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Dual Catalysis for the Copolymerisation of Epoxides and Lactones

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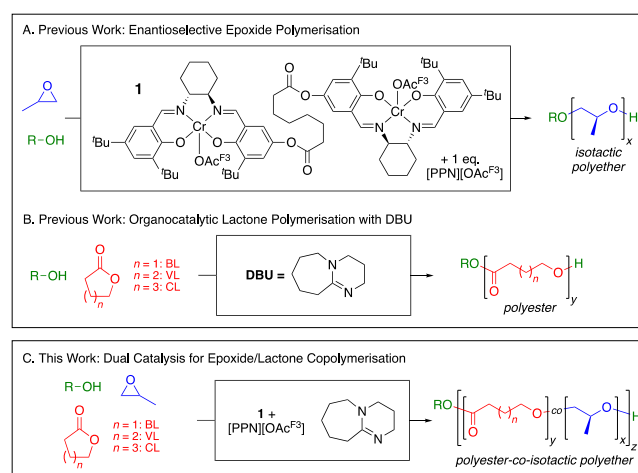
Abstract: A dual catalysis system was developed to synthesize hydrolyzable polyether-polyester copolymers from propylene oxide and cyclic esters such as γ -butyrolactone, δ -valerolactone, and ϵ -caprolactone. A bimetallic chromium catalyst active for the enantioselective polymerisation of propylene oxide and an organocatalyst active for the ring-opening polymerisation of lactones were used in conjunction with an alcohol chain shuttling agent to create new copolymers. The monomer and alcohol ratios were varied to yield a wide range of copolymers with varying monomer ratios, molecular weights, and crystallinities.

Copolymerisation is a common and versatile technique to optimize the macroscopic properties of polymeric materials by varying their microstructures. Polyether-polyester copolymers have been synthesized with a variety of monomers to access alternating,¹⁻³ blocky,³⁻¹² and statistical¹³ structures. Incorporation of ester functionality into the polymer backbone allows for hydrolytic degradation, a feature absent in polyether homopolymers.^{13,14} Additionally, incorporation of mechanically robust isotactic polyether segments could improve the physical properties of biodegradable polyesters, increasing their usefulness.¹⁵ With the improvement in physical properties, the copolymerisation of lactones and epoxides could produce materials that improve upon some of the shortcomings of current biodegradable plastics.

To the best of our knowledge, no polyether-polyester copolymers with stereoregular polyether segments have been reported. Polymer tacticity imparts improved thermal and mechanical properties; atactic poly(propylene oxide) (α PPO) is an amorphous material with a T_g of -70 °C, whereas isotactic poly(propylene oxide) (i PPO) is a semi-crystalline polymer with

a T_m of 67 °C.¹⁶ One of the largest industrial applications of telechelic α PPO is for the synthesis of polyurethanes.^{17, 18} We recently reported an immortal, enantioselective bimetallic chromium-salen catalyst (**1**, Scheme 1A) that polymerises racemic propylene oxide (PO), to give isotactic polymer with low dispersities and excellent control of molecular weight.¹⁹ This is the first system that achieves stereocontrol from a racemic monomer feed with control over molecular weight, whereas previous reports of bimetallic catalysts detail the synthesis of i PPO with less control over dispersity.^{16, 20, 21} The addition of an alcohol chain transfer agent (CTA) to **1** affords an immortal system that we recognized may be compatible with other polymerisation systems; the addition of other monomers and catalysts has the potential to afford i PPO copolymers with interesting and unexplored properties such as biodegradability.

