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Dependence of Copolymer Sequencing Based on Lactone Ring Size and ε-Substitution

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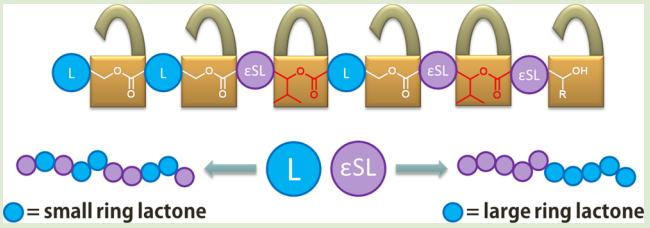
Supporting Information

ABSTRACT: The copolymerization of an ε-substituted ε-lactone, menthide (MI), and a range of nonsubstituted lactones (6-, 7-, 8-, and 9-membered rings) was investigated in order to determine the factors that affect the sequencing of the MI copolymers. Analysis by quantitative ^{13}C NMR spectroscopy showed the copolymerization of MI with a nonsubstituted lactone of ring size 7 or less produced a randomly sequenced copolymer, as a consequence of the smaller lactone polymerizing first and undergoing rapid transesterification as MI was incorporated. Conversely, copolymerization with larger ring lactones (ring size 8 and above) produced block-like copolymers as a consequence of MI polymerizing initially, which does not undergo rapid transesterification side reactions during the incorporation of the second monomer. Terpolymerizations of a small ring lactone, macrolactone, and menthide demonstrated methods of producing lactone terpolymers with different final sequences, depending on when the small ring lactone was injected into the reaction mixture.



The use of lactones in ring-opening polymerization (ROP) has been studied in a range of materials including biomedical materials,[1−6] polymer brushes,[7,8] cross-linked networks,[9−11] telechelic polymers,[12,13] and self-assembling copolymers.[14,15] However, a major drawback in the application of copolymer materials from lactones has been transesterification side reactions, including inter- and intramolecular transesterification, which has been shown to result in random copolymers with broad dispersities.[16−24] This has made advanced polymer architectures such as multiblock copolymers or sequence-controlled block copolymers difficult to achieve. While significant advances have been made in controlling the sequence of monomer addition using stereochemistry,[25−28] commonly, copolymerization of lactones in one pot leads to randomly sequenced copolymers as a consequence of transesterification side reactions occurring alongside ROP.[22−24,29,30] This is amplified in the ROP of large ring (macro)lactones, such as ambrettolide (Amb), in which the formation of low molecular weight cyclic species through the ring-expansion transesterification is an intrinsic aspect of the reaction;[31] however, the control over sequence of monomer addition could have significant effects on the subsequent behavior and degradation of the resultant materials.[16,32,33]

Transesterification side reactions can be curbed through careful choice of monomer. For example, small ring lactones polymerize rapidly and can be terminated before transesterification side reactions can occur. However, in order to produce a block copolymer in one pot, the sequence relies on differences in reactivity ratios between the monomers, one monomer must have a much slower rate of polymerization than the other, while avoiding competitive transesterification side reactions that randomize the polymer chain sequence. Despite these limitations, the one-pot copolymerization of a lactone with another monomer, such as a vinyl alcohol or a carbon dioxide/epoxy mixture, which rely on different polymerization techniques to produce block copolymers have been previously demonstrated.[34−36] Block copolymers of lactones have also been produced through sequential polymerization of each monomer, most frequently implemented in copolymerizations of lactide and ε-caprolactone (εCL).[3−5,19,20,29,37−39] Recently, however, Duchateau and co-workers showed that it is possible to produce a block copolymer of ε-decalactone (εDL) and ω-pentadecalactone (PDL).[21,22] Interestingly, the same study showed that the copolymerization of εDL with εCL yielded statistical copolymers. We further demonstrated the versatility of this approach to show that block-like copolymers are achievable in the copolymerization of PDL with ε-lactones that are functionalized on the ε-carbon as a consequence of hindered transesterification on the ester linkage that is formed.[40]

Observing the different polymer microstructures obtained in the copolymerization of εDL with lactones of different ring size, PDL (16-membered ring, block-like) and εCL (7-membered ring, statistical), we were curious to investigate the microstructure of polymers resulting from the one-pot copolymerization of ε-substituted ε-lactones (εSLs) and a nonsubstituted

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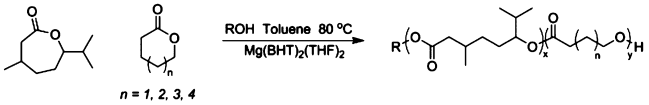
lactone of varying ring size, in order to potentially create complex materials with controllable behavior. We show for the first time that a monomer ring size of 8 is the critical point at which block copolymers become the preferred microstructure. Furthermore, we demonstrate the ability to overcome this inherent sequence control to produce random copolymers of the εSL, menthide, and macrolactones through terpolymerization.

