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Organic Catalyst-Mediated Ring-Opening Polymerization for the Highly Efficient Synthesis of Polyester-Based Star Polymers

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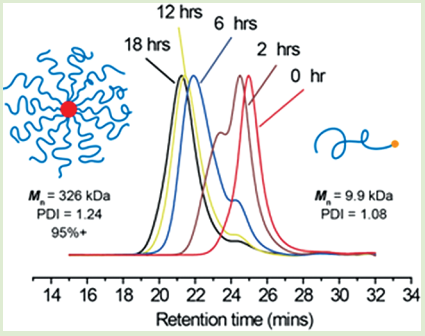
Supporting Information

ABSTRACT: A facile, highly efficient, and metal-free synthesis of well-defined polyester-based core cross-linked star (CCS) polymers with yields of up to 96 % was achieved via an organic catalyst (i.e., methanesulfonic acid) mediated ring-opening polymerization (ROP) at room temperature, through either a two-pot or a one-pot, two-step strategy. CCS polymers with narrow molecular weight distributions (PDI ≤ 1.3) and macroinitiator (MI) conversions of 90−96% were prepared using poly(ε-caprolactone) (PCL) MIs with molecular weights ranging from 9.9 to 36.2 kDa and [4,4′-bioxepane]-7,7′-dione (BOD) as the cross-linker. Furthermore, transesterification was identified as being responsible for the small percentage of unincorporated low molecular weight polymer remaining and star−star couplings in the star formation. Compared to CCS polymers synthesized via the methanesulfonic acid-mediated ROP, CCS polymers prepared via ROP mediated by high transesterification rate catalysts (i.e., stannous octoate ($Sn(Oct)_2$)) suffer from much lower star purity (ca. 70%) and star−star coupled products due to more prominent transesterification side-reactions.



Star polymers have a unique three-dimensional (3D) macromolecular architecture consisting of multiples arms radiating from a central core, which has endowed star polymers with exclusive rheological and chemical properties.[1] Compared to their linear analogues of similar molecular weight, star polymers not only possess lower intrinsic viscosities and better solubility characteristics but also contain higher end group functionalities, which make them useful materials for various applications including drug delivery,[2] membrane technologies,[3] and catalysis.[4] Star polymers can be synthesized via various controlled polymerization techniques[5] through either the "core-first"[6] or "arm-first" approaches.[1,7] Star polymers prepared through the latter approach have a distinct cross-linked network structure in the core[1] and are therefore referred to as core cross-linked star (CCS) polymers to highlight their unique core structure and distinguish them from other types of star polymers. Recently, we reported the synthesis of functionalized polyester-based poly(ε-caprolactone) (PCL) CCS polymers via ring-opening polymerization (ROP) and catalyzed by the organometallic complexes stannous octoate ($Sn(Oct)_2$) or stannous triflate ($Sn(OTf)_2$).[8] These functional polyester-based star polymers have attracted great attention due to their potential application to the research fields of nanofillers, degradable materials, and polymer therapeutics. Polyester-based CCS polymers are considered interesting candidates for in vivo drug delivery devices due to their biocompatibility, biodegradability, and large core size, which provides drug loading capacity.[2] However, the previously developed synthetic protocols for the preparation of functional PCL star polymers suffer from moderate yields, owing to the inefficient macroinitiator ("arm")-to-star conversion (typically <60%)[8c] and undesirable high molecular weight star−star coupled products leading to broad molecular weight distributions.[8b,9] Tedious and time-consuming purification processes are often required to isolate the pure star polymers from low and high molecular weight impurities, and this results in poor yields and reduces the widespread use and commercialization of these materials.[10]

