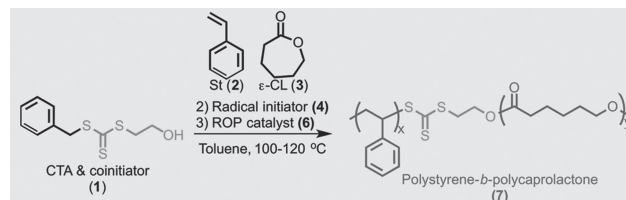


Controlled One-Pot Synthesis of Polystyrene-*block*-Polycaprolactone Copolymers by Simultaneous RAFT and ROP

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A convenient one-pot method for the controlled synthesis of polystyrene-*block*-polycaprolactone (PS-*b*-PCL) copolymers by simultaneous reversible addition–fragmentation chain transfer (RAFT) and ring-opening polymerization (ROP) processes is reported. The strategy involves the use of 2-(benzylsulfanylthiocarbonylsulfanyl)ethanol (1) for the dual roles of chain transfer agent (CTA) in the RAFT polymerization of styrene and co-initiator in the ROP of ϵ -caprolactone. One-pot polymerizations using the electrochemically stable ROP catalyst diphenyl phosphate (DPP) yield well-defined PS-*b*-PCL in a relatively short reaction time (≈ 4 h; $\overline{M}_n = 9600$ – $43\,600$ g mol⁻¹; $\overline{M}_w/\overline{M}_n = 1.21$ – 1.57). Because the hydroxyl group is strategically located on the Z substituent of the CTA, segments of these diblock copolymers are connected through a trithiocarbonate group, thus offering an easy way for subsequent growth of a third segment between PS and PCL. In contrast, an oxidatively unstable Sn(Oct)₂ ROP catalyst reacts with (1) leading to multimodal distributions of polymer chains with variable composition.



1. Introduction

Linear block copolymers have exerted a pivotal influence on advances in materials science and engineering.^[1–3] The great potential of such systems comes from the fact that a covalent linkage between different incompatible polymer chains in a mixture suppresses their tendency to undergo macrophase separation.^[2,4,5] As a result, they show significantly different behaviors in the ordered and disordered states,^[6] which can be ultimately controlled by macromolecular design.^[5]

The synthesis of block copolymers has a strong focus on the diblock architecture, to which many approaches can be taken, often combining mechanistically distinct polymerization techniques.^[7,8] With the current knowledge in macromolecular synthesis allowing for the combination of different strategies, the diversity in terms of diblock copolymer characteristics seems to be limited only by the innovative creativity of polymer chemists. In this regard, reversible addition–fragmentation chain transfer (RAFT) has been highly regarded as a versatile and powerful tool for the construction of next-generation complex macromolecular architectures.^[7,9–12] In most cases, however, the end product is obtained after successive reactions and purification steps.^[5]

The many applications of these advanced polymers in diverse fields have created a strong demand for easy access to them. Consequently, elegant ways of preparing these block copolymers in a one-step process are relevant not only to increasing the popularity of such systems in other areas but also to accelerating their industrial production.

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Pioneer studies carried out by the research groups of Howdle and co-workers^[13] and Barner-Kowollik and co-workers^[14] have indicated that RAFT polymerization and ring-opening polymerization (ROP) of aliphatic cyclic esters can occur simultaneously without significant changes in the reaction characteristics of each process. In the case of block copolymers, Howdle and co-workers^[13] showed that one-pot, simultaneous RAFT polymerization of styrene and ROP of ϵ -caprolactone (ϵ -CL) catalyzed by enzymes in $scCO_2$ results in block copolymers with a well-defined polystyrene (PS) block and a polycaprolactone (PCL) segment with a rather broad molar mass distribution. Li et al.^[15] devised a synthetic method consisting of simultaneous RAFT and ROP, of styrene and lactide, respectively, to prepare a diblock macromonomer that was subsequently used in a ring-opening metathesis polymerization “grafting through” reaction to produce double-brush copolymers. Recently, Youk’s group reported the successful one-pot synthesis of poly(alkyl methacrylate)-*block*-polyester and poly(vinylpyrrolidone)-*block*-polyester copolymers.^[16–18]

These straightforward strategies were facilitated by hydroxyl-functional molecules that worked concomitantly as a chain transfer agent (CTA) for RAFT and co-initiator for ROP. However, there is a fundamental difference between the approaches of Howdle and co-workers^[13] and Li et al.^[15] and Youk and co-workers^[16–18] that arises from the addition–fragmentation mechanism; in the former case, the CTA was 2-(benzylsulfanylthiocarbonylsulfanyl)ethanol (1), of which the alcohol function is part of the Z activating group, whereas the free radical leaving group R is not involved in the ROP. As a consequence, the segments of an AB diblock copolymer will be covalently bound by a trithiocarbonate group situated between A and B. Alternatively, in the synthetic methods of Li and Youk the co-initiator for ROP is attached to the leaving group R, thus leaving the main CTA moiety at the chain end of the RAFT polymer. In addition, if the decomposition of the radical initiator for the RAFT process does not generate primary radicals I^\cdot with hydroxyl groups and such radicals do not preferably add directly to the CTA,^[19] then a fraction, defined by the reaction stoichiometry, of the RAFT chains will probably exist in the medium as a homopolymer, because only chains derived from reinitiation by hydroxyl-functionalized fragment radicals R^\cdot from the CTA will take part and act as a co-initiator in the ROP process. This is a consequence of the fact that the number of polymer chains corresponds to the sum of the primary radicals I^\cdot and fragment radicals R^\cdot .^[20,21]

The choice of the method to be applied is obviously dependent on the purpose of the synthesis, but it can have several implications in relation to the final material properties both when a homopolymer is present in the medium and when further reactions are to be performed

on the resulting diblock copolymers. For example, one advantage of placing the CTA main group between the A and B blocks is that the diblock copolymer can be chain-extended by the RAFT polymerization of another monomer to produce a new block that will be located between A and B, thus offering, for example, an easy cross-linking strategy to impart chemical stability to self-assembled nanostructures, as demonstrated by Stenzel’s group.^[22] A disadvantage of locating the alcohol functionality on Z is that any process that cleave the trithiocarbonate linkage will also cleave the block copolymer.

