipped with a SCK-10A controller, DGU-20A degassing unit, LC-10AD solvent delivery module, CTO-20A column oven, and RID-10A refractive index and SPD-20A UV–vis detectors. Calibration was performed using a series of near-monodisperse polystyrene (PS) standards. The molar mass distribution for PCL homopolymers has been corrected using the appropriate Mark–Houwink parameters ($K = 13.95 \times 10^{-5}$ dL g^{-1} and $\alpha = 0.786$).[23]

2.3.3. UV–Vis Spectroscopy

UV–vis spectra were recorded using a Shimadzu UV2600 spectrophotometer. For the measurements, 3.0 mL of solution was placed in a 10 mm square quartz cell. All spectra were recorded in the wavelength range of 300–900 nm at a scan rate of 600 nm min^{-1} (0.1 s integration per 1.0 nm) for air-equilibrated thermostated solutions under stirring.

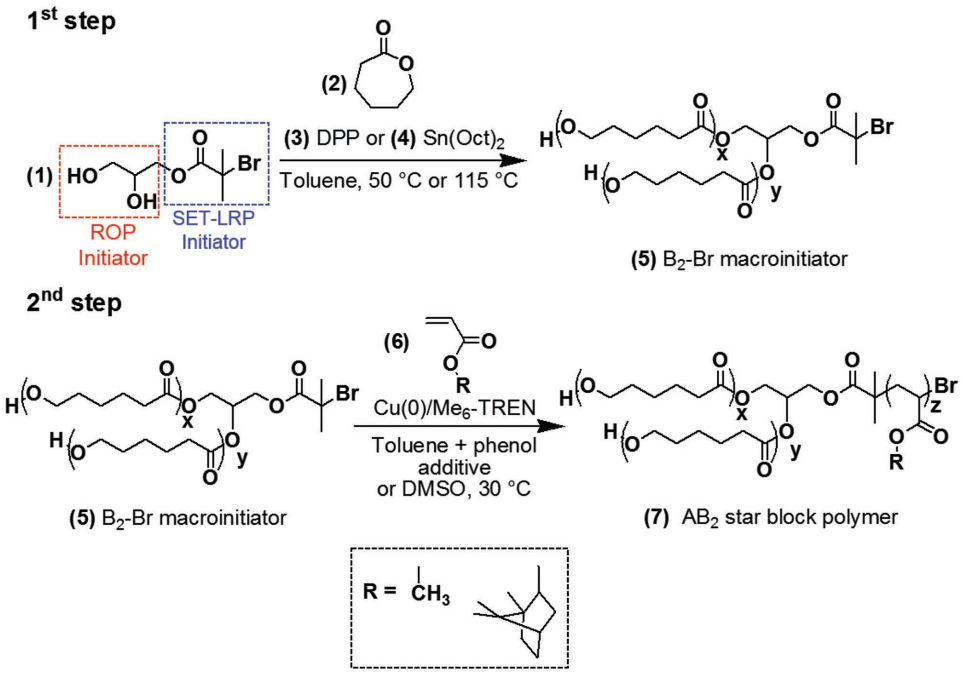
3. Results and Discussion

The synthesis strategy developed in this study is shown in **Scheme 1**. The main challenge encountered in performing a one-pot polymerization of two monomers by two distinct reaction mechanisms in a multicomponent system is to find adequate experimental conditions under which the two processes can occur independently, and promote the controlled growth of polymer chains. ROP and SET-LRP techniques feature striking differences in terms of reaction media polarity. While ROP is preferably carried out in aprotic organic solvents of low polarity such as toluene,[24–28] THF,[28,29] and dioxane,[27,28] SET-LRP is particularly sensitive to experimental conditions. The latter requires polar media[5,6] or, alternately, binary mixtures of solvents containing a polar component[30] or specific polar additives[31,32] for the crucial step of self-regulated disproportionation of the Cu(I)X/L into extremely reactive Cu(0) nanoparticles and Cu(II)X/L. Such a process depends on the nascent Cu(0) reactivity that is ultimately related to the nature of ligand and its concentration,[5,33,34] the solvent–ligand combination,[34–37] and its ability to stabilize Cu(0) colloidal particles.