Recently, very high yielding CCS polymer synthesis has been achieved using various controlled polymerization techniques. For controlled radical polymerization, Matyjaszewski and co-workers have reported the synthesis of CCS polymers in >98% yields via activator generated by electron transfer (AGET)-ATRP,[11] and our own research group has reported the >99% yield synthesis of CCS via ruthenium-catalyzed living radical polymerization.[12] Recently, Boyer and co-workers have optimized the synthesis of star polymers via RAFT polymerization to achieve much improved yields of >90%.[13] Similarly, Aoshima et al. reported the >99% yield of poly(vinyl ether) CCS polymers via living cationic polymerization.[14] CCS polymers prepared via these aforementioned methods have high star purity, and therefore, further purification is generally not required. Nevertheless, these synthetic approaches have their own inherent weaknesses. Controlled radical polymerization techniques suffer from termination reactions (i.e., radical dimerization and disproportionation) and are sensitive to the radical scavengers (e.g., oxygen) or require the addition of excess reducing agents (e.g., AGET-ATRP).[15] In comparison, living cationic polymerization requires even more stringent reaction conditions, being susceptible to both oxygen and

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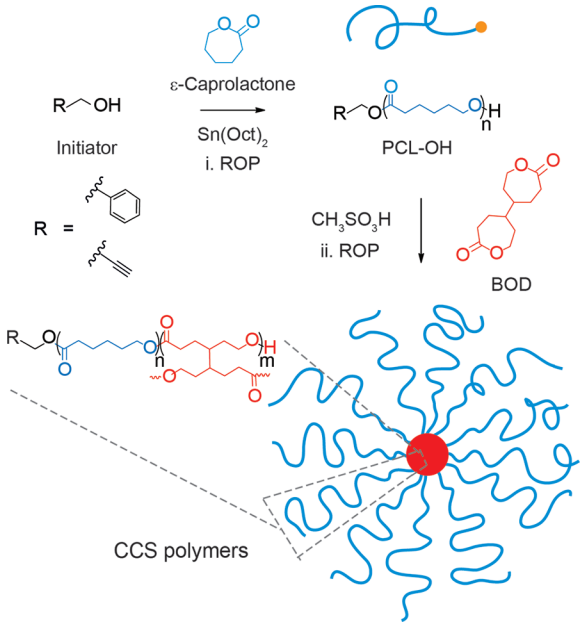
protic impurities (e.g., water). In contrast, the ROP of lactones and lactams requires far less stringent reaction conditions since it is inert to oxygen and reasonably tolerant of water, although under certain conditions water can act as a polymer chain initiator during polymerization.[16] However, for the synthesis of CCS polymers via ROP, water impurities may not be detrimental since the initiation of the bislactone-based cross-linkers would lead to the formation of reactive cross-linked nanonetworks that would be expected to facilitate cross-linking of MIs to yield star polymers. Therefore, ROP may be considered a valuable approach for both laboratory- and industrial-scale synthesis of star polymers, especially if the arm-to-star conversion can be maximized eliminating the need for purification.

ROP mediated by the tin(II) organometallic complexes $Sn(Oct)_2$ and $Sn(OTf)_2$ follows a coordination−insertion mechanism,[17] which often requires elevated reaction temperatures to achieve a fast reaction rate. Thus, the synthesis of CCS polymers via ROP using tin(II) complexes requires reaction temperatures of 65−110 °C to achieve a satisfactory star formation rate.[8a,c] However, elevated reaction temperatures are disfavored, especially for industrial scale processes where energy conservation is particularly important from a cost and environmental perspective. Furthermore, tin(II) based organometallic complexes are strong transesterification agents.[17,18] Therefore, ROP mediated by tin(II) complexes might suffer from intramolecular transesterification reactions, leading to the formation of cyclic impurities and broad polymer molecular weight distributions, and these transesterification reactions would be more prominent at elevated reaction temperatures. This is particularly important during star synthesis as cyclization of the polyester MIs (arms) leads to the formation of noncross-linkable ("dead") cyclic polymer chains without "active" terminal groups, which cannot take part in star formation.[19] It is also speculated that bulky tin(II) complexes cannot diffuse effortlessly out of the cross-linked core of the performed star polymers to catalyze further cross-linking of the unbounded MIs or low molecular weight star precursors.[8c] As a result of insufficient catalysis, the star formation process often requires lengthy reaction times to achieve moderate arm-to-star conversions. Evidently, given the aforementioned issues associated with the previously reported CCS polymer synthesis via ROP, more robust catalysts with a small molecular size, higher catalytic activity, and lower transesterification rates are required to allow the formation of well-defined stars at low reaction temperatures and fast reaction rates. Recent advances in organo-catalysis have introduced several robust catalysts (e.g., *N*-heterocyclic carbenes (NHCs),[20] bifunctional thioureas,[21] triazabicyclodecene,[22] and sulfonic acid derivatives[23]) that can efficiently catalyze the controlled ROP of cyclic esters under mild reaction conditions and offer comparable reaction rates[20] to organometallic catalytic systems operating at elevated temperatures. More importantly, previous studies have shown that organic catalysts have low transesterification rates even at high monomer conversions.[21,23,24]