This communication describes a convenient, one-pot method for the preparation of polystyrene-*block*-polycaprolactone (PS-*b*-PCL) diblock copolymers by simultaneous RAFT and ROP processes in organic medium using (1) as a CTA, which was also prepared in a facile, one-pot, universal procedure previously reported by Skey and O’Reilly.^[23] The possible effect of ROP catalysts (diphenyl phosphate and stannous octoate) on the RAFT process is discussed. We demonstrate for the first time that well-defined polystyrene-*b*-polycaprolactone copolymers with a RAFT agent moiety at the junction of the blocks, can be synthesized through the simple, and cost-effective experimental procedure described herein.

2. Experimental Section

2.1. Materials

Styrene (St) (Aldrich, $\geq 99\%$, 100 ppm of BHT stabilizer) and ϵ -caprolactone (CL) (Aldrich, 97%) were distilled under reduced pressure over CaH_2 before polymerization. 1,1'-Azobis(cyclohexanecarbonitrile) (VAZO catalyst 88) (98%), diphenyl phosphate (DPP) (99%), stannous octoate ($Sn(Oct)_2$) ($\approx 95\%$), anisole (99%), 2-mercaptoethanol ($\geq 99\%$), potassium phosphate ($\geq 98\%$), benzyl bromide (99%), carbon disulfide (CS_2) ($\geq 99\%$), acetone, petroleum ether, methanol, tetrahydrofuran, and toluene were of the highest purity available from Sigma-Aldrich, and used without any further purification.

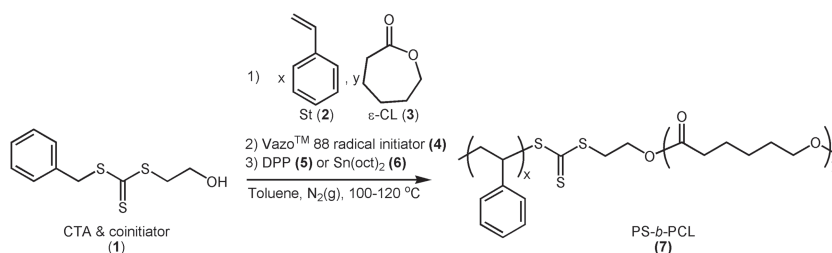
2.2. Synthesis Procedures

2.2.1. 2-(Benzylsulfanylthiocarbonylsulfanyl)ethanol (1)

The title compound was prepared following a one-pot procedure previously described elsewhere.^[23] Briefly, 2-mercaptoethanol (0.50 g, 6.4 mmol) was added to a suspension of K_3PO_4 (1.35 g, 1.26 mmol) in acetone (10 mL) in a round-bottom flask, and the mixture was stirred for 10 min. CS_2 (1.46 g, 19.25 mmol) was then added to the vessel and the resulting yellow solution was stirred for another 10 min before benzyl bromide (1.10 g, 6.42 mmol) was finally added to the reaction. After a further 10 min of stirring, the solids were filtered off and the solvent was removed from the organic filtrate under reduced pressure. The resulting yellow oil was further purified by column chromatography on



silica using petroleum ether as the eluent to yield a bright yellow oil (1) that crystallized when stored under cold conditions. Yield = 90%. ^1H NMR (CDCl_3 , 400 MHz, 298 K, δ): 7.40–7.23 (5H, m, Ph), 4.63 (2H, s, $\text{CH}_2\text{-Ph}$), 3.89 (2H, t, $\text{S-CH}_2\text{-CH}_2$), 3.62 (2H, t, $\text{S-CH}_2\text{-CH}_2$), 1.95 (1H, br s, CH_2OH).



Scheme 1. Envisaged approach to synthesizing polystyrene-*b*-polycaprolactone diblock copolymers through a one-pot procedure comprising simultaneous RAFT and ROP using diphenyl phosphite or stannous octoate catalysts.

2.2.2. One-Pot RAFT and ROP Polymerization Procedure for the Synthesis of (7)

In a typical reaction, the RAFT agent and ROP co-initiator (5) (42.7 mg, 0.175 mmol), monomers (2) (1.82 g, 17.46 mmol) and (3) (1.99 g, 17.46 mmol), radical initiator VAZO-88 (4) (10.7 mg, 0.044 mmol), anisole (10%/styrene, as internal reference for NMR spectroscopy conversion analysis), and dry toluene (1.90 mL) were placed in a dry 100 mL Schlenk flask. The tube was closed, subjected to three freeze–pump–thaw cycles, and subsequently backfilled with nitrogen gas. The ROP catalyst DPP (44.0 mg, 0.175 mmol) or $\text{Sn}(\text{Oct})_2$ (35.0 mg, 0.087 mmol) was then added under gentle nitrogen flow and the flask was closed and immediately immersed in an oil bath at 100 °C (for DPP) or 120 °C (for $\text{Sn}(\text{Oct})_2$) to start the polymerization, unless otherwise indicated. Samples were taken periodically 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 and diluting with toluene. The final product was obtained after precipitation in cold methanol and vacuum drying.