On devising the one-pot experiment by observing the above-mentioned differences between the two polymerization techniques, it became soon clear that ROP would have to be performed in the first place because SET-LRP necessitates reactants and solvents that would be not suitable compatible with controlled ROP. This is the case of phenol as an additive, DMF and DMSO as a component of the solvent in SET-LRP. To the best of our knowledge, and according to the comprehensive review of Labet and Thielemans,[38] no experimental approaches were successful in synthesizing PCL with controlled molar mass distribution in the presence of aforementioned chemicals.

We investigated DPP **(3)** and $Sn(Oct)_2$ **(4)** as catalysts, which have been previously proven to be very efficient for the ROP of ε-CL using alcohols as initiators. Kakuchi's group showed that DPP-catalyzed ROP of lactones proceeds through an activated monomer mechanism, with kinetic and chain extension experiments confirming the controlled nature of the process in toluene at room temperature.[25,39] $Sn(Oct)_2$ is a well-established catalyst as well,[29,38] but requires reaction temperatures higher than DPP does.

Following the understanding reached in a recent study by our group on one-pot synthesis of polystyrene-*b*-polycaprolactone copolymers by simultaneous RAFT and ROP,[40] we chose similar experimental condition to perform, in the first place, the ROP of ε-CL using either DPP or $Sn(Oct)_2$. The NMR spectrum of the PCL polymer obtained from a ROP that used $(OH)_2$-SK-Br initiator **(1)** and DPP or $Sn(Oct)_2$ is provided in



Scheme 1. Envisioned approach to synthesizing polyacrylate-(polycaprolactone)$_2$ three-arm AB$_2$ star block polymers through a one-pot, two-step procedure comprising first ROP using DPP phosphate or Sn(Oct)$_2$ catalysts, and then SET-LRP either in toluene/toluene + phenol or toluene/DMSO solvent systems.

Figure S1 (Supporting Information). The characteristic peaks of the PCL and initiator **(1)** are evident. The monomer conversion after 1.0 h was nearly quantitative regardless of the catalyst, and the PCL obtained consisted of fairly narrowly distributed chains, as evidenced from the monomodal GPC trace shown in Figure S2 (Supporting Information) and physico-chemical characteristics summarized in **Table 1**. The dispersity was remarkably low (M_w/M_n = 1.08) and the M_n(GPC) values were close to the M_n(target) calculated from the initial ratio of [ε-CL]$_0$/[**(1)**] (Table 1, entries 1 and 2). The molar mass distribution for PCL homopolymers has been corrected using the appropriate Mark–Houwink parameters (see the Experimental Section).

The (OH)$_2$-SK-Br **(1)** works as initiator for both the ROP and the SET-LRP processes, but having two hydroxyl groups, it leads to a three-arm AB$_2$ star block polymer. Therefore, the ROP generates a homopolymer with two PCL branches denoted here as B$_2$, which have half the degree of polymerization estimated from the ratio [ε-CL]$_0$/[**(1)**]. Comprehensive NMR studies indicated that both hydroxyl groups of **(1)** are indeed able to initiate the ROP (see Figure S3, Supporting Information), in agreement with previous studies published elsewhere.[41,42]

After stopping the synthesis of PCL by ROP, reactants for the SET-LRP step were to be loaded into the same reaction vessel. Already present in the reaction medium were the B$_2$-Br SET-LRP macroinitiator (with B standing for PCL branches), the solvent (toluene), and the ROP catalyst (DPP or Sn(Oct)$_2$). Among these components, the catalyst is the only one with high potential to interfere with the next and sensitive SET-LRP process.

We therefore elected to clarify whether DPP or Sn(Oct)$_2$ can disrupt the controlled nature of SET-LRP. Polymerizations of MA and IBA monomers performed in presence of Sn(Oct)$_2$ at [I]:[Sn(Oct)$_2$]:[acrylate monomer]:[Me$_6$-TREN] = 1:0.5:100:0.1

Table 1. Experimental conditions and properties of PCL and PMA homopolymers synthesized by ROP and SET-LRP processes, respectively.

Entry	[I]:[cat.]:[CL]:[MA]:[Me$_6$-TREN]	Solvent in ROP/SET-LRP	ROP reaction time [h]	SET-LRP reaction time [h]	Conversion of CL [%]	Conversion of MA [%]	M_n (target) [g mol^{-1}]	M_n (theo) [g mol^{-1}]	M_n(GPC) [g mol^{-1}]	M_w/M_n
cat. = DPP										
1	1:1:50:–:–	Toluene	1	–	99	–	5950	5900	3300	1.08
cat. = Sn(Oct)$_2$										
2	1:0.5:–:–	Toluene	14	–	100	–	5950	5950	3500	1.35
3	1:0.5:–:100:0.1	DMSO	–	1	–	96	8850	8500	7800	1.06
cat. = DPP										
4	1:1:–:100:0.1	DMSO	–	15	–	18	8850	1600	ND[a)]	ND
5	1:1:–:100:1	DMSO	–	2	–	97	8850	8600	7900	1.08

[a)]ND = Not determined.