In this paper, we report the highly efficient synthesis of PCL-based CCS polymers via ROP using the organic catalyst methanesulfonic acid (CH_3SO_3H),[23] through either a two-step or a one-pot sequential addition strategy. The robust nature of methanesulfonic acid was exploited to catalyze the ROP of lactones to form CCS polymers at ambient temperature. Compared to the previously published systems utilizing tin(II) complexes as catalysts, the new approach provides low polydispersity (<1.3) star polymers in very high yields (>95%) and at faster reaction rates, without the formation of star−star coupled side-products.

The synthesis of PCL CCS polymers was achieved in two steps, involving (i) the ROP of ε-caprolactone (CL) using benzyl alcohol (BnOH) or propargyl alcohol (PgOH) as the initiator to afford living poly(ε-caprolactone) "arm" macroinitiators (PCL−OH) (Scheme 1, i), followed by (ii) ROP of

Scheme 1. Synthesis of PCL CCS Polymers via ROP and the "Arm-First" Approach



the bislactone cross-linker, [4,4′-bioxepane]-7,7′-dione (BOD), using the PCL−OH macroinitiators and methanesulfonic acid (CH_3SO_3H) as the catalyst (Scheme 1, ii). Initially, four PCL MIs with different molecular weights (MWs) (Bn-PCL-OH 1a−d, Table 1) were prepared via ROP, using BnOH as the initiator and $Sn(Oct)_2$ as the catalyst at 110 °C in toluene. All reactions were terminated at monomer conversions of <80% to avoid undesirable transesterifications, which might arise at high conversion (>90%).[25] Gel permeation chromatography (GPC) revealed that Bn-PCL-OH 1a−d have number average molecular weights ($M_{n,GPC}$) values ranging from 9.9 to 36.2 kDa. The $M_{n,GPC}$ values of Bn-PCL-OH 1a−d and their number average MWs calculated based upon ^{1}H NMR spectroscopic analysis ($M_{n,NMR}$) and theoretical number average MWs ($M_{n,theo}$) based upon monomer conversion (via GC-MS analysis) were all in good agreement (Supporting Information (SI), Table S1). The GPC RI chromatograms of Bn-PCL-OH 1a−d revealed monomodal distributions with narrow polydispersities (PDI < 1.2) (Figure 1A−D, t = 0 h). These results suggest that the occurrence of inter- or intramolecular transesterifications during MI synthesis is negligible[19,25] and that all of the MIs are living with "active" hydroxy termini suitable to initiate ROP of the cross-linker (BOD) in the subsequent star formation step. Subsequently, star formation using macroinitiators Bn-PCL-OH 1a−d was conducted at room temperature in dichloromethane using methanesulfonic acid as the catalyst to afford CCS 1a−d, respectively. In all cases the reactions were followed over time by GPC (Figure 1A−D). Very high final arm-to-star conversions, ranging from 90−96%,

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Table 1. Characterization of $PCL_{arm}PBOD_{core}$ CCS Polymers via ROP and the Arm-First Approach

polymer[a]	catalyst[b]	macroinitiator (MI)	expt. condition $[MI]_0/[BOD]_0/[Cat]_0$	MI $M_{n,GPC}$[c] (kDa)	MI conv.[d]	CCS $M_{n,GPC}$[e] (kDa)	CCS M_w/M_n	CCS N_{arm}[f]
CCS 1a	CH_3SO_3H	Bn-PCL-OH 1a	1:30:3	9.9	0.95	326	1.25	19
CCS 1b	CH_3SO_3H	Bn-PCL-OH 1b	1:55:3	15.6	0.92	488	1.32	17
CCS 1c	CH_3SO_3H	Bn-PCL-OH 1c	1:90:3	24.8	0.96	680	1.28	15
CCS 1d	CH_3SO_3H	Bn-PCL-OH 1d	1:128:3	36.2	0.90	550	1.18	8
CCS 2[g]	CH_3SO_3H	Bn-PCL-OH 2		12.2	0.95	295	1.23	15
CCS 3	CH_3SO_3H	HC≡C-PCL-OH 3	1:30:3	11.8	0.94	286	1.30	15
CCS 4	$Sn(Oct)_2$	Bn-PCL-OH 1a	1:30:0.5	9.9	0.85	364	1.20	21