2.3. Physical Methods and Techniques

2.3.1. Nuclear Magnetic Resonance (NMR) Spectroscopy

^1H and ^{13}C NMR (400 MHz for H and 100 MHz for C) spectra were acquired using an Avance DPX 400 spectrometer with CDCl_3 as the solvent.

2.3.2. Gel Permeation Chromatography (GPC)

Number-average molar mass (\overline{M}_n) and polydispersity index ($\overline{M}_w/\overline{M}_n$) values were determined by GPC in THF at a flow rate of 1.0 mL min^{-1} using SKgel H_{XL} guard and TSKgel G3000 H_{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 ($K = 13.95 \times 10^{-5} \text{ dL g}^{-1}$ and $\alpha = 0.786$ for PCL,^[24] and $K = 14.1 \times 10^{-5} \text{ dL g}^{-1}$ and $\alpha = 0.70$ for PS^[25]).

2.3.3. UV–Vis Spectroscopy

UV–vis spectra were recorded using a Shimadzu UV2600 spectrophotometer. For the measurements, 3.0 mL of solution ready for polymerization was placed in a 10 mm square quartz cell

under inert conditions. All spectra were recorded in the wavelength range of 360–600 nm at a scan rate of 600 nm min^{-1} (0.1 s integration per 1.0 nm) for 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 the simultaneous 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. Considering a typical RAFT polymerization, the additional components in the present case are the ϵ -CL monomer (3) and the ROP catalyst. Whereas the former has almost no effect on the controlled nature of the radical process, the same is not always applicable to the latter. We investigated (5) and (6) as catalysts, which have been previously proven to be very efficient for the ROP of ϵ -CL using alcohols as co-initiators. However, they behave very differently according to the reaction temperature and depending on this experimental parameter it is possible to dispense with the use of a radical initiator for the RAFT polymerization of styrene.

Recently, Kakuchi and co-workers^[26,27] showed that DPP-catalyzed ROP of trimethylene carbonates and lactones proceeds through an activated monomer mechanism, with kinetic and chain extension experiments confirming the controlled nature of the process and quantitative chain end functionalization in toluene at room temperature. Initially, we therefore performed a similar reaction using (1) as the co-initiator at 100 °C, where the 1,1'-azo bis(cyclohexanecarbonitrile) radical initiator decomposes, thus initiating the RAFT polymerization of styrene. The NMR spectrum of the reaction produced provided in Figure S1 (Supporting Information) shows the characteristic peaks of the PCL polymer and co-initiator (1). The monomer conversion after 1.0 h at 100 °C was nearly quantitative, and the PCL obtained consisted of

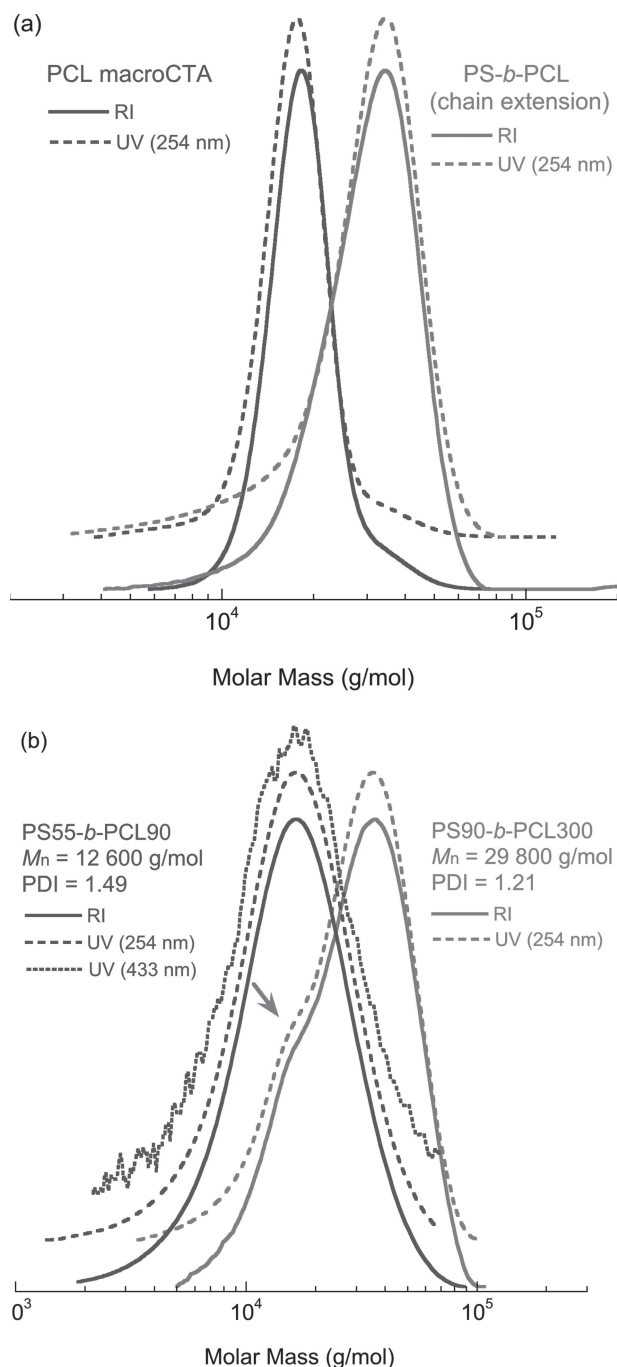


Figure 1. a) GPC chromatograms for a PCL macro-CTA prepared using DPP as the catalyst for the ROP process (Table 1, entry 1), and corresponding chain extension by RAFT polymerization of styrene (Table 1, entry 2); b) GPC chromatograms for PS-*b*-PCL diblock copolymers prepared in a one-pot approach consisting of simultaneous RAFT and ROP processes (Table 1, entries 4 and 8).