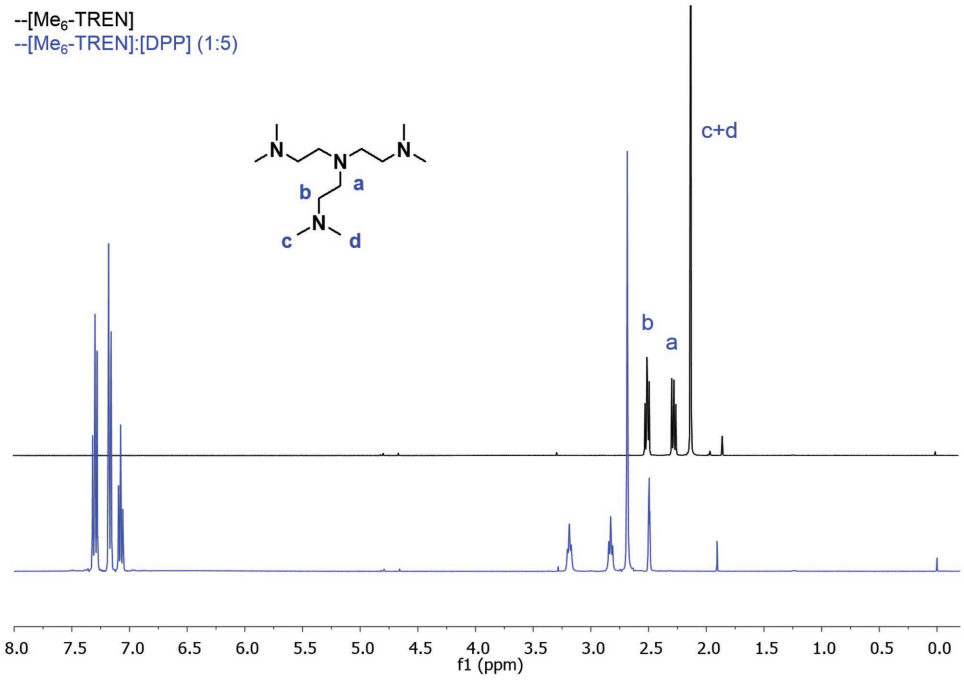


Figure 1. ^{1}H NMR spectra for 0.027 M solution of Me_6-TREN in DMSO-d_6 before and after addition of 5 eq. of DPP, as indicated.

ratio were found to be controlled processes with linear first-order kinetic plots, predictable molar mass, and uniform distribution of chains (Table 1, entry 3). This was quite surprising to us since $Sn(Oct)_2$ is an electrochemically active compound which, at first glance, would have been avoided in simultaneous polymerization involving controlled radical processes. We found earlier that it did interfere with RAFT process, for instance.[40]

On the other hand, DPP interacted with the Me_6-TREN ligand and caused major effects on SET-LRP. Monomer conversion in presence of DPP was very low at 18% after a 15 h long period of time (Table 1, entry 4), when it should otherwise (in absence of DPP) be very fast. This happened because DPP is acidic enough to protonate tertiary amino groups of Me_6-TREN. The acid–base interaction was confirmed by ^{1}H NMR in DMSO-d_6 (**Figure 1**). The addition of five equivalents of DPP to a Me_6-TREN solution in DMSO-d_6 provoked an acid–base reaction that resulted in the protonation of tertiary amino groups with consequent downshift in the typical Me_6-TREN ^{1}H NMR signals. This reaction affects the set of complex equilibriums involving copper species inherent of the SET-LRP mechanism, as corroborated by UV–vis spectra of the disproportionation of CuBr/Me_6-TREN under conditions simulating those employed in one-pot two-step polymerizations (**Figure 2**). The absorbance attributed to Cu(0) nascent nanoparticles and $CuBr_2$/Me_6-TREN complex, which is seen in Figure 2 at 730 and 870 nm[34] for [DPP]:[Me_6-TREN] = 1:1, practically disappears when the acid amount is increased to [DPP]:[Me_6-TREN] = 4:1 (i.e., stoichiometrically equivalent to the number of tertiary amino groups) or [DPP]:[Me_6-TREN] = 10:1.