[a]Experimental conditions: For CCS 1a–d, 2, and 3, $[MI]_0$ = 50 mg/mL, room temperature, dichloromethane. For CCS 4, $[MI]_0$ = 50 mg/mL, 110 °C, toluene. MI and cross-linker (BOD) conversion were monitored via GPC and GC-MS, respectively. [b]Catalyst utilized in the star formation reaction. [c]M_n of MI determined by GPC MALLS using dn/dc = 0.078 mL/g.[26] [d]Macroinitiator conversion based upon the area fraction ratio of star polymers, determined by deconvolution of the GPC RI chromatograms using a Gaussian function. [e]M_n of functionalized stars determined by GPC MALLS and based upon the assumption of 100% mass recovery. [f]Number-average value of arms per star polymer calculated from equation S1 (SI). [g]Experimental conditions for one-pot synthesis: $[PhCH_2OH]_0/[CL]_0/[BOD]_0/[CH_3SO_3H]_{tot}$ = 1:100:30:3, where $[CH_3SO_3H]_{tot}$ is the total methanesulfonic acid concentration in the star formation reaction.

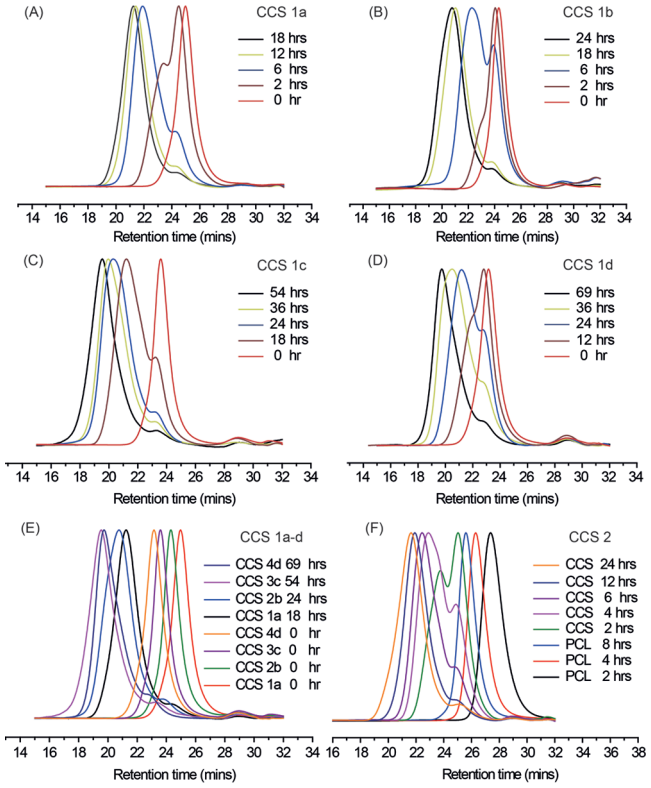

Figure 1. GPC RI chromatograms over time for the synthesis of CCS polymers: (A) CCS 1a, MI; Bn-PCL-OH 1a, $M_{n,GPC}$ = 9.9 kDa, PDI = 1.08 (Table 1, entry 1); (B) CCS 1b, MI; Bn-PCL-OH 1b, $M_{n,GPC}$ = 15.6 kDa, PDI = 1.04 (Table 1, entry 2); (C) CCS 1c, MI; Bn-PCL-OH 1c, $M_{n,GPC}$ = 24.8 kDa, PDI = 1.06 (Table 1, entry 3); (D) CCS 1d, MI; Bn-PCL-OH 1d, $M_{n,GPC}$ = 24.8 kDa, PDI = 1.08 (Table 1, entry 4). (E) Summary of GPC-RI chromatograms of MI 1a–d and CCS 1a–d at reaction end point (Table 1, entry 1–4). (F) One-pot synthesis of CCS 2: MI; Bn-PCL-OH 2, t = 8 h; CL monomer conversion (GC) = 93%; $M_{n,GPC}$ = 12.2 kDa, PDI = 1.12 (Table 1, entry 5).

