

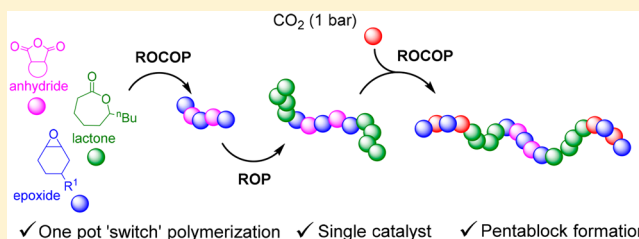
Pentablock Copolymer from Tetracomponent Monomer Mixture Using a Switchable Dizinc Catalyst

Thomas T. D. Chen, Yunqing Zhu, and Charlotte K. Williams*

Department of Chemistry, Chemistry Research Laboratory, 12 Mansfield Road, Oxford OX1 3TA, U.K.

Supporting Information

ABSTRACT: Well-defined pentablock copolymers are prepared using a single catalyst, in one pot, from four different monomers: anhydride, epoxide, lactone, and CO₂. The dizinc catalyst bridges three distinct polymerization cycles and performs a double switch in polymerization mechanism to produce pentablock copolymers. The new materials are hydroxyl-telechelic and are efficiently postfunctionalized to introduce polar and nonpolar side-chains.



Nature synthesizes molecules with exquisite product selectivity.¹ Synthetic chemistry struggles with selective reactivity from mixtures, although catalysis could solve the problem if directing of reaction pathways were better understood. Such selective catalysis could simplify process chemistry by obviating intermediate isolations and purifications, thereby reducing energy usage and costs. In polymerization catalysis, such selectivity may also deliver well-defined copolymer sequences.² The most widely investigated block polymers have AB or ABA structures, and applications include thermoplastic elastomers, toughened plastics, and drug delivery. More complex block structures are difficult to prepare (e.g., the number of potential block order variations are proportional to the factorial of the number of monomers used) but are expected to show superior properties.³ Multiblock copolymers are usually prepared using macroinitiators, followed by intermediate isolations and purifications, or by multiple timed monomer additions.^{4–8} A simpler strategy is to switch a single catalyst between different polymerization cycles, thus allowing the enchainment of a much greater variety of monomers. For example, Kamigaito and co-workers pioneered a trithiocarbonate initiator that switched between controlled radical acrylate and cationic vinyl ether polymerizations.⁹ Aoshima and co-workers applied B(C₆F₅)₃ to catalyze both cationic polymerization of vinyl ethers and epoxides.¹⁰

We target sustainable block copolymers featuring degradable ester/carbonate linkages and utilizing CO₂.¹¹ These materials may be prepared using lactone ring-opening polymerization (ROP) to form poly(lactones) or epoxide/CO₂ (anhydride) ring-opening copolymerization (ROCOP) to form alternating polyesters/polycarbonates (PE/PC).^{12–14} While terpolymerizations using a single mechanism are well-known,^{15,16} polymerizations applying both mechanisms are less investigated.^{17–19} Tandem catalysis, applied by Darensbourg and Wu, enabled linking of the catalytic cycles to form ABA block polymers.^{20,21} We reported a single catalyst active using mixtures of epoxides/CO₂/lactones, switching between

ROCOP and ROP, to produce block copolymers.^{19,22,23} Subsequently, CO₂ was replaced for anhydrides to form ABA block copolyesters.^{24,25} In 2017, Rieger and co-workers reported another dizinc catalyst selective for three-component monomer mixtures.²⁶ Recently, we reported how to switch a commercial Cr-Salen catalyst so as to prepare ABA triblocks (again from three component mixtures).²⁷ Until now, all studies applied only mixtures of three different monomers limiting the resulting sequence to AB(A). A previous DFT study of three-component mixtures suggested that a clear future target should be to investigate mixtures of four monomers, accessing three different catalytic cycles.²³ Here, we experimentally demonstrate such a selective catalysis using mixtures of four monomers and a single catalyst (Scheme 1).