fairly narrowly distributed chains, as evidenced from the monomodal GPC trace shown in Figure 1 (panel a) and physicochemical characteristics summarized in Table 1. The polydispersity was remarkably low ($\overline{M}_w/\overline{M}_n = 1.07$)

and the $\overline{M}_n(\text{GPC})$ value was close to the $\overline{M}_n(\text{target})$ calculated from the initial ratio of $[\epsilon\text{-CL}]_0/[\mathbf{1}]$ (Table 1, entry 1). PCL molar masses were determined using the appropriate Mark-Houwink parameters.^[24,25] Similar profiles of GPC traces obtained from RI and UV (254 nm and 433 nm) detectors (Figure 1 panel a, and Figure S2, Supporting Information) strongly suggest the presence of a UV absorbing CTA moiety at the chain ends since no other species absorb at the λ_{max} of (**1**) (433 nm; selective detection of the CTA residue). The amount of CTA present in this sample is consistent with quantitative functionalization of all polymer chains with a trithiocarbonate group (Figure S3, Supporting Information). A chain extension experiment using this PCL sample as a macro-RAFT agent for the polymerization of styrene at 100 °C initiated by 1,1'-azobis(cyclohexanecarbonitrile) further confirmed the quantitative functionalization of PCL with a CTA fragment. This was clear from the shift to a higher molar mass for the PS-*b*-PCL diblocks as compared with the PCL macro-CTA, without a significant contribution from the latter (Figure 1 and Table 1, entry 2).

The one-step approach was then tested according to Scheme 1. In this case, the ROP catalyst DPP was added to the solution immediately before immersion in the oil bath, otherwise the ROP of $\epsilon\text{-CL}$ could start at a low temperature during the degassing procedure. Figure 1 (panel b) shows representative GPC traces of representative samples with the target degrees of polymerization for $[\text{St}]:[\epsilon\text{-CL}]$ of 100:100 and 300:300, corresponding to entries 4 and 8 in Table 1. Block polymers synthesized through this straightforward method showed a monomodal distribution of molar masses. However, for high target polymerization degrees ($\text{DP}(\text{target})$ $[\text{St}]:[\epsilon\text{-CL}] = 300:300$), a low molar mass shoulder was always evident (see arrow in Figure 1, panel b). In general, the molar mass distributions ($\overline{M}_w/\overline{M}_n$) calculated from the GPC traces were moderate, lying in the range of 1.21–1.57, but still satisfactory considering the synthesis strategy. These polydispersity indexes are considerably lower than those reported in the simultaneous RAFT of styrene and ROP of $\epsilon\text{-CL}$ mediated by enzymes in scCO_2 ($\overline{M}_w/\overline{M}_n = 1.5\text{--}2.1$),^[13] but higher than those obtained by Youk's group for the one-pot synthesis of poly(alkyl methacrylate)-*b*-polyester block copolymers which were remarkably low ($\overline{M}_w/\overline{M}_n < 1.21$).^[18] Theoretical molar masses ($\overline{M}_n(\text{theo})$) and polymerization degrees ($\text{DP}(\text{theo})$) were calculated from the conversion of styrene determined by ¹H NMR spectroscopy analysis of a reaction aliquot containing anisole as the internal reference, assuming a quantitative efficiency of (**1**), and from the ¹H NMR spectroscopy integral ratio corresponding to PS and PCL protons (Figure S4, Supporting Information). The efficient initiation involving (**1**) was verified by the good agreement between $\overline{M}_n(\text{theo})$ and $\overline{M}_n(\text{GPC})$ of PS (same as standards) and PCL

Table 1. Experimental conditions and properties of PS-*b*-PCL copolymers synthesized by in a one-pot polymerization reaction involving simultaneous RAFT and ROP processes.

Entry	[CTA]:[I]:[cat]: [St]:[CL]	[St] ₀ [M]	[CL] ₀ [M]	<i>T</i> [°C]	Time [h]	DP(theo) [St]:[CL]	$\bar{M}_n(\text{target})$ [g mol ⁻¹]	$\bar{M}_n(\text{theo})$ [g mol ⁻¹]	$\bar{M}_n(\text{GPC})$ [g mol ⁻¹]	\bar{M}_w/\bar{M}_n
Catalyst: DPP										
1	1:--:1:--:100	–	2.80	85	1	n.d.	11 400	n.d.	11 000 ^{a)}	1.07
2	1:0.25:--:200:--	2.81	–	100	8	n.d.	31 900	n.d.	29 500	1.09
3	1:0.25:1:050:100	2.80	4.14	100	2	21:100	16 900	13 600	17 400	1.57
4	1:0.25:1:100:100	2.80	2.80	100	4	55:90	22 100	15 600	12 600	1.49
5	1:0.25:1:100:100	1.40	1.40	100	4	33:100	22 100	14 900	8 900	1.36
6	1:0.25:1:100:200	1.40	2.80	100	4	57:200	33 500	28 700	20 600	1.45
7	1:0.25:1:200:200	2.81	2.81	100	4	60:200	43 900	29 000	23 700	1.26
8	1:0.25:1:300:300	2.00	2.00	100	4	90:300	65 700	43 600	29 800	1.21
9	1:0.25:1:300:100	2.80	0.94	100	8	144:100	42 900	26 400	27 400	1.25
Catalyst: Sn(Oct) ₂										
10	1:--:0.5:--:100	–	1.45	120	22	n.d.	11 700	n.d.	13 600 ^{a)}	1.19
11	1:0.25:--:200:--	2.80	–	120	12	125:45	32 500	24 900	36 900	1.32
12	1:--:0.5:100:200	1.72	3.43	120	12	53:184	33 200	26 800	17 500	1.29
13	1:--:0.5:200:200	2.87	2.87	120	12	108:176	43 900	31 300	34 500	1.40
14	1:0.25:0.5:100:100	2.88	2.88	120	24	93:82	22 100	19 000	14 000	1.32
15	1:0.25:0.5:100:200	1.45	2.89	120	21	65:200	33 500	n.d.	22 300	1.30
16	1:0.25:0.5:200:200	2.88	2.88	120	24	140:73	43 900	22 900	19 200	1.22