Normally, ROP of CL initiated by a hydroxyl group and catalyzed by DPP is performed at [I]:[DPP] ratio of 1:1. On the other hand, the [I]:[Me_6-TREN] ratio in SET-LRP is usually much lower at around 1:0.1, although significant variations are common.[34] The simple combination of both cases would lead to a system with [I]:[DPP]:[Me_6-TREN] = 1:1:0.1. With a [DPP]:[Me_6-TREN] = 10:1 ratio, disproportionation of Cu(I) species is compromised, and the SET-LRP does not proceed with controlled characteristics. The problem can be minimized by a tenfold increase in the Me_6-TREN concentration in the medium so that [I]:[DPP]:[Me_6-TREN] = 1:1:1. From a stoichiometry point of view, 25% of the amino groups can still be protonated

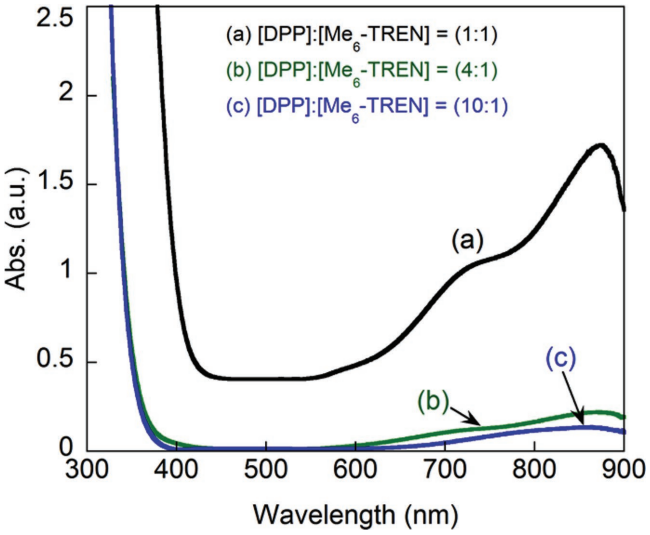


Figure 2. UV–vis spectra of the disproportionation of CuBr/Me_6-TREN in the presence of DPP, as indicated, under conditions otherwise simulating those employed in SET-LRP. Experimental conditions: [CuBr]:[Me_6-TREN]:[DPP] = 1:1:*x* (indicated), toluene/DMSO = 1:1 (v/v), *T* = 25 °C.

under such conditions, but this extent is low enough to reach monomer conversion of 97% in the SET-LRP of MA in only 2 h in a controlled manner (Table 1, entry 5).

From this part of the study, we concluded that SET-LRP can be performed as a second polymerization step in the same reaction pot where ROP had been carried out first, but the concentration of Me_6-TREN should be augmented whenever DPP is present in the system. In the case of $Sn(Oct)_2$ we tested both cases (i.e., [I]:[Me_6-TREN] = 1:0.1 and [I]:[Me_6-TREN] = 1:1) and verified no significant changes in the overall characteristics of the reaction and reactions products, apart from the SET-LRP rate that was faster at the highest [Me_6-TREN].

As already stated above, a polar component[30] or a specific polar additive[31,32] is necessary for the crucial step of self-regulated disproportionation of the Cu(I)X/L of SET-LRP. We tested two approaches: (i) keeping the same solvent (toluene) and adding a specific polar additive (phenol), hereinafter denoted as toluene/toluene + phenol solvent system, and (ii) changing solvent composition to toluene/DMSO, hereinafter denoted as toluene/DMSO solvent system. Phenol has been used as an additive to enhance the rate of SET-LRP in toluene at ambient temperature, and its influence on the SET-LRP mechanism has been the subject of previous studies.[31,32] DMSO and mixtures of toluene/DMSO have been established as efficient solvent systems to mediating SET-LRP.

In the first approach, typical reactants for SET-LRP along with toluene and phenol were added to the reaction vessel, and polymerization was carried out according to standard procedures (see the Experimental Section), without any other special care.