Catalyst 1, [LZn₂Ph₂], was activated using *trans*-1,2-cyclohexanediol (CHD) to form the zinc alkoxide complex *in situ* (see Scheme S1 for the activation of 1 and Scheme S2 for ROP and ROCOP mechanisms).²⁸ This catalyst is selected because it is highly controlled, yielding only hydroxyl-telechelic polymers with monomodal molar mass distributions in each separate polymerization.^{24,28} The latter is paramount since most other ROCOP catalysts result in bimodal molar mass distributions with differing end-groups.^{20–22,24,29,30} Such bimodality prevents selective multiblock formation as it causes contamination by lower block sequences (i.e., AB/ABC/ABCB type).^{31,32} The catalyst system was reacted with four monomers (phthalic anhydride (PA)/cyclohexene oxide (CHO)/ε-decalactone (DL)/CO₂), at 0.1 mol % catalyst loading, and 100 °C under CO₂ (1 bar pressure). DL was chosen as the model lactone as it affords a secondary metal alkoxide propagating species when ring-opened which results in well-balanced kinetics and resistance to transesterification; both features are expected to be important for effective

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Scheme 1. Four Monomer Selective Polymerization, Using $[LZn_2Ph_2]$ (**1**)/*trans*-1,2-Cyclohexanediol (CHD) Catalytic System (See Scheme S1 for *in Situ* Activation of the Catalyst)

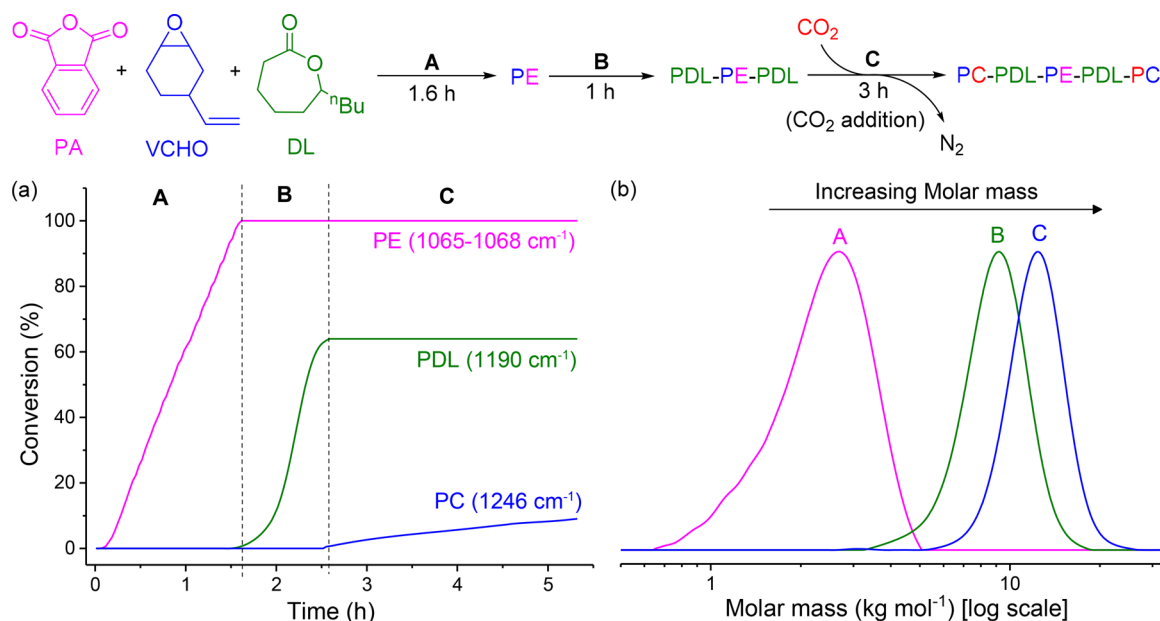
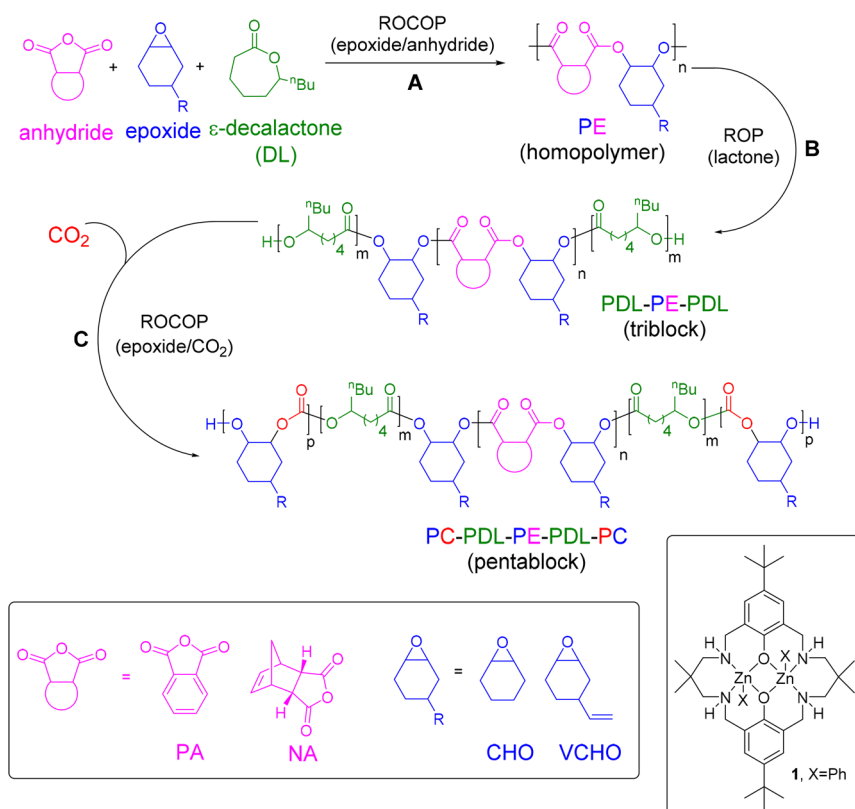