were obtained for all stars CCS 1a–d (Table 1) as determined by deconvolution of the GPC RI chromatograms (SI, Figure S1). It was observed that as the MW of the MIs Bn-PCL-OH 1a–d increased from 9.9 to 36.2 kDa so did the reaction time (18 to 69 h) required to obtain high arm-to-star conversion (Figure 1E), and the number-average value of arms per star (N_{arm}) decreased from ca. 19 to 8. These are common observations for the synthesis of star polymers via the arm-first approach; high MW MIs generally require long reaction times, and the resulting stars have lower arm-to-star conversions and lower N_{arm} due to steric limitations.[1a,14]

In addition, the preparation of PCL CCS polymers could be conducted in a one-pot, two-step strategy without isolation of the intermediate MIs. Initially, the PCL MI was prepared via ROP of CL at room temperature using BnOH as the initiator and methane sulfonic acid as the catalyst. Once the CL conversion reached 90%, the cross-linker BOD was added to the reaction to induce star formation. Using this approach, CCS 2 (Figure 1F) was prepared with targeted MI and BOD degree of polymerization (DP) values of 100 and 30, respectively. GPC analysis of CCS 2 provided a $M_{n,GPC}$ of 295, PDI of 1.23, and an arm-to-star conversion of 95%, which is comparable to CCS 1a prepared using a similar MW MI (Table 1). No further improvements in arm-to-star conversion were observed after the addition of excess amounts of BOD or BnOH initiator (results not shown).

The GPC characterization of CCS 1a–d and 2 indicates the presence of side-reactions that prevent 100% incorporation of the linear MIs into star polymers. In general, for the synthesis of CCS polymers via controlled radical polymerization (CRP) the loss of chain end functionality through radical termination events results in unincorporated linear polymers remaining, although it has been demonstrated that the selection of a catalytic system with low propagating radical concentration can suppress these termination events to give higher star yields.[11,12] For the synthesis of CCS polymers via living cationic polymerization, the selection of the initiation system (e.g., the base-stabilizing system rather than the counterion system to ensure a more stable living chain end) was the key to achieving the quantitative synthesis of CCS polymers.[14] Motivated by these CCS synthetic systems, it was speculated that the unincorporated polymers in the designed ROP system must result from the loss of the active hydroxy terminus of these polymers during star formation. To test this hypothesis, CCS 3 was prepared using an α-alkyne, ω-hydroxy PCL MI, HC≡C-PCL-OH 3 (Table 1), which was synthesized via ROP of CL using propargyl alcohol (PgOH) as the initiator and $Sn(Oct)_2$ as the catalyst at 110 °C in toluene. PgOH was selected as the initiator due to its MW (55.6 g/mol), which is significantly different to the MW of the CL repeat unit (114.14 g/mol), as opposed to BnOH, which has a MW of 108.14 g/mol. This is