Kinetic experiments confirmed the classic behavior of controlled radical polymerizations for both MA and IBA monomers. **Figure 3** shows representative first-order kinetic plots, dependence of M_n(GPC) and M_w/M_n on monomer conversion, and GPC chromatograms relative to chain extension after the second step of the synthesis for the SET-LRP of MA monomer. The polymerization exhibited a linear pseudo-first-order kinetics in the concentrations of monomer and propagating radicals with k_p^{app} = 0.0180 min^{-1} (Figure 3a). A linear dependence of the experimental number-average molar mass determined by GPC (M_n(GPC)) with conversion was observed, accompanied by narrow molar mass distributions at all conversions (Figure 3b). The value of M_w/M_n decreased with the increasing of the monomer conversion (Figure 3b), as expected for controlled polymerizations.[43] The dynamics of exchange involving dormant and short-lived active sites as well as the exchange rate compared to propagation are at the origin of this behavior, which was studied in detail in a seminal work by Litvinenko and Müller.[44]

The $(PCL)_2$-Br macroinitiator synthesized in the first step efficiently initiated the second step; there was a clear shift to a higher molar mass for the $(PCL)_2$-*b*-PMA star block copolymers as compared with the $(PCL)_2$-Br macroinitiator, without a significant contribution from the latter (Figure 3c).

Essentially the same comments also apply to data collected for the SET-LRP of IBA monomer shown in **Figure 4**, apart from the two linear kinetics domains (Figure 4a). The first and faster linear domain shows k_{p1}^{app} = 0.0066 min^{-1} and persists up to ≈50% of conversion. Then, a second linear domain with