^{a)} \bar{M}_n (exp) for PCL was determined using the appropriate Mark–Houwink parameters.^[24,25]

(determined using the appropriated Mark–Houwink coefficients^[24,25]) homopolymers. $\bar{M}_n(\text{NMR})$ was not determined because the resonance of protons from the CTA fragment, which is located at the junction between PS and PCL, became almost undetectable for long polymer chains (Figure S1, Supporting Information), due to reasons discussed in the literature.^[28]

Evidence for the formation of the block copolymer architecture was obtained from the GPC traces monitored by RI and UV detectors. The similar shapes registered with three detection systems (RI and UV set at 254 and 433 nm) means that the chain architecture and composition are homogeneous, and that the trithiocarbonate group is present in all polymer chains. The low signal-to-noise ratio observed in the GPC trace recorded at 433 nm is due to the low concentration of CTA. The diblock copolymers were composed of segments with distinct lengths due to the distinct polymerization rates of styrene and ϵ -CL. For example, the polymerization conducted with DP(target) [St]:[ϵ -CL] = 200:200 produced block copolymers with DP(theo) [St]:[ϵ -CL] = 60:200, thus implying that each block has an \bar{M}_n value, which would be distinguishable in GPC analysis if there were homopolymers in the medium. Side reactions in the RAFT of styrene and ROP of ϵ -CL were not observed when these polymerizations were

conducted separately under similar experimental conditions; both processes were well-controlled as confirmed by the good agreement between $\bar{M}_n(\text{target})$ and $\bar{M}_n(\text{GPC})$, and low polydispersity indexes (data now shown).

Further confirmation of the presence of a block copolymer was obtained through a commonly applied test involving the hydrolytic degradation of the polyester segment.^[13] The sample described in Table 1 entry 4 was subjected to hydrolysis, leading to the PS homopolymer as the only reaction product, with the removal of PCL being verified by ¹H NMR spectroscopy (Figure S5 and S6, Supporting Information).

The clear advantage of this one-pot/single-step methodology is the convenience and simplicity of the procedure allowing for easy access to PS-*b*-PCL diblock copolymers.

The main limitation associated with this approach is the huge difference in terms of polymerization rates for the RAFT of styrene and ROP of ϵ -CL at 100 °C. Near quantitative conversion is normally reached after 24 h at 27 °C in the ROP of δ -valerolactone and ϵ -CL.^[27] The higher reaction temperature employed in this study (100 °C) meant that the ϵ -CL monomer was fully converted into polymer within the time scale of the experiments described herein (up to 8 h). Meanwhile, the conversion of styrene ranged

from 30% to 57%. When high DP(target) values were chosen (DP(target) [St]:[ϵ -CL] = 200:200, or higher), the reaction mixture eventually became opaque due to the precipitation of small visible particles. We observed that the reaction should be stopped before this point in order to avoid the presence of multiple distributions of molar masses. In all cases, a remarkable increase in the viscosity of the reaction medium was observed soon after the polymerization began.

The ROP of ϵ -CL can also be mediated by Sn(oct)₂, which is probably the catalyst most commonly used for this purpose. The special attention given to this compound arises from its biological tolerance. Polymerization is also carried out in the presence of active hydrogen compounds (e.g., alcohols) as co-initiating species. When no active hydrogen compound is added, impurities in the medium are believed to initiate the polymerization.^[29,30] The reaction pathway in the presence of an Sn(oct)₂/ROH catalyst/initiator system is rather complex, and at least two mechanisms have been proposed, one of them being the activated monomer mechanism.^[29]

An important point related to the use of Sn(Oct)₂ is that ROP requires a high temperature, typically in the range of 90 to 130 °C. Under this condition, the RAFT polymerization of styrene can then be thermally initiated and, consequently, the use of a radical initiator is no longer necessary. In addition, the rate of ϵ -CL polymerization is slower with Sn(Oct)₂ than with DPP, indicating that the viscosity of the reaction medium as a function of reaction time must be quite different.