The copolymerization of menthide (MI) with PDL has been shown to produce copolymers with block-like sequencing as a consequence of the rapid polymerization of MI, followed by the incorporation of PDL, with no transesterification side reactions occurring in the MI block.[40] In order to determine whether all MI-lactone copolymers are block-like, the copolymerization of MI was investigated with other nonsubstituted lactones; δ-valerolactone (δVL), εCL, ζ-heptalactone (ζHL), and η-caprylolactone (ηCL) of varying ring size (Scheme 1, Table 1) using $Mg(BHT)_2(THF)_2$ as a catalyst. All polymerizations proceeded to high monomer conversions (≥75%), however the dispersity ($Đ_M$) for each copolymer was high, which indicates that transesterification side reactions of the nonsubstituted lactones occurred in each case, consistent with MI/PDL copolymerization.[40] DOSY NMR spectroscopy confirmed that, in each copolymerization, only one polymer species had been formed, that is, only copolymers were produced in the copolymerization and no homopolymer species resulted (Figure S1).

Scheme 1. Copolymerization of Menthide with Nonsubstituted Lactones Catalysed by $Mg(BHT)_2(THF)_2$



The MI/δVL copolymer was analyzed by quantitative ^{13}C NMR spectroscopy (Figure 1a). Each carbonyl diad resonance observed (MI*−MI, MI*−δVL, δVL*−MI, δVL*−δVL, where * denotes the observed carbonyl) had equivalent integrals and, therefore, equal quantities of each type of carbonyl within the copolymer, which is characteristic of a random copolymer (Table 1, entry 1). In a previous study, it was determined that when using $Mg(BHT)_2(THF)_2$ as a catalyst, the polymerization of δVL to DP50 is extremely rapid (under 5 min).[16] Hence, transesterification moves a chain end MI unit to the middle of the chain before another MI unit is added to the chain end. As the transesterification side reactions are randomly placed, the final copolymer would be completely random in sequence once all MI has been incorporated. This is the opposite to the copolymerization of MI and PDL, where the unsaturated

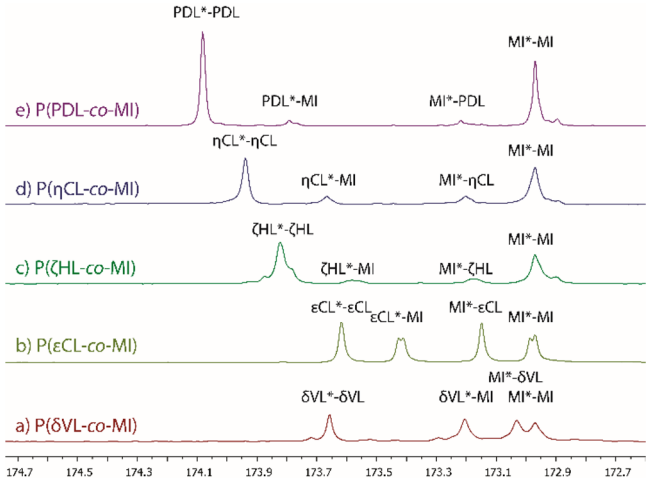


Figure 1. Quantitative ^{13}C NMR spectra of the carbonyl region for copolymers of menthide with (a) δ-valerolactone, (b) ε-caprolactone, (c) ζ-heptalactone, (d) η-caprylolactone, and (e) ω-pentadecalactone at 1:1 mol % monomers with a total DP of 100 (125 MHz, $CDCl_3$, 298 K).

lactone polymerizes after the substituted lactone and is a consequence of the higher affinity of δVL to the catalyst as well as its higher ring strain compared to MI and PDL. As PMI is thought to exhibit little to no transesterification, the ester linkage in PMI could be "locked" against transesterification side reactions. The prevention of transesterification side reactions by the isopropyl group in esters MI*−MI and δVL*−MI means transesterification only occurs on the esters, δVL*−δVL and MI*−δVL. Similarly, copolymerization of MI and εCL was also found to result in randomly sequenced copolymers (Figure 1b). Again, the rapid homopolymerization of εCL (cf. MI)[40] is postulated to result in ROP of ε-CL, but again, as MI is added to the chain-end, transesterification side reactions occur before the addition of another MI unit (i.e., the rate of transesterification of PCL is greater than the rate of ROP of MI), which causes a random copolymer to form.