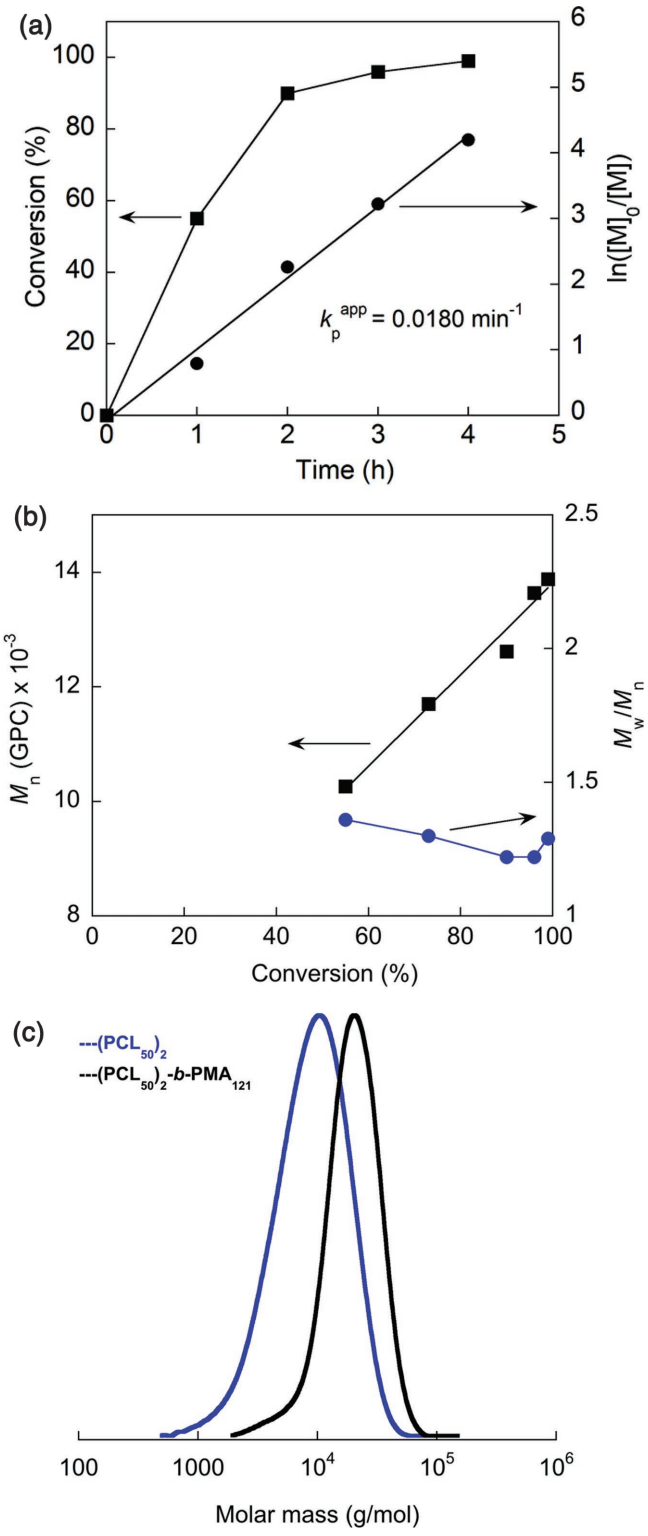


Figure 3. a) First-order kinetic plots, b) dependence of M_n(GPC) and M_w/M_n on monomer conversion, and c) GPC chromatograms showing chain extension after the second step of the synthesis for the SET-LRP of MA carried out using $(PCL)_2$-Br macroinitiator prepared using $Sn(Oct)_2$ as the catalyst for the ROP process. Experimental conditions (Table 2, entry 2): [I]:[$Sn(Oct)_2$]:[CL]:[MA]:[Me_6-TREN] = 1:0.5:50:123:1, $[CL]_0$ = 2.86 M (first step), $[MA]_0$ = 2.78 M (second step).

Table 2. Experimental conditions and properties of AB_2 star block copolymers synthesized by one-pot two-step reaction involving ROP and SET-LRP techniques.

Entry	[I]:[cat.]:[CL]:[M]:[Me_6-TREN]	Solvent system in ROP/SET-LRP	SET-LRP reaction time [h]	Conversion of M [%]	M_n(target) [g mol^{-1}]	M_n(theo) [g mol^{-1}]	M_n(GPC) [g mol^{-1}]	M_w/M_n
Toluene/toluene + additive solvent system								
cat. = $Sn(Oct)_2$; M = MA								
1	1:0.5:50:123:1	1/0 + 20 eq. phenol	3	98	16 500	16 300	12 500	1.30
2	1:0.5:100:123:1	1/0 + 20 eq. phenol	4	99	22 200	22 100	13 900	1.28
3	1:0.5:50:123:1	1/1 + 20 eq. phenol	6	98	16 500	16 300	17 000	1.24
4	1:0.5:50:123:1	1/1 + 20 eq. benzyl alcohol	6	97	16 500	16 200	13 200	1.39
cat. = $Sn(Oct)_2$; M = IBA								
5	1:0.5:50:25:1	1/1 + 20 eq. phenol	4	87	11 100	10 500	9000	1.35
6	1:0.5:50:52:1	1/1 + 20 eq. phenol	6	91	16 700	15 800	10 100	1.36
7	1:0.5:50:50:1	1/2 + 20 eq. phenol	6	75	16 400	13 800	13 800	1.17
8	1:0.5:50:157:1	1/3 + 20 eq. phenol	6	54	38 600	23 600	26 500	1.37
cat. = DPP; M = MA								
9	1:1:50:100:1	1/2 + 20 eq. phenol	17	95	18 700	18 100	24 100	1.18
cat. = DPP; M = IBA								
10	1:1:50:100:1	1/2 + 20 eq. phenol	17	83	26 800	23 200	19 300	1.14
Toluene/DMSO solvent system								
cat = DPP; M = MA								
11	1:1:30:90:1	1/1	2	86	11 400	10 400	10 400	1.16
12	1:1:30:180:1	1/2	3	95	19 200	18 400	21 200	1.13
13	1:1:50:100:1	1/1	4	98	14 500	14 400	14 400	1.29

a second slower rate constant of k_{p2}^{app} = 0.0032 min^{-1} becomes evident. In spite of this change in the polymerization kinetics, linear dependence of M_n with conversion was still consistent with a controlled polymerization process. Percec's group already reported this behavior for several cases.[30,45] It might be the result of lower solubility of the growing chains in the solvent system.[46] Indeed, solubility of growing PIBA chains was a tricky aspect to control in the present case, as further discussed below.

The results of this study are summarized in **Table 2**. In general, the molar mass distributions (M_w/M_n) calculated from the GPC traces were moderate, lying in the range of 1.08–1.39, but still satisfactory considering the synthesis strategy. Theoretical molar masses (M_n(theo)) of star block copolymers were calculated from the conversion of acrylate monomer determined by ^{1}H NMR spectroscopy analysis of a reaction aliquot, assuming a quantitative efficiency of **(1)**. This was validated through the good agreement between the M_n(theo) and M_n(GPC) values for the homopolymers. In the case of star block copolymers, the M_n(GPC) values are slightly offset in some cases due to the use of standards with hydrodynamic volumes distinct from that of the samples.