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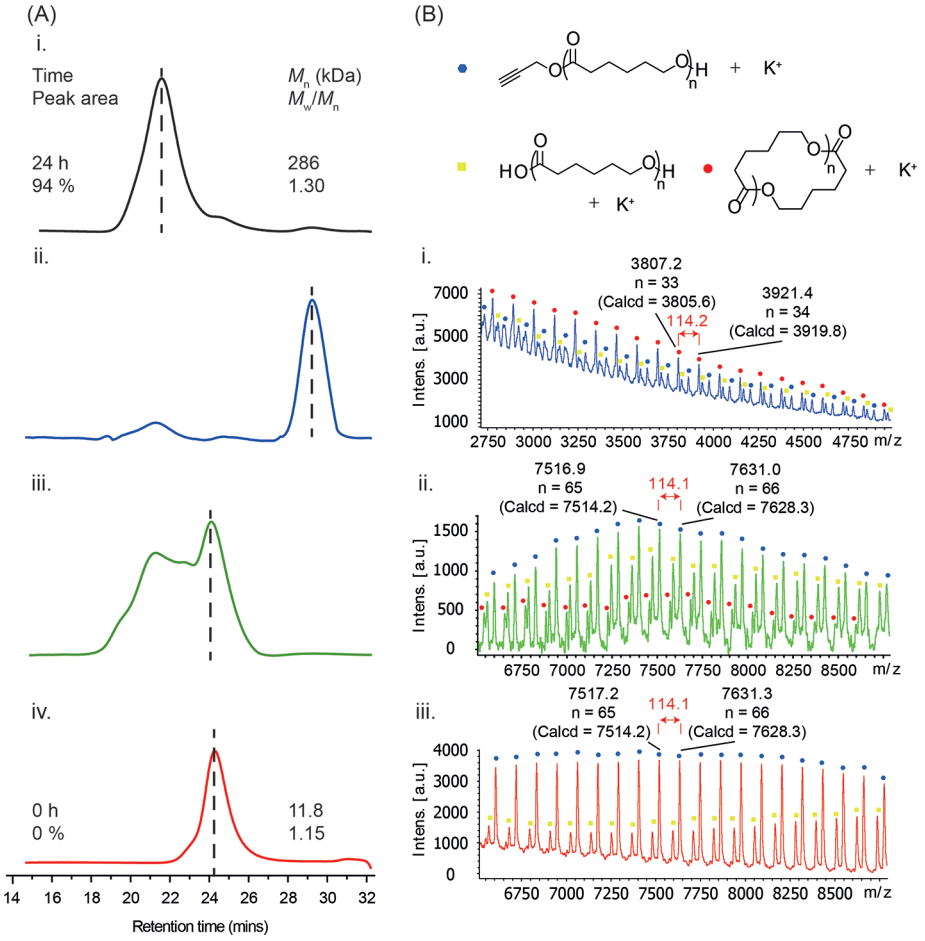

Figure 2. (A) GPC RI chromatograms of (i) CCS 3, (ii) fractionated unincorporated cyclic PCL (*c*-PCL), (iii) fractionated unincorporated linear PCL (*l*-PCL), and (iv) macroinitiator HC≡C-PCL-OH 3; $M_{n,GPC}$ = 11.8 kDa, PDI = 1.15 (Table 1, entry 5). (B) MALDI-ToF mass spectra of (i) fractionated unincorporated cyclic PCL (*c*-PCL), (ii) fractionated unincorporated linear PCL (*l*-PCL), and (iii) macroinitiator HC≡C-PCL-OH 3. MALDI ToF mass spectra were acquired in linear/positive mode using α-cyano-4-hydroxycinnamic acid and potassium trifluoroacetate (KTFA) as the matrix and cationization agent, respectively.

particularly important when conducting end-group analysis of polymers via matrix-assisted laser desorption/ionization time-of-flight (MALDI ToF) mass spectrometry, since cyclic PCL (*c*-PCL) impurities can be more easily identified as there would not be the overlapping mass peaks between HC≡C-PCL-OH and *c*-PCL series, whereas this complication might arise in the case of Bn-PCL-OH. CCS 3 was prepared using the same reaction conditions used for CCS 1a, and after 24 h a final arm-to-star conversion of 94% was achieved. Similarly to CCS 1a−d and 2 (Figure 1), the GPC RI chromatogram of CCS 3 revealed a trimodal peak profile (Figure 2A), with the peak corresponding to the star polymers at a retention time of 19−24 min also being accompanied by peaks at higher retention times of 23−27 and 28−30 min.