As in the first part of the study, we initially investigated whether a PCL macro-CTA synthesized by ROP using the Sn(Oct)₂/(1) catalyst/co-initiator system at 120 °C can be quantitatively chain extended by a subsequent RAFT process. Figure S7 (Supporting Information) reveals a shift to high molar mass in the GPC traces as the PCL macro-CTA is RAFT-extended to yield the PS-*b*-PCL diblock copolymer, even though a weak shoulder is seen with \overline{M}_n characteristic of the PCL macro-CTA. Stenzel's group previously reported both the preparation of polylactide macro-CTA using the same approach and the successful chain extension with RAFT-made poly(*N*-isopropylacrylamide).^[22]

The outcome of one-pot reactions carried out with (1) functioning simultaneously as the RAFT agent and ROP co-initiator along with Sn(Oct)₂ was both interesting and intriguing. The polymers exhibited GPC traces that had different shapes depending on the detection system (RI or UV) (Figure 2), indicating that they consisted of a mixture of chains with variable compositional characteristics. Provided that light absorption at 254 nm is dominated by the benzene rings of PS, the results in Figure 2 reveal the presence of a low molar mass PCL-rich distribution (low UV absorption). The GPC profile recorded at 433 nm was similar, although with a low signal-to-noise ratio (see

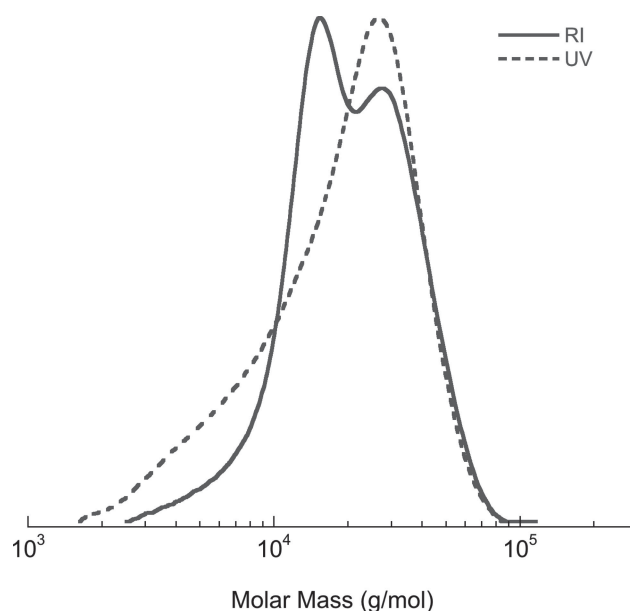


Figure 2. GPC chromatograms of the polymer sample resulting from a one-pot polymerization experiment involving simultaneous RAFT and ROP processes in the presence of Sn(Oct)₂ catalyst (Table 1, entry 12).

Figure S8 in the Supporting Information, and discussion below). The same was also observed in the presence of a radical initiator for other samples listed in Table 1 (entries 14–16).

A chain extension experiment using samples with a bimodal molar mass distribution, such as macro-CTA, for the RAFT polymerization of styrene revealed, in all the cases, that one of the distributions remains unchanged (Figure S9, Supporting Information). The main chemical functionality for a controlled RAFT processes is therefore partially lost during the one-pot process with Sn(Oct)₂, the effect of which is related to the addition–fragmentation step.

Considering the results reported above, further experiments were devised to clarify the origin of side polymerization reactions. In one of these tests, the one-pot synthesis was conducted in two-steps; all reactants apart from Sn(Oct)₂ were placed in the flask, and the RAFT polymerization of styrene was first carried out for 10 h at 120 °C. The reaction mixture was then opened to air and cooled down to room temperature (i.e., the RAFT of styrene was stopped) before the addition of a small aliquot of Sn(Oct)₂ in toluene. The solution was degassed again and the flask was re-immersed in the same oil bath at 120 °C for a further 11 h. This procedure promoted the onset of the ROP of ϵ -CL, which would occur simultaneously with the thermally initiated RAFT of styrene from this point onwards. The characteristics of the polymers thus obtained are shown in Figure 3. In the first part, only well-defined PS chains were formed



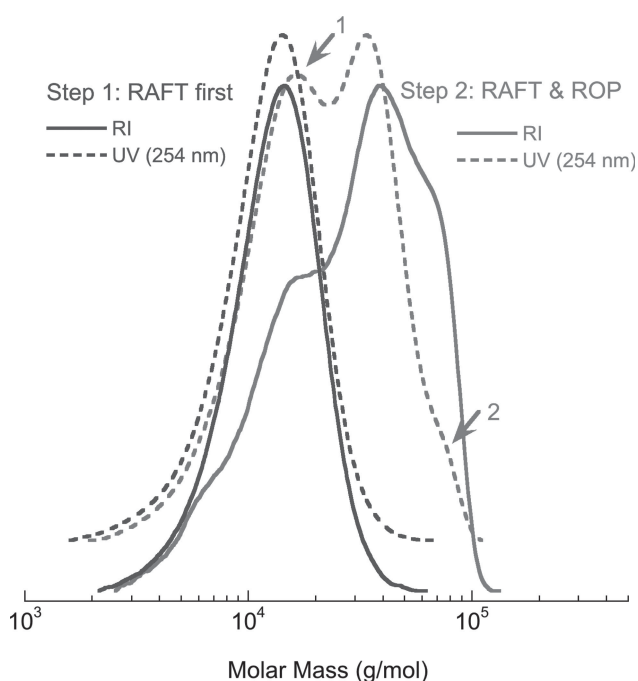


Figure 3. GPC chromatograms of polymer samples obtained in a one-pot/two-step polymerization experiment involving (a) RAFT first (step 1, 7 h), and then (b) simultaneous RAFT (thermally initiated) and ROP processes in the presence of $\text{Sn}(\text{Oct})_2$ catalyst (step 2, + 5 h, conv.(St) = 73%, conv.(CL) = 77%). Experimental conditions: $[\text{CTA}]:[\text{I}]:[\text{Sn}(\text{Oct})_2]:[\text{St}]:[\text{CL}] = 1:0.25:0.5:200:200$, $[\text{St}]_0 = [\text{CL}]_0 = 2.88 \text{ M}$, $T = 120^\circ \text{C}$.