Use of bifunctional CTAs such as 1,6-hexanediol (HD) in conjunction with **1** enables multiple chains to be synthesized by every metal centre. This process affords a telechelic polyether, with polymer chains bearing alcohol end-groups when grown



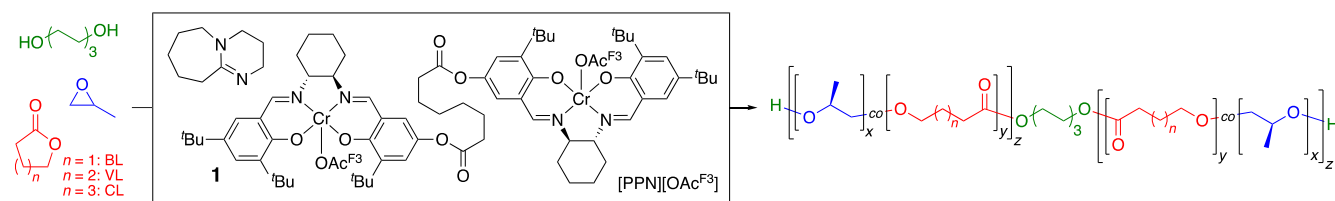
Scheme 1. A. Enantioselective epoxide polymerisation by complex **1**. B. Ring-opening polymerisation of lactones by DBU. C. Copolymerisation of propylene oxide and lactones (γ -butyrolactone ($n = 1$: BL), δ -valerolactone ($n = 2$: VL), ϵ -caprolactone ($n = 3$: CL)) using dual catalysis.

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Table 1. Effect of varying lactone (L) monomer identity, [PO]₀: [L]₀ feed ratios, and 1,6-hexanediol CTA loading on copolymerisation behaviour.^a

Entry	Lactone (L)	PO:L	HD:1	Conv. L ^b (%)	Conv. PO ^c (%)	% Ester ^b	M _n theo. ^d (kDa)	M _n GPC ^e (kDa)	Đ ^e	[mm] ^f	T _m ^g	ΔH _{fus} ^g (J/g)
1	VL	100:1	5	24	16	1.5	9.7	9.4	1.10	92	55	52
2	VL	100:1	10	45	29	1.1	10.5	17.0	1.09	96	58	53
3	VL	100:1	20	65	10	4.0	1.7	- ^h	- ^h	95	19	46
4	VL	10:1	10	22	18	7.4	7.6	9.8	1.16	97	45	59
5	VL	1:1	10	25	23	56.1	22.4	11.1	1.20	- ⁱ	17	3
6	BL	10:1	10	3	9 ^b	2.7	3.2	5.5	1.14	95	53	55
7	CL	10:1	10	5	21	1.6	8.4	9.4	1.08	96	54	66

^a Polymerisation conditions: 2.0 mg **1**; [PO]₀: [L]₀: [[PPN][OAcF₃]]₀: [DBU]₀ = 6000:1:1:5; t_{rxn} = 6h. ^b Determined by ¹H NMR spectroscopy. ^c Determined gravimetrically.

^d [(g lactone) × (% conversion lactone)/100] + [(g PO) × (% conversion PO)/100] / (mmol HD + mmol Cr cat). ^e Determined by GPC relative to polystyrene standards at 30 °C in THF. ^f Determined by ¹³C NMR spectroscopy. ^g Determined by DSC. ^h Not determined because peak fell outside calibration region. ⁱ no [mm] peaks resolvable in the ¹³C NMR spectrum.

off the CTA. We therefore sought to copolymerise PO with other monomers, which once polymerised, also result in alcohol chain ends. Waymouth²²⁻²⁷ and others²⁸⁻³⁰ have utilized base catalysts to accomplish the ring-opening polymerisation (ROP) of cyclic esters and carbonates to afford hydroxyl end-functional polymers (Scheme 1B). We hypothesized that given a base that is both active for ROP of lactones and compatible with the conditions necessary for the **1**-mediated enantioselective polymerisation of PO, chain shuttling between the two catalysts would produce *i*PPO-polyester copolymers.

Homopolymerisation of PO by **1** with [PPN][OAcF₃] ([PPN]⁺ = [Ph₃P–N=PPh₃]⁺) cocatalyst in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) proceeded to 12% conversion in 10 hours, as compared to 17% conversion in the absence of DBU (See Figure S8 in the SI). Likewise, a homopolymerisation of *L*-lactide by DBU in the presence of one equivalent of a monometallic Cr(salen) complex relative to DBU proceeded to 71% conversion in 12 hours as compared to 89% in the absence of Cr(salen) (See Figure S7 in SI). This result was unsurprising since DBU has previously been used in conjunction with a similar Cr(salen) catalyst to synthesize polyester-polycarbonate block copolymers.⁷ While the presence of an additional catalyst moderately slowed both homopolymerisations, appreciable monomer conversions were reached, signifying the compatibility of these catalyst systems. Thus, we determined that a DBU and Cr(salen) dual catalyst system could be viable for the copolymerisation of cyclic esters and epoxides.