To identify the species responsible for the peaks at 23−27 and 28−30 min, CCS 3 was fractionated utilizing a fractional precipitation technique (SI) to isolate the unincorporated polymers into two fractions (Figure 2A, ii and iii). The fractionated polymers were subsequently analyzed via MALDI ToF mass spectroscopy and compared with the MALDI ToF mass spectrum of the MI HC≡C-PCL-OH (Figure 2 B). The MALDI ToF mass spectrum of the MI HC≡C-PCL-OH revealed two apparent oligomeric mass series: the major series correspond to HC≡C-PCL-OH and the minor series correspond to linear PCL with an α-carboxylic acid end group (i.e., HOOC-PCL-OH) (Figure 2B, iii). The presence of HOOC-PCL-OH could potentially originate from the ROP of CL initiated by water present in the PgOH initiator or water produced from esterification of PgOH with octanoic acid liberated from the Sn(Oct_2) catalyst at elevated temperatures (>100 °C).[27] Another plausible explanation for the presence of HOOC-PCL-OH is the fragmentation of propargylic ester end groups of the MI HC≡C-PCL-OH during the mass spectroscopy ionization process, as the relative peak intensity of the HOOC-PCL-OH oligomeric series varies in the MALDI ToF mass spectra under different acquisition conditions, for example, matrix and laser power (SI, Figure S2). Mass peaks observed corresponding to the *c*-PCL oligomeric series were negligible (<0.5% of the total peak area) compared to the HC≡C-PCL-OH and HOOC-PCL-OH oligomeric series (Figure 2B, iii). In comparison, the mass peaks corresponding to the *c*-PCL oligomeric series can be clearly observed in the mass spectra of the fractionated unincorporated PCL polymers (Figure 2B, i and ii). For example, *c*-PCL is the dominant oligomeric series in the MALDI ToF mass spectrum (Figure 2B, i) of the unincorporated PCL polymers with a GPC RI retention time of 27.5−30 min (Figure 1A, ii), and accounts for ca. 50% of the sample composition as determined by peak area integration. These results suggest that the intramolecular transesterification or backbiting process[19] of MIs takes place

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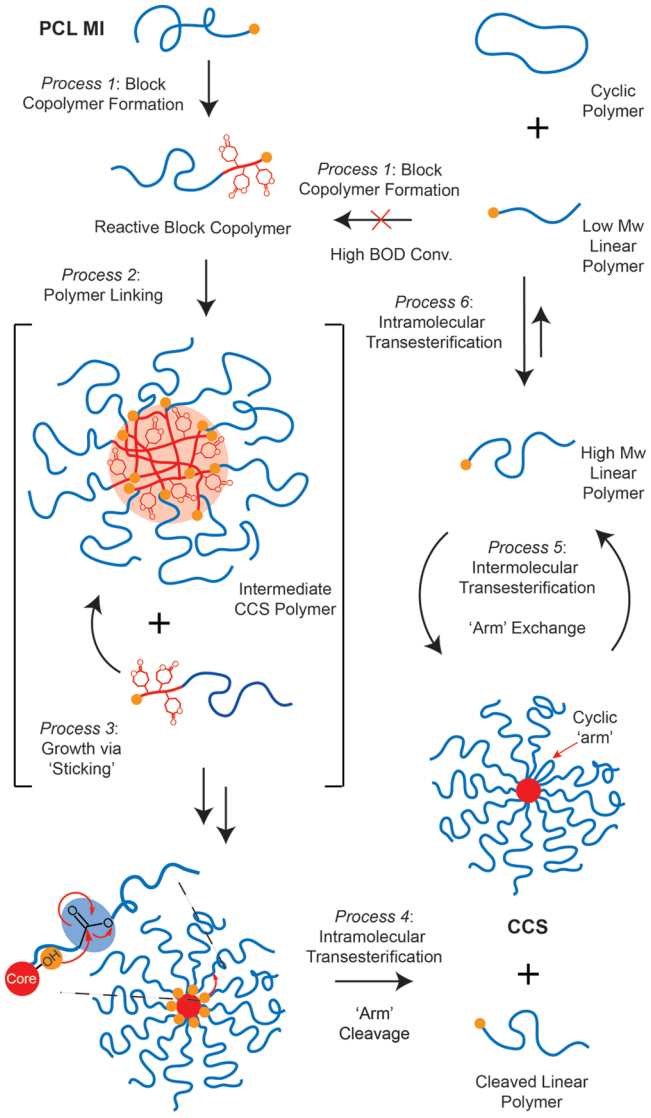
during the star formation process, leading to the formation of low MW *c*-PCL, which cannot be integrated into stars. Surprisingly, the MALDI ToF mass spectra of both fractionated unincorporated polymers (Figure 2B, i and ii) revealed an oligomeric series corresponding to the telechelic PCL polymers, HC≡C-PCL$_n$–OH and HOOC-PCL$_n$-OH. The presence of unincorporated telechelic PCL with "active" hydroxyl termini can only result from the intramolecular transesterification of the performed star polymers, during which the hydroxyl functional groups embedded in the core of the CCS polymers attack the ester groups on the linear arms to cleave and liberate *l*-PCL polymer (Scheme 2, Process 4).