Figure 1. Polymerization of tetracomponent monomer mixture: PA/VCHO/DL/CO₂; $[1]/[CHD]/[PA]/[DL]/[VCHO] = 1/4/50/200/1000$, 100 °C, (A, B) N₂ and (C) CO₂, 1 bar. (a) Conversion vs time plot illustrating block formation: A (anhydride/epoxide ROCOP), B (lactone ROP), and C (epoxide/CO₂ ROCOP). Conversions obtained using *in situ* ATR-IR spectroscopy and calibrated using ¹H NMR spectroscopy (Figure S4). (b) SEC traces illustrating the increase in M_n and retention of D as the polymerization progresses (calibrated with narrow dispersity polystyrene standards).

polymerization control.³³ The reaction yielded only the PC–PE–PC triblock formed by ROCOP. To drive DL ROP, the CO₂ was completely removed, but poly(ϵ -decalactone) (PDL) block formation was not observed even after 20 h (Figure S3).

Rather, the *trans*-cyclic carbonate byproduct slowly evolved. The formation of *trans*-cyclohexene oxide indicates that chain backbiting occurred from the metal alkoxide intermediate (Scheme S3).³² Thus, while it is clear that the metal alkoxide

Table 1. Four Monomer Polymerizations Using Anhydride, Epoxide, Lactone, and CO₂^a

monomer combination	conversion ^b (%)			M _n (kg mol ⁻¹) [Đ] ^c			TOF ^d (h ⁻¹)		
	anhydride	lactone	epoxide ^e	A	B	C	PE ROCOP	PDL ROP	PC ROCOP
P1 PA/CHO/DL/CO ₂	>99	69	11	1.7 [1.12]	7.5 [1.15]	8.8 [1.11]	27	160	6
P2 PA/VCHO/DL/CO ₂	>99	64	14	2.1 [1.16]	8.4 [1.08]	12.1 [1.05]	32	128	30
P3 NA/CHO/DL/CO ₂	>99	79	12	1.4 [1.15]	6.5 [1.12]	8.4 [1.08]	4	126	9
P4 NA/VCHO/DL/CO ₂	>99	80	16	1.5 [1.15]	7.1 [1.11]	10.2 [1.14]	8	160	44

^a[1]/[CHD]/[anhydride]/[lactone]/[epoxide] = 1/4/50/200/1000, 100 °C, (A, B) N₂ and (C) CO₂, 1 bar. PA, NA, DL, CHO, and VCHO denote phthalic anhydride, *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride, ϵ -decalactone, cyclohexene oxide, and 4-vinyl-1-cyclohexene 1,2-epoxide, respectively. ^bObtained from ¹H NMR spectra (Figures S4 and S26–28). ^cMeasured by SEC, calibrated with polystyrene (Figures S23–S25). ^dCalculated from molar monomer conversion per mole of catalyst per hour. ^eNote: the apparently low overall conversions for epoxide are due to its dual use as monomer and solvent.

intermediate is accessed, the rate of backbiting reaction is proposed to occur faster than the initiation of DL ROP. This problem was overcome by a simple change in monomer addition order. First, the catalyst system was reacted with PA/CHO/DL, forming the desired PDL–PE–PDL copolyester (Scheme 1A,B). Thereafter, the N₂ atmosphere was replaced with 1 bar pressure of CO₂, resulting in selective PC–PDL–PE–PDL–PC pentablock formation.