The solubility properties of MA monomer and PMA polymer allowed for the SET-LRP to be performed without dilution of the former ROP solution in toluene (Table 2, entries 1 and 2). In such a case, polymerization was fast, reaching near quantitative conversion (>95%) after 3 h when the reaction mixture was already highly viscous. Chains were uniform in distribution as verified by monomodal GPC curves with rather low dispersity indexes ($M_w/M_n \approx 1.3$). Upon dilution prior to the second step, the time required to full conversion increased (Table 2, entry 3; comparatively, monomer conversion was 85% after 3 h). However, the solution was not much less viscous at the end, and dispersity indexes were consistently lower (M_w/M_n = 1.25). Benzyl alcohol can replace phenol as additive for SET-LRP at the expense of the dispersity (Table 2, entry 4), in agreement with findings reported by Wright et al.[31]

In the case of the bulkier IBA monomer, attempts to perform SET-LRP without further dilution of the reaction mixture with toluene were unsuccessful because it gelified within minutes of polymerization, and magnetic stirring was no longer possible. Using a mixture of toluene/toluene + phenol at 1/1 + 20 eq. ratio, the second step could be carried out until near-quantitative conversion for targeted polymerization degree of ≈50, generating well-defined star block copolymer (Table 2, entries 5 and 6). Further dilution to toluene/toluene + phenol at 1/2 + 20 eq. (Table 2, entry 7), aimed at controlling (decreasing) the viscosity near the end of the reaction, contributed for a better control of the SET-LRP process as deduced from lowered dispersity index (M_w/M_n = 1.17 at 1/2 + 20 eq. as compared to ≈1.35 at 1/1 + 20 eq.). IBA and PIBA concentration is very critical for the herein undertaken approach, with dilution being required whenever the targeted polymerization degree is augmented. This is exemplified in Table 2 entry 3, which summarizes experimental