($\overline{M}_n(\text{GPC}) = 11400 \text{ g mol}^{-1}$; $\overline{M}_w/\overline{M}_n = 1.20$), but after a further 11 h of reaction the GPC traces indicated virtually the same behavior as that discussed above, that is, multimodal distributions with different compositions ($\overline{M}_n(\text{GPC}) = 18\,600 \text{ g mol}^{-1}$; $\overline{M}_w/\overline{M}_n = 1.73$). The changeable relative intensities of the different peaks in each detector (RI and UV at 254 and 433 nm) are indicative of the existence of a main distribution and, at least, one low molar mass PS-rich (remaining from step 1) and one high molar mass PCL-rich distribution (see arrows 1 and 2, respectively) in this particular case. GPC analyses with UV detector set at 254 nm (absorption dominated by PS) and 433 nm (detection of CTA fragment only), shown in Figure S10 (Supporting Information), revealed that a significant fraction of PS chains produced in step 1 (RAFT first) lost the trithiocarbonate chain-end functionality after reacting with $\text{Sn}(\text{Oct})_2$ in step 2 (RAFT and ROP). Consequently, these polymer chains were not extended. The low signal-to-noise ratio observed at 433 nm (see relative intensities in Figure S2 (DPP) and Figure S10 ($\text{Sn}(\text{Oct})_2$), Supporting Information) reflects a low concentration of polymer-bound CTA fragments in the sample synthesized with $\text{Sn}(\text{Oct})_2$. Therefore, the trithiocarbonate fragment is partially destroyed or released from the polymer in presence of $\text{Sn}(\text{Oct})_2$ in a simultaneous one-pot RAFT and

ROP process. An experiment in which a small aliquot of degassed $\text{Sn}(\text{Oct})_2$ toluene solution was injected into the reaction mixture without cooling (i.e., RAFT of styrene was not stopped) yielded the same result.

Other relevant observations made in this study include: i) the simultaneous RAFT of St and $\text{Sn}(\text{Oct})_2$ -catalyzed the ROP of CL producing white polymer powder samples, thus indicating that the trithiocarbonate fragment, which usually renders the polymer slightly yellow, is lost; ii) the RAFT of St in the presence of $\text{Sn}(\text{Oct})_2$ yield PS with a huge difference between the $\overline{M}_n(\text{theo})$ and $\overline{M}_n(\text{GPC})$ data ($\overline{M}_n(\text{GPC}) \gg \overline{M}_n(\text{theo})$), suggesting that pre-equilibrium and chain equilibration RAFT steps are disrupted by $\text{Sn}(\text{Oct})_2$ so that a significant fraction of (1) is not involved in the polymerization; iii) hydrolysis of multimodal samples, similar to that shown in Figure 2, yields a PS homopolymer with quite a broad molar mass distribution ($\overline{M}_w/\overline{M}_n \approx 1.40$), indicating a loss of RAFT polymerization control; and iv) high conversion is observed in the ROP process in spite of the poorly defined systems.

Considering the fact that stannous compounds are oxidatively unstable, the data reported above appear to verify that the interaction between $\text{Sn}(\text{Oct})_2$ and dormant and active species carrying a trithiocarbonate function involved in the reversible chain transfer and chain equilibration steps of the RAFT mechanism (mechanism as proposed in the first publication on this topic^[31] and further discussed by Moad and Barner-Kowollik^[9]) is at the origin of the formation of multimodal distributions, and, therefore, electrochemically active compounds should be avoided in simultaneous polymerization involving controlled radical processes.

The stability of (1) during simultaneous RAFT and ROP processes was investigated by in situ UV-vis spectroscopy. Figure 4 shows UV-vis spectra recorded at selected stages of indicated temperature-time program during polymerization reactions (insets). When DPP was used as ROP catalyst (Figure 4, panel a), a small bathochromic shift of the characteristic λ_{max} of (1) (433 nm), accompanied by a decrease in the absorption intensity, was observed as the temperature was raised to 90°C . At this temperature, the RAFT polymerization already initiated, and no further changes were detected during the polymerization time. Upon cooling the reaction mixture, the initial profile was fully recovered, corroborating that the trithiocarbonate group of (1) is stable under such conditions. On the contrary, irreversible changes to the CTA structure occurred in presence of $\text{Sn}(\text{Oct})_2$ (Figure 4, panel b). In such a case, the absorption intensity at λ_{max} after the polymerization was markedly lower than that observed before the reaction. In fact, (1) quickly reacts with $\text{Sn}(\text{Oct})_2$ (Figure 4, panel c), changing solution color from yellow to the characteristic bronze of stannic sulfide precipitates (see inset digital photograph taken before and after the reaction).