The tetracomponent mixture polymerization was generalized to include a functionalized epoxide (vinylcyclohexene oxide, VCHO). Throughout the polymerization, aliquots were analyzed using ¹H NMR spectroscopy to quantify the monomer conversions against an internal standard (mesitylene) (Figure S4) and by SEC to quantify molar masses (Figure 1b). The initial ¹H NMR spectrum showed complete consumption of anhydride (8.02 and 7.90 ppm) and concurrent formation of polyester (7.66 and 7.50 ppm). The alternating copolymerization with VCHO was also confirmed (5.35 and 5.22 ppm). PDL blocks were only observed once all anhydride was consumed (4.84 ppm). The sequential block formation is also observed using *in situ* ATR-IR spectroscopy, where formation of PE (1065–1068 cm⁻¹) is followed by PDL (1190 cm⁻¹). To demonstrate the high selectivity, CO₂ was added before full DL conversion and an immediate switch from DL ROP to VCHO/CO₂ ROCOP occurred, as evidenced by the PC formation (1246 cm⁻¹). The ¹H NMR spectrum at this stage also showed the growth of a signal at 4.76 ppm assigned to PC (Figure S4). All IR and ¹H NMR resonances were assigned by comparison with resonances observed in the constituent polymers (Figures S5–S18).

It is important to note that high polymer conversions are achieved in each block, but as the epoxide is applied as both reagent and solvent its conversion appears lower. Nonetheless, the epoxide conversion is fully consistent with the formation of perfectly alternating PE and PC blocks. SEC analyses show a clear increase in molar mass with retention of narrow dispersity (Đ < 1.17) (Figure 1b). The catalyst maintains its activity throughout polymerization, with differing rates for each stage (Table 1). ³¹P{¹H} NMR spectroscopy enables characterization of chain end groups (Figure S19).^{24,34} During stage A peaks are observed at 146.7–146.8 ppm (assigned to PE) that shifted to a single peak for PDL (147.1 ppm) after stage B. Stage C revealed peaks consistent with PC formation (146.6–146.9 ppm). At all stages, hydroxyl end-group signals are observed. ¹H DOSY NMR analysis of the pentablock shows a single diffusion coefficient for all resonances, suggesting all blocks are joined (Figure S20, top). In contrast, a blend of the appropriate polymers, at related molar masses, shows three different diffusion coefficients (Figure S20, bottom). The

extent of transesterification must be understood since it could scramble block structure.³⁴ The pentablock copolymer showed no detectable transesterification: the ¹³C NMR spectrum showed three major carbonyl peaks, corresponding to each of the three blocks; furthermore, SEC analysis reveals narrow dispersity values throughout the polymerization (Figure S21). Purification of the crude pentablocks did not change their composition; i.e., there is no significant homopolymer contamination (Figure S22). Overall, the characterization data are consistent with selective pentablock copolymer formation. This polymerization breaks new ground in proceeding with *two switches* between *different polymerization mechanisms*, specifically from epoxide/anhydride ROCOP to lactone ROP, followed by epoxide/CO₂ ROCOP.

