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How to better control polymer chemistry

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DOI:

[10.1126/science.aaw9863](https://doi.org/10.1126/science.aaw9863)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Foster, JC & O'Reilly, RK 2019, 'How to better control polymer chemistry', *Science*, vol. 363, no. 6434, pp. 1394-1394. <https://doi.org/10.1126/science.aaw9863>

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A Paradigm Shift in Polymerization Control

OR

Organo-Catalysts Turn Over a New Leaf in Functional Materials

Jeffrey C. Foster, Rachel K. O'Reilly

Polymer chemists have long endeavoured to gain control over the precise chemical structures of the polymers they synthesize. Polymers can have variable lengths and length distributions, chemically programmed units at each chain end, and different spatial arrangements of the pendant side chain atoms—a characteristic known as stereochemistry. Controlled polymerization techniques developed in the past three decades have provided excellent control over polymer length and chain end functionality;¹ however, new examples of stereo-controlled polymerizations are sporadic and few methods have been developed to a sufficient level for commercialization. Perhaps the most successful example of stereo-controlled polymerization was the development of metal-organic polymerization catalysts by Karl Ziegler and Giulio Natta in the early 1950s,² leading to the eventual market dominance of polyolefins such as polyethylene (PE) and polypropylene (PP) and a Nobel prize in chemistry for Ziegler and Natta in 1963.³ In the 70 years since this discovery, several key advances have been made toward stereo-controlled copolymerization of functional monomers with ethylene or propylene to expand the chemical diversity of stereo-controlled polymerization.⁴⁻⁹ On page XXX of this issue, Teator *et. al.* report an alternative strategy for preparing functional polymers with well-defined stereochemistry using organo-catalysts which exact exquisite control over the microstructure of poly(vinyl ethers)—oxygen rich analogues to PE/PP.

While PE/PP may have captured a majority of the plastics market, these materials are limited in their chemical diversity. In particular, these polymers, which are entirely comprised of carbon and hydrogen, have poor adhesion capability which limits their applications as adhesives, coatings, and in biomedical devices. In contrast, poly(vinyl ethers) (PVEs) possess excellent adhesive properties due to their high oxygen content.¹⁰ Until recently this improved adhesion came at a cost, as PVEs have low stereo-regularity based on the way they are synthesized, leading to poor mechanical performance.

A new report from Teator *et. al.* is poised to shift the materials paradigm towards highly functional materials with mechanical properties competitive to PE/PP by precisely controlling the stereochemistry of PVEs. The authors designed a new catalyst-controlled approach for the preparation of isotactic PVEs *via* cationic polymerization. This approach makes use of an organo-catalyst, which have advantages over inorganic catalysts which are used to make PE/PP including their low cost and low toxicity.¹¹ By carefully designing their catalyst to be stereoselective—the geometry of the catalyst complex influences the orientation of the monomers as they are polymerized—enchainment is directed towards one a single face of the propagating chain end, resulting in the formation of polymers with high structural regularity. This method was discovered to be compatible with a variety of vinyl ether monomers, implying broad scope for future industrial processes.

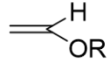
Even more impressive is the fact that the resulting PVEs produced using the author's catalytic method were found to possess mechanical properties comparable to commercial low-density polyethylene (LDPE) while also exhibiting adhesion that was more than an order of magnitude stronger. Endowing PE-like materials with strong adhesion could open up possibilities for next-generation adhesives, coatings, and biomedical devices, among other applications. These findings, coupled with the scalability of the polymerization procedure and the high processability (wide thermal window) of the resulting polymeric material signify an important breakthrough in the plastics field.

Moreover, translation of this simple and effective concept to other polymerization systems represents a logical progression and could rapidly push plastics manufacturing towards more highly functional materials. Indeed, the prospect of introducing control over polymer tacticity in non-hydrocarbon systems is a necessary and significant stepping stone in the direction of designing high-value, recyclable and degradable materials to meet global challenges.

The findings of Teator *et. al.* serves as a reminder that careful consideration of fundamental polymerization concepts can revitalize existing materials. Whilst research in the polymer community has trended towards polymers with increasingly complex chemistry and architecture, this work reinforces the importance of the central principles underlying the behaviour of polymer chains—in this case, the stereoregularity of the repeating units—with respect to their impact on the macroscopic properties of the resulting material.

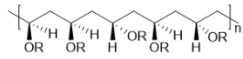
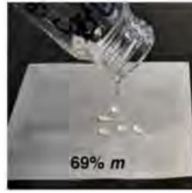
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Free radical
polymerization



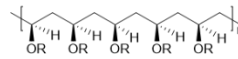
Stereo-controlled
polymerization

Amorphous
polymer



Atactic polymer sequence

Crystalline
polymer



Isotactic polymer sequence