In contrast, quantitative ^{13}C NMR spectroscopic analysis (Figure 1c) of the copolymerization of MI with ζHL (an 8-membered ring lactone) showed the carbonyl diad resonances to have unequal integrals, with larger resonances observed for ζHL*−ζHL and MI*−MI carbonyl diad resonances than ζHL*−MI and MI*−ζHL carbonyl diad resonances. The sequencing of the polymer chain is therefore block-like and not random. Copolymerization of MI with ηCL (a 9-membered ring lactone) similarly produced copolymers that exhibited the same block-like behavior as P(ζHL-*co*-MI). Thus, copolymerizations of MI with lactones containing larger ring size than 7 (εCL) have been found to only form block-like copolymers,

Table 1. Copolymerizations of Menthide with a Linear Lactone at 1:1 mol % Targeting an Overall DP of 100

		conversion[a] (%)								diads[c]				
lactone (L)	ring size	MI	L	total	M_{p}[b] (GPC) (kDa)	M_{n}[b] (GPC) (kDa)	M_{w}[b] (GPC) (kDa)	$Đ_M$[b]	M_{n}[a] (NMR) (kDa)	L*−L	L*−MI	MI*−L	MI*−MI	sequencing
δVL	6	60	90	75	5.8	23.9	5.5	2.3	9.7	0.22	0.28	0.26	0.25	random
εCL	7	60	97	79	37.7	28.0	40.9	1.5	10.7	0.24	0.24	0.25	0.27	random
ζHL	8	74	87	81	11.6	3.8	11.9	3.1	11.9	0.45	0.05	0.09	0.42	block-like
ηCL	9	57	94	76	19.2	18.4	28.1	1.5	10.9	0.40	0.08	0.09	0.43	block-like

[a]Determined by ^1H NMR spectroscopy. [b]Determined by SEC in $CHCl_3$ against poly(styrene) standards. [c]Determined by quantitative ^{13}C NMR spectroscopy, with * defining the carbonyl analyzed.

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which is potentially a consequence of the lower activity of the catalyst toward these larger ring lactones.

As such, we postulate that the polymer microstructure is dependent on reactivity of the monomers (which, in turn, is dependent on their ring strain, among other factors). While all nonsubstituted lactones do undergo transesterification at some point in the copolymerization, as evidenced by a broad $Đ_M$ in each case, the effect on the polymer sequencing is dependent on whether MI has already been polymerized. For monomers that are less reactive than MI in ROP, consumption of the comonomer after MI, combined with the much lower rates of transesterification for PMI, which is a result of steric hindrance around the linear ester results in a block of linear lactone formed second that can only undergo transesterification within itself. However, if the comonomer is more reactive than MI, a PMI block is not formed and hence, transesterification side reactions that occur concurrently with MI incorporation results in randomly sequenced copolymers.

Further investigation of the transesterification behavior in these systems showed that the homopolymerization of MI under the same conditions led to only a small increase in dispersity ($Đ_M$ = 1.3) after 1 week (after 5 h: 75% monomer conversion, $Đ_M$ = 1.26) broadening further to $Đ_M$ = 1.5 after 2 weeks. These results show that transesterification side reactions are occurring, albeit very slowly in comparison to poly(εCL). This is most likely an effect of the ε-substituent sterically hindering the transesterification of the PMI. In order to determine if transesterification occurred between adjacent MI units (MI*−MI), the transesterification of a DP_5 PCL and a DP_{50} PMI (M_n = 650 and 8400 g·mol^{-1}, respectively) was studied in a 1 M solution in toluene, with $Mg(BHT)_2(THF)_2$ at 80 °C. After 72 h, SEC analysis of the resultant polymer showed two distinct molecular weight peaks that correspond to the original homopolymers (Figure S2). Further analysis of the final material by quantitative ^{13}C NMR spectroscopy showed less than 1% of carbonyl diad resonances were attributable to adjacent εCL and MI repeat units, thus, confirming that transesterification into MI−MI sequences is severely retarded, unlike as commonly observed in other polyester blends.[16,24]