The generality of the four monomer switchable catalysis was investigated using various anhydride/epoxide combinations (Table 1). High selectivity for pentablock formation was observed in all mixtures. The anhydride was investigated using *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (NA) (Table 1, P3 and P4). Both reactions occurred first through NA/epoxide ROCOP (A), followed by DL ROP (B) and finally by epoxide/CO₂ ROCOP (C), as confirmed using *in situ* ATR-IR and ¹H NMR spectroscopy (Figures S24–S28). The SEC analyses show molar mass increases and narrow dispersity in all samples (Đ < 1.17) (Figures S24 and S25). The pentablock structures were once again confirmed using a range of techniques (*vide supra*) (Figures S29–S35). In all reactions, even though DL ROP is the faster reaction, the slower epoxide/anhydride ROCOP occurs first (Table 1). This selectivity is proposed to arise from the zeroth-order rate dependence on the insertion of anhydride and CO₂ into the zinc alkoxide intermediate (Figure 2).^{32,35} In addition, DFT investigations highlight the relative linkage stability as well as the overall barrier in controlling selectivity; the zinc carboxylate/carbonate intermediates (anhydride/CO₂ insertion) are significantly more stable than the alternative zinc alkoxide (lactone insertion).²³ Overall, the chemistry of the zinc chain end group controls the monomer selectivity, linking the three different polymerizations and controlling monomer discrimination.

Several of the pentablock copolymers contain alkene groups that were postfunctionalized to install different side chains. Generally, functionalized lactones are difficult to synthesize and polymerize which has limited investigation of functionalized, degradable polyesters. Recently, ROCOP was used to prepare various alkene-substituted polyesters and carbonates that were later efficiently reacted without compromising the polymer backbone.^{29,36–40} Here, the well-known thiol–ene reaction is applied to install alkane or hydroxyalkane

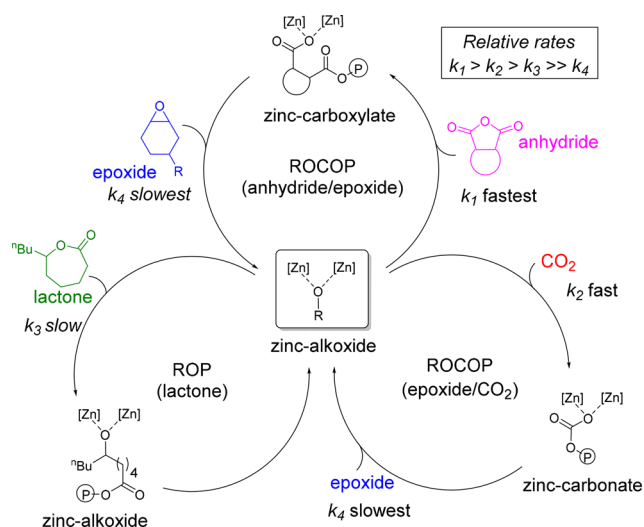


Figure 2. Proposed mechanisms occurring during polymerization of anhydride, epoxide, lactone, and CO_2 , highlighting the central role for the zinc alkoxide intermediate (P = growing polymer chain).

substituents.⁴¹ UV-initiated reactions were performed on pentablock **P2** using either 1-butanethiol or 2-mercaptoethanol (Figure 3). The reactions reached complete conversion within 2 h, as shown by ^1H NMR spectroscopy (Figure S37). The

double-bond resonances are consumed during the reaction (5.76 and 5.01–5.09 ppm), but all the other resonances remain unchanged (Figure S22). New resonances confirm attachment of the butyl thioether (2.51, 0.90 ppm) or hydroxyl ethyl thioether groups (3.72, 2.71, and 2.55 ppm). The functionalized polymers show slightly higher molar masses compared to the starting pentablocks with retention of monomodal, narrow dispersity; these findings suggest the polymer backbone remains intact. The pentablock copolymers **P3** and **P4** were also successfully reacted to produce analogous functionalized polymers (Table S1 and Figures S38–S41). In the case of the block copolymer **P4**, both internal and terminal double bonds react with the thiol reagent.

Preliminary assessment of pentablock copolymers' thermal properties indicates a single T_g for all polymers, suggesting amorphous structures with miscible blocks (Table S2). The block miscibility is tentatively attributed to the lower overall molar masses, since the propensity to undergo phase separation is directly correlated to degree of polymerization. Interestingly, the T_g was easily varied over the range -35 to 20 $^\circ\text{C}$. Moreover, the T_g can be further adjusted by side-chain functionalization: addition of hydroxyl alkyl side-chains increases the T_g (typically >20 $^\circ\text{C}$) compared to the precursor, presumably due to hydrogen bonding.⁴² The pentablocks' controllable, low T_g , low molar masses, and hydroxyl-telechelic structures indicate they are suited for further development as