Due to their prevalence, we pursued the polymerisation of propylene oxide with γ -butyrolactone (BL), δ -valerolactone (VL), and ϵ -caprolactone (CL).³¹ δ -Valerolactone can be polymerised by a variety of organic bases.²⁵ We found that this monomer was compatible with PO polymerisation by **1**. Once compatibility was established, initial screens to assess optimal catalyst, cocatalyst, and monomer loadings showed that optimal conversion of both monomers was obtained at a molar ratio of [1]₀: [[PPN][OAcF₃]]₀: [DBU]₀ = 1:1:5 with no solvent at 23 °C.

Having established optimal catalyst loadings, monomer feed ratios were studied (Figure 1; Table 1, Entries 2, 4–5). Modest conversions of both monomers were observed in well-controlled polymerisations at monomer feed ratios of [PO]₀: [VL]₀ = 100:1, 10:1, and 1:1 (Figure 1). In all cases, F₁ ≈ f₁, consistent with a statistical polymerisation. Copolymers produced at [PO]₀: [VL]₀ = 100:1 most closely resembled the homopolymer of *i*PPO, with a T_m of 58 °C (Table 1, Entry 2), compared to 67 °C for highly isotactic homo-*i*PPO. The final copolymer is comprised of 1.5% VL monomer units (Figure 2). The copolymer has a VL-rich segment at the beginning of the polymer chains, but no blocks are observed as there are no consecutive VL units (by ¹H NMR, see SI for more information). Only 1% of all PO units are followed by a unit of VL.

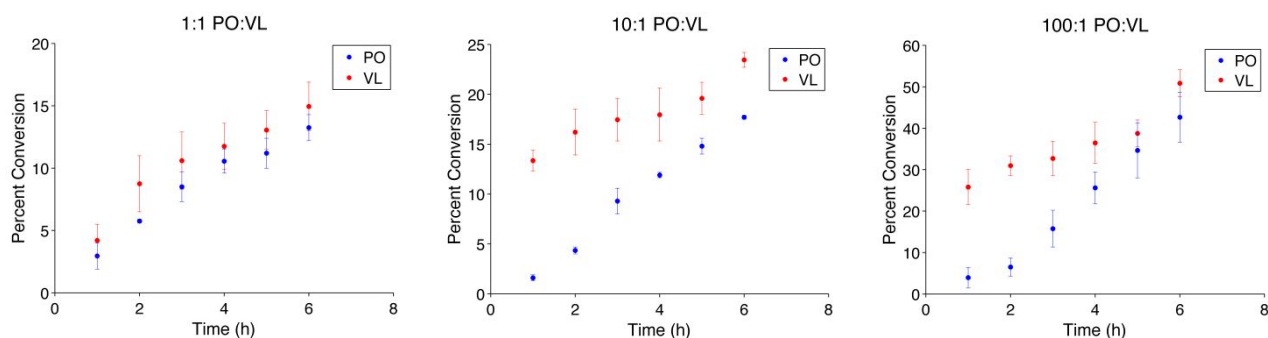


Figure 1. Polymerisation kinetics for the copolymerisation of PO and VL into PPO-PVL at monomer feed ratios of $[PO]_0:[VL]_0 = 1:1, 10:1,$ and $100:1$.

Decreasing the $[PO]_0:[VL]_0$ feed ratio drastically changes the properties of the resultant material. At a monomer feed ratio of $[PO]_0:[VL]_0 = 10:1$, the copolymer has a T_m of 45 °C (Table 1, Entry 4). Again, there is a VL-rich segment in the beginning of the polymer. This early enrichment yields a polymer in which 18.8% of VL monomers are followed by another VL even though VL only comprises 7.4% of the final material.