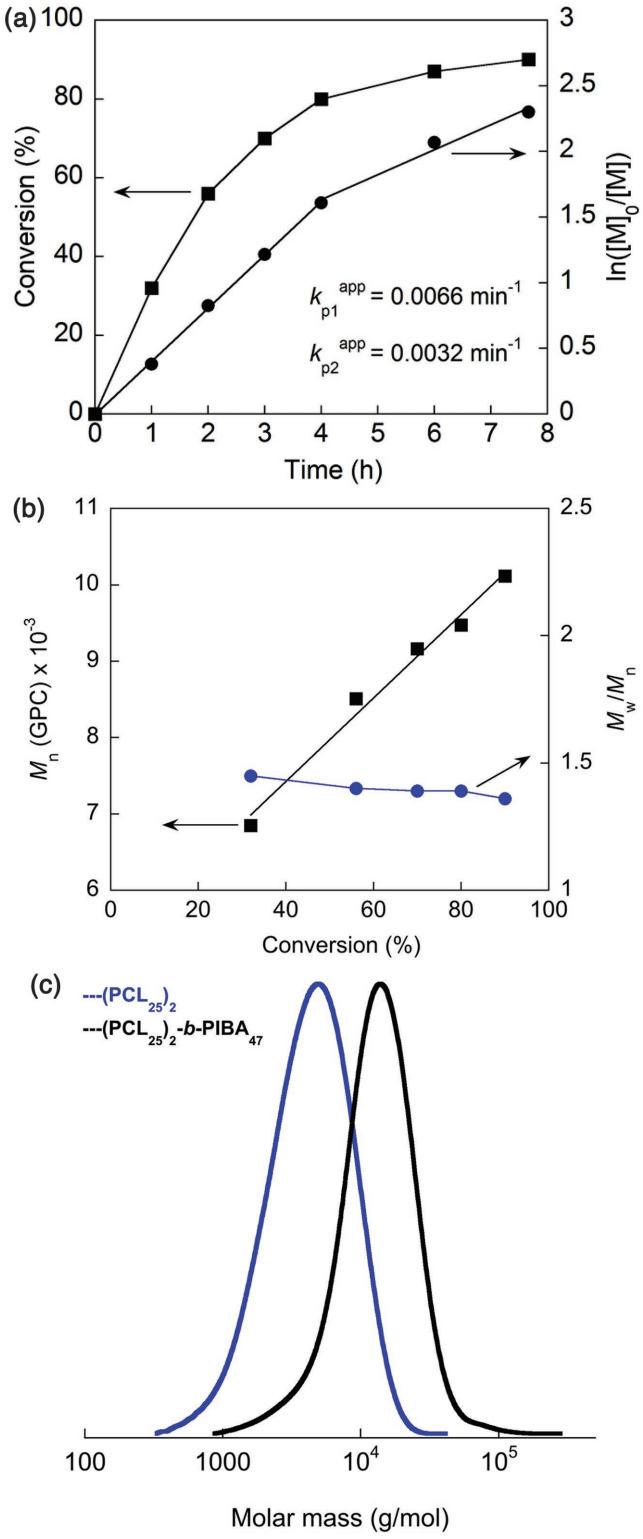


Figure 4. a) First-order kinetic plots, b) dependence of M_n(GPC) and M_w/M_n on monomer conversion, and c) GPC chromatograms showing chain extension after the second step of the synthesis for the SET-LRP of IBA carried out using $(PCL)_2$-Br macroinitiator prepared using $Sn(Oct)_2$ as the catalyst for the ROP process. Experimental conditions (Table 2, entry 6): [I]:[$Sn(Oct)_2$]:[CL]:[IBA]:[Me_6-TREN] = 1:0.5:50:52:1, $[CL]_0$ = 3.00 M (first step), $[IBA]_0$ = 1.35 M (second step).

conditions under which uniform (i.e., dispersity lower than 1.4) star block copolymers could be obtained.

In this toluene/toluene + phenol solvent system, the SET-LRP was much slower when DPP had been used as ROP catalyst in the first step. It required more than 15 h to reach conversions higher than 95%, although the resulting polymers were still well-defined (Table 2, entries 8 and 9). These results are attributed to the interaction between DPP and Me_6-TREN already addressed above.

The effect of such an acid–base interaction, and the consequent drawback (slow reaction), is minimized in toluene/DMSO. Near full conversion of MA was observed after approximately the same elapsed time (≈4 h) as that registered for toluene/toluene + phenol. The physical chemical characteristics of macromolecules shown in Table 2 entries 10–12 are consistent with formation of well-defined star block copolymers.

Finally, we addressed the synthesis of block copolymers from the commercially available dual initiator 2,2,2-tribromoethanol. The alcohol function initiated the ROP of ε-CL catalyzed either by DPP or $Sn(Oct)_2$, as it can be anticipated for a primary alcohol. The polyhalogenated group behaves as a monofunctional initiator in atom transfer radical polymerization (ATRP) initiator.[47,48] The same also hold for SET-LRP. The 2,2,2-tribromo-terminated PCL was successfully chain extended by SET-LRP of MA and IBA (Supporting Information). Therefore, the synthesis of block copolymers was a straightforward application of the methodology described above.

4. Conclusion

A straightforward one-pot two-step synthesis method comprising ROP first then SET-LRP processes allowed easy access to well-defined polycaprolactone-*b*-polyacrylate star block copolymers. The proposed method did not require intermediate purification steps. Uniform polymers (dispersity indexes lower than 1.4) could be obtained within no more than ≈8 h of experiment under certain experimental conditions (e.g., ROP of ε-CL catalyzed by DPP followed by SET-LRP of an acrylate monomer in toluene/DMSO with [I]:[Me_6-TREN] = 1:1) using standard glassware and reactants.

The critical point in devising one-pot reactions involving ROP and SET-LRP techniques is related to the acid–base interaction between DPP (the ROP catalyst) and Me_6-TREN (the SET-LRP N-ligand). Protonation of amino groups disrupts the crucial step of self-regulated disproportionation of the Cu(I) X/L into reactive Cu(0) nanoparticles and Cu(II)X/L species. Increasing the Me_6-TREN concentration in the medium can minimize interference of the ROP catalyst with the SET-LRP process. High conversions of MA monomer, for instance, can be achieved after only 2 h of reaction when the protonation extent does not exceed 25% of the amino groups ([I]:[Me_6-TREN] = 1:1). On the other hand, the electrochemically active compound $Sn(Oct)_2$, with partially filled d-orbitals of the metallic center, does not provoke detectable changes in the outcome of the SET-LRP.

The method reported here is also suitable for the synthesis of well-defined block copolymers in a one-pot reaction from commercially available dual initiators such as 2,2,2-tribromoethanol.

The limitations found in this study were mainly related to monomer reactivity and polymer solubility as for many regular SET-LRP reactions, but not to the combination of ROP and SET-LRP techniques.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

radical polymerization, ring-opening polymerization, star polymers, synthesis

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