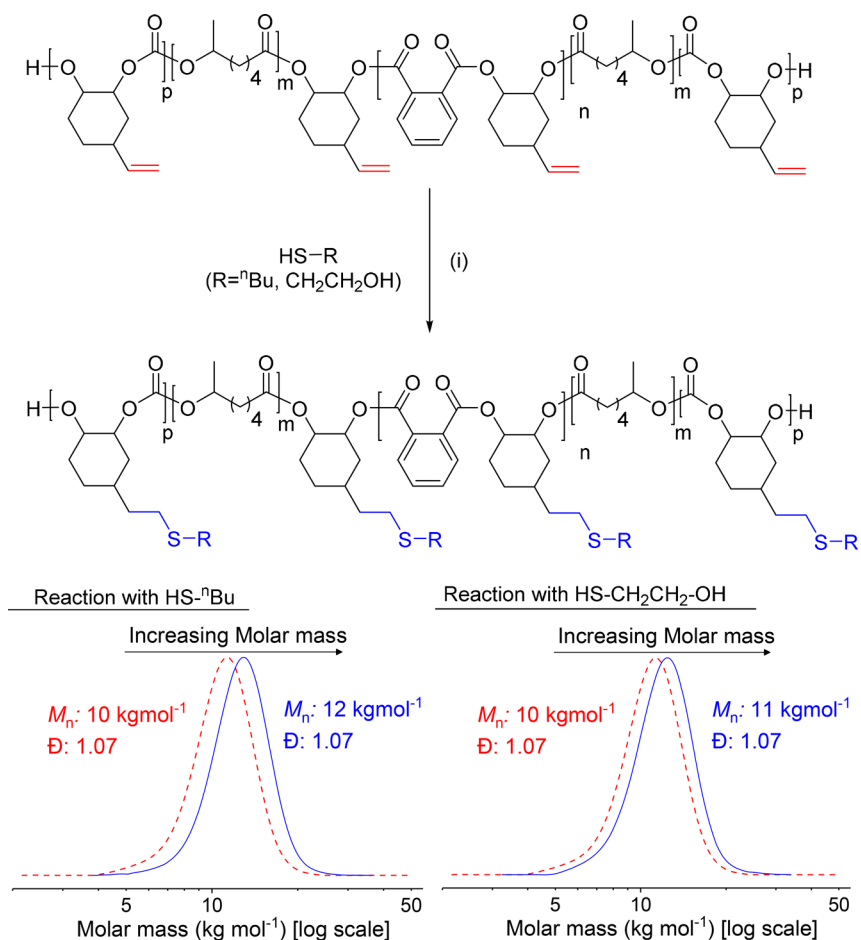


Figure 3. Thiol–ene functionalization of the pentablock copolymers. (i) 2,2-Dimethoxy-2-phenylacetophenone (DMPA, photoinitiator)/alkene/thiol reagent = 1/2.5/10, UV, 2 h, 25 $^\circ\text{C}$, CDCl_3 . Dashed red and solid blue lines illustrate the molar mass distributions before and after reaction, respectively.

polyols. Recently, polycarbonate polyols, produced using carbon dioxide ROCOP, are being commercially investigated for polyurethane manufacture; these new pentablocks significantly expand the range of carbon dioxide containing polyols.⁴³

In summary, switchable catalysis is demonstrated using mixtures of four monomers to selectively produce pentablock copolymers. The method applies a single catalyst in one pot to yield hydroxyl-telechelic pentablocks. Fundamentally, the catalyst accesses three different polymerization cycles and switches mechanism twice. Overall, the work demonstrates the high selectivity and complexity of block structures that can be delivered using switchable catalysis. More generally, it should be applicable to other catalysts and monomer combinations. Applications for the new pentablock polyols in areas such as semirenewable coatings, cross-linked resins, and polyurethane manufacture are recommended.⁴⁴ Finally, the switchable catalysis is expected to enable variation in polymer composition, block volume fraction, and molar mass producing new thermoplastic elastomers, toughened plastics, and even functionalized medical materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b01224.

Experimental section; Schemes S1 and S2, Figures S1–S52, Tables S1 and S2 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Charlotte.williams@chem.ox.ac.uk (C.K.W.).

ORCID

Charlotte K. Williams: 0000-0002-0734-1575

Notes

The authors declare the following competing financial interest(s): C.K.W. is a director and CSO of Eonic Technologies.

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