Interestingly, the VL enrichment effect observed early in the 10:1 $[PO]_0:[VL]_0$ copolymer lessened with a monomer feed ratio of 1:1. This material is amorphous at room temperature with a T_m of 17 °C (Table 1, Entry 5). With no VL enrichment at the beginning, composition of the copolymer is consistent throughout the polymerisation (Figure 2). VL comprises 51.6% of the final copolymer, and PO accounts for 48.4% (Figure 2). As evidenced by the thermal properties, the effect of semi-crystalline isotactic polyether is lost with such a high incorporation of lactone. The triad signals normally used to evaluate tacticity in *i*PPO are no longer observable in the NMR (Table 1, Entry 5).

To better understand the structure of the synthesized copolymers, the loading of a chain shuttling agent, 1,6-hexanediol (HD), was varied between 5 equivalents and 20 equivalents (Table 1, Entries 1–3). An increase in HD loading leads to an increase in shuttling between catalysts, resulting in a decrease in size of the *i*PPO blocks formed. Consequently, an

increase in chain shuttling agent also corresponds to a decrease in crystallinity with a melting temperature of 19 °C.

Having evaluated the copolymerisation behaviour of δ -valerolactone, we pursued copolymerisation of PO with ϵ -caprolactone (CL) and γ -butyrolactone (BL). CL behaved similarly to VL, with efficient incorporation of lactone into the copolymer (Table 1, Entry 7). Increasing the loading of lactone or 1,6-hexanediol decreased polymer crystallinity (See Table S1 in SI). Excitingly, BL, a monomer known for its difficulty to homopolymerise,^{32, 33} incorporates with the existing copolymerisation system, without requiring an increase in reaction temperature. BL behaved similarly to the other lactones, with incorporation increasing with higher BL loadings and crystallinity decreasing with increased chain shuttling agent loading (Table 1, Entry 6). While both CL and BL were incorporated into copolymers, their ratios of incorporation were consistently lower than that of VL (See Table S1 in SI). Although *L*-lactide was investigated as a comonomer, unfortunately only polylactide was formed. Since other groups have also experienced difficulty polymerising other monomers after lactide,^{3, 6} we suspect the lactate may form a chelate with **1**, sequestering it from further polymerisation activity.

In conclusion, we have synthesized a variety of new copolymers from propylene oxide with γ -butyrolactone, δ -valerolactone, and ϵ -caprolactone. Through variation of monomer and alcohol loadings, we can synthesize polymers with targeted ester content and crystallinity. Increased crystallinity afforded by the presence of *i*PPO is promising for improved polyester material properties, and incorporation of ester units into polyether materials increases the probability of biodegradability. These materials are the first examples of enantioselective polyether formation in polyether-polyester copolymers.

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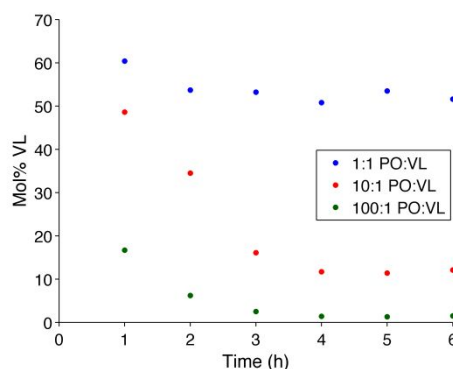


Figure 2. Mole percent valerolactone in the copolymer as a function of time.

Conflicts of interest

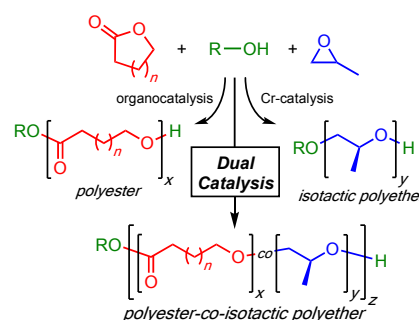
There are no conflicts to declare.

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Table of Contents Entry:

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