As a consequence of this reduced transesterification within poly(εSL)s, the production of random copolymers is difficult to achieve. Both εSL monomers and macrolactones are known to produce random copolymers with small nonsubstituted lactones; therefore, we postulated that a terpolymerization of an εSL monomer with a macrolactone and smaller lactone could produce polymers with random sequencing. From the above results and previous work,[16] it can be assumed that the rate of consumption of each monomer will be εCL ≫ MI > PDL, and as shown, transesterification of εCL will occur while MI is consumed to form a random copolymer. While midchain MI would be "locked-in", when PDL is added to the chain end, transesterification of "unlocked" esters (εCL*−εCL and MI*−εCL) would still occur, thus, randomizing the polymer sequence, albeit with the absence of PDL*−MI resonances. As such, the terpolymerization of equimolar quantities of εCL, MI, and PDL under the conditions used in this study was conducted. ^{1}H NMR spectroscopy showed complete consumption of εCL within 1 h of polymerization, with PDL consumed more rapidly than MI over the next 5 h (Figure 2). The quicker consumption of PDL compared to MI is possibly a consequence of the preference of MI for propagation from a menthide chain end (evidenced by the slow initiation from benzyl alcohol).[40] Analysis of the final copolymer by

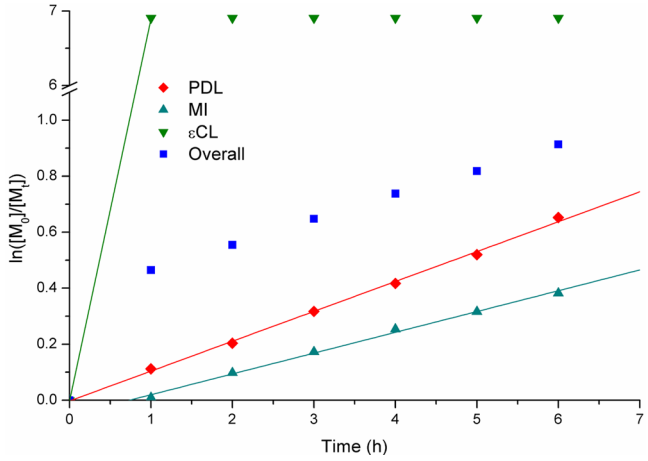

Figure 2. Semilogarithmic kinetic plot for the terpolymerization of ε-caprolactone, menthide and pentadecalactone, conducted at 80 °C in toluene with $[εCL]_0/[PDL]_0/[MI]_0/[BnOH]_0/[cat.]_0$ = 50:50:50:1:1.

quantitative ^{13}C NMR spectroscopy showed that, in contrast to our expectation, the final copolymer contained all nine possible carbonyl diad resonances (Figure 3). The relative integrals for each of the εCL and MI carbonyl diad resonances were all equivalent, suggesting random sequencing of these