Scheme 2. Proposed Mechanism of CCS Polymer Formation via ROP



Based upon the results obtained, a mechanism of PCL CCS polymer formation via ROP can be proposed (Scheme 2), whereby four distinct and sequential processes occur: (1) reactive block polymer formation (i.e., chain-extension of MI with BOD); (2) polymer linking to form CCS polymers; (3) growth of CCS polymers, and (4) cleavage of *l*-PCL arms as a result of intramolecular transesterification. The cleaved *l*-PCL can either attack the preformed star polymers through (5) intermolecular transesterification with the arms, which leads to the generation of new *l*-PCL chains without any overall change in the amount of *l*-PCL, or (6) intramolecular backbiting to give *c*-PCL and another *l*-PCL with lower MW.

To demonstrate the effectiveness of the organic catalyst-mediated ROP for star polymer synthesis, CCS 4 was prepared via ROP catalyzed by Sn(Oct)$_2$ in toluene at 110 °C over 48 h (while keeping all other reaction conditions constant) and compared to CCS 1a (Table 1). Comparison of the GPC results for both CCS 4 and CCS 1a (SI, Figure S3) reveals several important differences. For example, the GPC RI chromatogram of CCS 4 shows a large shoulder peak (Figure S3A, i) and a higher percentage of unincorporated polymers (Figure S3, ii and iii). The large shoulder peak most likely corresponds to high MW star–star coupled products that formed as a result of elevated reaction temperature (110 °C) and long reaction time (48 h) (Figure S3A).[28] Since Sn(Oct)$_2$ has a high rate of transesterification even at relatively low monomer conversions,[18] transesterifications are more pronounced in Sn(Oct)$_2$-catalyzed star formation, which leads to a larger amount of the unincorporated polymers (i.e., cyclic oligomers *c*-PCL and cleaved linear polymers *l*-PCL) (Figure S3, ii and iii). Therefore, CCS 4 only contains approximately 85% star polymers, even taking the star–star coupled products into account. In contrast, CCS 1a synthesis was completed within 24 h, the GPC RI chromatogram shows no formation of star–star coupled products (Figure S3B), and the final yield of the star was 95%. Overall, this comparison reveals that by performing star polymer synthesis using organic catalysts (e.g., methanesulfonic acid) with low rates of transesterification, at low reaction temperatures, the amount of unconverted *l*-PCL and *c*-PCL (Figure S3, ii and iii) caused by inter- or intramolecular transesterification reactions can be significantly reduced, but not completely eliminated (Figure S3B).

In summary, we have demonstrated the facile and near-quantitative synthesis of PCL-based star polymers via the arm-first approach using organic catalyst (i.e., methanesulfonic acid) mediated ROP. The star polymers can be prepared either using a two-pot or a one-pot two-step strategy in high yields of 90–96% (macroinitiator-to-star conversion) from PCL macroinitiators with molecular weights ranging from 9.9 to 36.2 kDa. Detailed characterization of the reaction products, including the unincorporated PCL-based polymers, suggests that transesterification prevents the quantitative synthesis of PCL-based CCS polymers via ROP. Compared to the previously published synthetic approach catalyzed by the organometallic complex stannous octoate, the new reaction system utilizing the organic catalyst displays improved yields, but most importantly no star–star coupling products, which is attributed to the lower reaction temperatures, fast star formation rate, and lower transesterification rates. This study provides a facile, high yielding approach for the synthesis of CCS polymers via organic catalyst-mediated ROP and requires far less demanding reaction conditions than other controlled polymerization techniques. Hence, we anticipate that the reported synthetic approach will be applicable to the synthesis of a wide variety of polyester-based functional star polymers and aid in the development of advanced materials, commercial applications, and academic research.

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■ ASSOCIATED CONTENT

Supporting Information

Text giving materials and experimental and characterization procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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