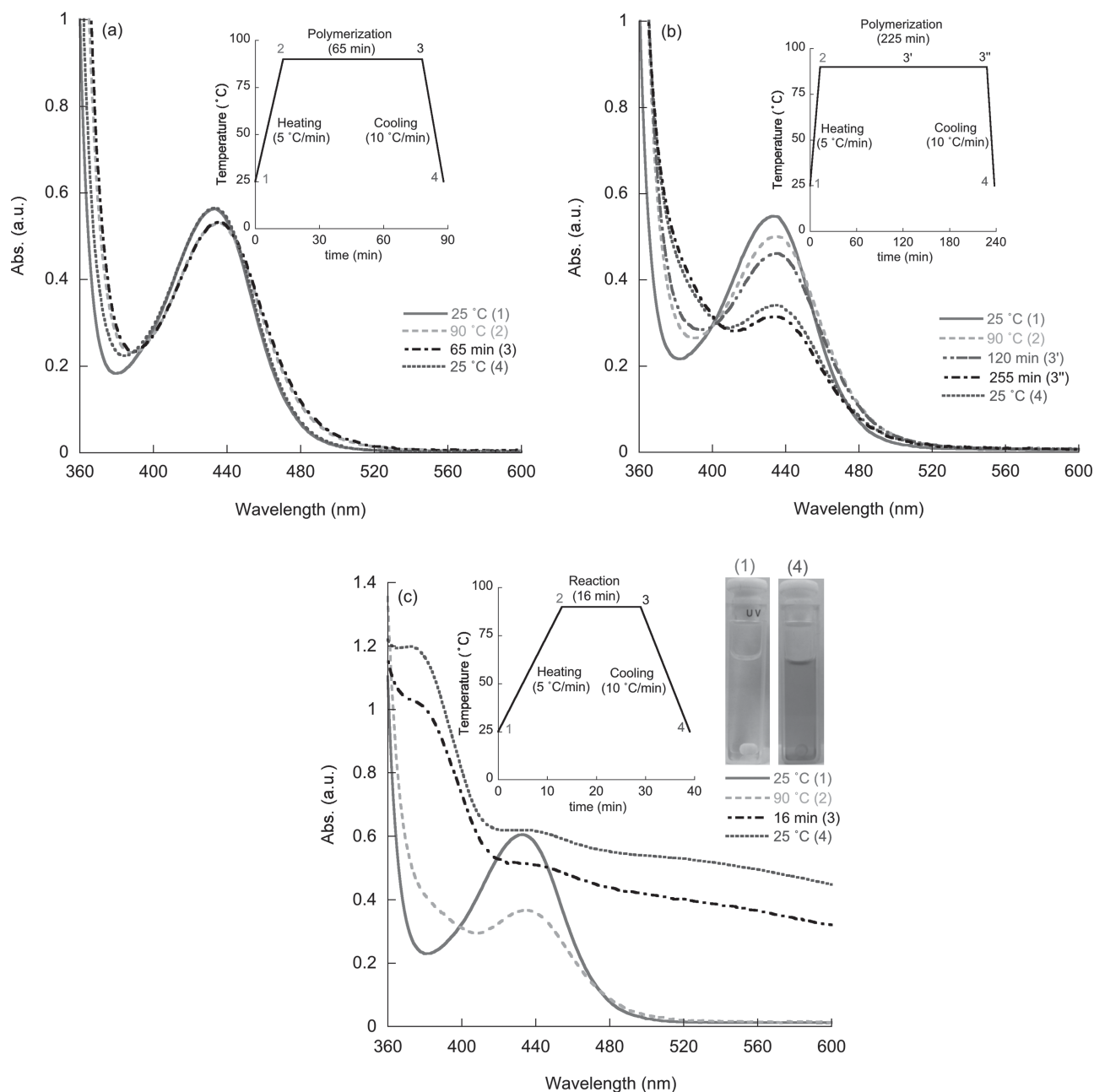


Figure 4. UV-vis spectra recorded at selected stages of the indicated temperature-time program (inset) during simultaneous polymerization reactions using (a) DPP and (b) Sn(Oct)₂ ROP catalysts, and (c) during a reaction between (1) and Sn(Oct)₂. Experimental conditions: [CTA]:[AIBN]:[catalyst]:[St]:[CL] = 1:0.25:0.5:10:10, [St]₀ = [CL]₀ = 0.288 M.

These precipitates cause the strong background absorption detected at points 3 and 4. The same behavior manifested for another RAFT agent of trithiocarbonate type (2-(dodecylthiocarbonothioylthio)-2-methylpropanoic acid). Although the reaction seems to be slower during the simultaneous RAFT and ROP processes (no precipitates were observed), it can certainly be at the origin of multimodal distributions of polymer chains with variable compositions verified when Sn(Oct)₂ is used as ROP catalyst.

4. Conclusion

A novel straightforward one-pot synthesis method comprising simultaneous RAFT and ROP processes allowed easy access to well-defined PS-*b*-PCL diblock copolymers. The proposed method did not require intermediate purification steps, and diblock polymers with molar masses reaching up to 50 000 g mol⁻¹ and polydispersity indexes in the range of 1.20–1.60 were obtained within

approximately 4 h of reaction. 2-(Benzylsulfanylthiocarbonylsulfanyl)ethanol can efficiently perform the dual roles of CTA in the RAFT polymerization of styrene and of co-initiator in the ROP of ϵ -caprolactone. Having the hydroxyl function as part of the Z substituent of the CTA, the possibility of homopolymer formation is suppressed, and the resulting diblock copolymers consist of PS and PCL segments connected through a trithiocarbonate group so that subsequent growth of a third middle segment between PS and PCL is thus feasible.

The critical point in devising one-pot reactions involving RAFT and ROP is related to the electrochemical stability of the ROP-catalyst, which should not react with radical species inherent to the RAFT process. DPP yielded excellent results, but it can mediate the ROP process even at room temperature. Therefore, DPP should be added immediately before the polymerization starts if the standard RAFT procedure (i.e., comprising a degassing step) is applied. In the case of Sn(Oct)₂, partially filled d-orbitals of the metallic center favor redox reactions with species containing trithiocarbonate groups, leading to multimodal distributions of polymer chains with variable compositions.

Supporting Information

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

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