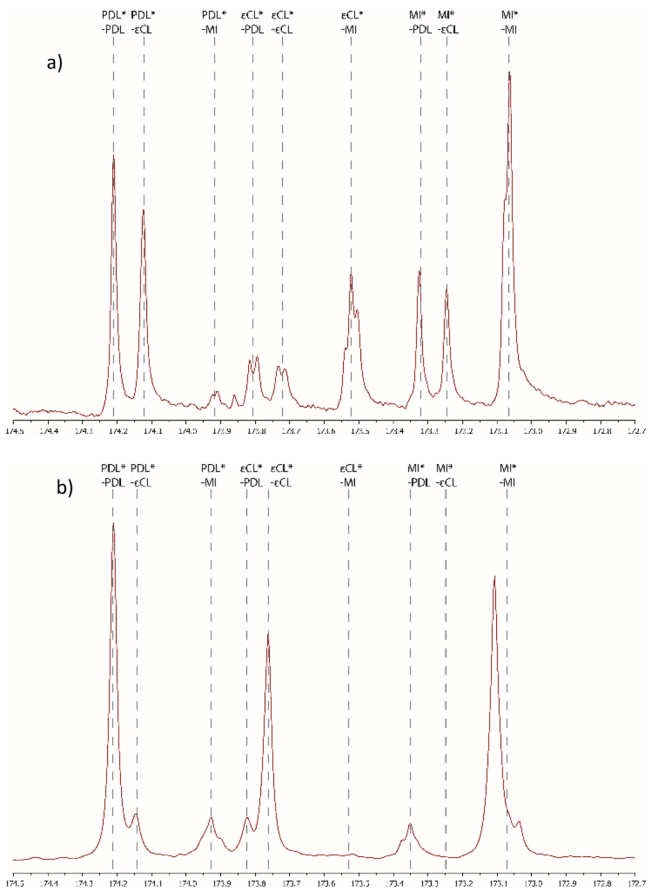

Figure 3. Quantitative ^{13}C NMR spectra of the carbonyl region for (a) the one-pot terpolymerization of equimolar quantities of ε-CL, MI, and PDL with an initial concentration of $[εCL]_0/[MI]_0/[PDL]_0/[BnOH]_0/[cat.]_0$ = 50:50:50:1:1, and (b) the copolymerization of equimolar quantities of MI and PDL with a timed injection of ε-CL (125 MHz, $CDCl_3$, 298 K).

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monomers throughout the polymer chain (Table S2). However, in the case of PDL carbonyl diad resonances only PDL*−PDL and PDL*−εCL diad resonances exhibited similar integrals and the integral corresponding to the PDL*−MI carbonyl diad resonance accounted for less than 1% of the carbonyl diad resonances, which can only be accounted for by PDL monomer being added to the chain end immediately after a MI monomer is added and before transesterification side reactions have occurred.

As the terpolymerization of εCL, MI and PDL is shown to occur with more rapid PDL incorporation than MI incorporation, reducing the molar ratio of εCL with respect to PDL and MI should allow for more transesterification during MI incorporation, producing a more prevalent PDL*−MI carbonyl diad resonance and therefore closer to random polymer sequencing. As such, the terpolymerization of εCL, MI, and PDL was carried out at a molar ratio of 10:50:50 εCL/MI/PDL. Analysis of the resultant material by quantitative ^{13}C NMR spectroscopy revealed the presence of all nine expected carbonyl diad resonances, however two carbonyl diad resonances (PDL*−PDL and MI*−MI) appear prominently and with larger relative integrals than would be expected with a randomly sequenced terpolymer (Table S2). In contrast to our expectations, this procedure yields block-like copolymers, most likely as a consequence of the low quantity of εCL reducing the amount of transesterification.

We also postulated that the introduction of ε-caprolactone into a P(MI-*co*-PDL) prepolymer could randomize the chain through transesterification side reactions during εCL incorporation, similar to the sequential polymerization of PDL followed by εCL.[16] This could then be used to produce a MI block-like copolymer with a tunable, degradable segment.[16] The copolymerization of equimolar quantities of PDL and MI was undertaken before addition of a 1 M solution of εCL in toluene after 8 h. After a total 24 h of polymerization, the resultant polymer was shown to possess block-like sequencing of all monomers by ^{13}C NMR spectroscopy (Figure 3b). Interestingly, the only carbonyl diad resonances observed relating to εCL incorporation were PDL*−εCL, εCL*−PDL, and εCL*−εCL, no εCL*−MI or MI*−εCL diads were observed. Furthermore, the significant difference in integration between the large PDL*−PDL and εCL*−εCL carbonyl diad resonances compared to the smaller PDL*−εCL and εCL*−PDL carbonyl diad resonances is indicative of a more block-like sequencing with a gradation between these blocks also. This is unexpected given previous sequential additions of εCL to PDL polymerizations;[16,17,23,24] however, this does provide a method for the one-pot production of a εCL block-like terpolymer with two other lactones.

The copolymerization of the ε-substituted-ε-lactone, menthide, with nonsubstituted lactones of varying size has been shown to enable unique ROP behavior. The presence of the ε-substitution has been shown to severely hinder transesterification side reactions that enable the synthesis of statistical or block copolymers, depending on the relative polymerization rates of the monomers. The differences in ROP and transesterification reactivities of MI, small ring lactones and macrolactones were then used to demonstrate the production of terpolymers with different polymer sequences resulting from the time at which the smaller lactone is introduced into the polymerization.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00940.

SEC chromatograms and ^{13}C NMR spectra (PDF).

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Notes

The authors declare no competing financial interest.

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