Pentablock Copolymer from Tetracomponent Monomer Mixture Using a Switchable Dizinc Catalyst

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ABSTRACT: Well-defined pentablock copolymers are prepared using a single catalyst, in one pot, from four different monomers: anhydride, epoxide, lactone, and CO$_2$. 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. 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. 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. Multiblock copolymers are usually prepared using macroinitiators, followed by intermediate isolation and purifications, or by multiple timed monomer additions. A simpler strategy is to switch a single catalyst between different polymerization cycles, thus allowing the enrichment of a much greater variety of monomers. For example, Kamiigaito and co-workers pioneered a trihydrocarbonate initiator that switched between controlled radical acrylate and cationic vinyl ether polymerizations. Aoshima and co-workers applied B(C$_6$F$_3$)$_3$ to catalyze both ring-opening copolymerization (ROCOP) and ring-opening polymerization (ROP) to form poly(lactones) or epoxide/CO$_2$ (anhydride) copolymers. Specifically, CO$_2$ was replaced for anhydrides to form ABA block copolymers. In 2017, Rieger and co-workers reported another dizinc catalyst selective for three-component monomer mixtures. Recently, we reported how to switch a commercial Cr-Salen catalyst so as to prepare ABA triblocks (again from three component mixtures). 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. Here, we experimentally demonstrate such a selective catalysis using mixtures of four monomers and a single catalyst (Scheme 1). Catalyst 1, [LZn$_2$Ph$_2$], 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). This catalyst is selected because it is highly controlled, yielding only hydroxyl-telechelic polymers with monomodal molar mass distributions in each separate polymerization. The latter is paramount since most other ROCOP catalysts result in bimodal molar mass distributions with differing end-groups. Such bimodality prevents selective multiblock formation as it causes contamination by lower block sequences (i.e., AB/ABC/ABCB type). The catalyst system was reacted with four monomers (phthalic anhydride (PA)/cyclohexene oxide (CHO)/ε-decalactone (DL)/CO$_2$), at 0.1 mol % catalyst loading, and 100 °C under CO$_2$ (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...
polymerization control.\textsuperscript{33} The reaction yielded only the PC−PE−PC triblock formed by ROCOP. To drive DL ROP, the CO\textsubscript{2} was completely removed, but poly(\(\varepsilon\)-decalactone) (PDL) block formation was not observed even after 20 h (Figure S3). Rather, the trans-cyclo carbonate byproduct slowly evolved. The formation of trans-cyclohexene oxide indicates that chain backbiting occurred from the metal alkoxide intermediate (Scheme S3).\textsuperscript{32} Thus, while it is clear that the metal alkoxide...
Table 1. Four Monomer Polymerizations Using Anhydride, Epoxide, Lactone, and CO$_2$\textsuperscript{ab}

| monomer combination | anhydride (%) | lactone (%) | epoxide (%) | conversion\textsuperscript{b} (%) | $M_n$ (kg mol$^{-1}$) | [D]\textsuperscript{c} | PE ROCOP | PDL ROC | PC ROCOP | TOF\textsuperscript{d} (h$^{-1}$) |
|---------------------|---------------|-------------|------------|----------------|------------------|-------|--------|--------|--------|-----------|----------------|
| P1                  | >99           | 69          | 11         | 1.7 [1.12]     | 7.5 [1.15]       | 8.8 [1.11] | 27     | 160    | 6      |          |
| P2                  | >99           | 64          | 14         | 2.1 [1.16]     | 8.4 [1.08]       | 12.1 [1.05] | 32     | 128    | 30     |          |
| P3                  | >99           | 79          | 12         | 1.4 [1.15]     | 6.5 [1.12]       | 8.4 [1.08] | 4      | 126    | 9      |          |
| P4                  | >99           | 80          | 16         | 1.5 [1.15]     | 7.1 [1.11]       | 10.2 [1.14] | 8      | 160    | 44     |          |

\textsuperscript{a}4/50/200/1000, 100 °C, (A, B) N$_2$ and (C) CO$_2$. 1 bar, PA, NA, DL, CHO, and VCHO denote phthalic anhydride, cis-5-norbornene-endo-2,3-dicarboxylic anhydride, e-decalactone, cyclohexene oxide, and 4-vinyl-1-cyclohexene 1,2-epoxide, respectively. \textsuperscript{b}Obtained from $^1$H NMR spectra (Figures S4 and S26–S28). \textsuperscript{c}Calculated from molar monomer conversion per mole of catalyst per hour. \textsuperscript{d}Note: the apparently low overall conversions for epoxide are due to its dual use as monomer and solvent.
substituents. 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. The pentablocks’ controllable, low $T_g$, low molar masses, and hydroxyl-telechelic structures indicate they are suited for further development as...
polyls. Recently, polycarbonate polyls, produced using carbon dioxide ROCOP, are being commercially investigated for polyurethane manufacture; these new pentablocks significantly expand the range of carbon dioxide containing polyls.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 polyls 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 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

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**Notes**

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

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