

Metal Complexes for Catalytic Polymerizations

The production of polymers occurs worldwide on a scale exceeding 350 million tons/year, and polymerization catalysis is central to controlling the resulting polymers' physical-chemical properties and delivering cost-effective manufacturing.^{1,2} Catalyst selection is, therefore, critical—just the same as in the production of small-molecule commodity chemicals. In contrast to small-molecule catalysis, polymerization catalysts also control the polymerization rate, selectivity, and productivity that govern the resulting materials' properties: for example, polymer crystallinity, decomposition temperature, viscosity, rheology, and mechanical performance. Catalyst selection may also be used to tune polymer molecular weight, dispersity, chain composition, chain architecture, and regio- and/or stereochemistry. Innovation in polymerization catalysis requires understanding both inorganic chemistry and the polymer macromolecular properties; for this reason, research in this field is naturally highly interdisciplinary.

To reflect this interdisciplinarity, we present this Virtual Issue, “Metal Complexes for Catalytic Polymerizations,” depicting a collaboration between two leading ACS journals that publish research at the heart of this chemistry: *Inorganic Chemistry* and *Macromolecules*. The selection of articles necessarily focuses on recent work, the majority being published within the past two years. The articles we chose to feature are, of course, personal and reflect our own research interests, enthusiasms, and perspectives. Because we both carry out research using homogeneous metal-based polymerization catalysts, and because this issue is being coproduced by *Inorganic Chemistry*, our selection mostly focuses on metal catalysts. We have grouped the selections into themes and topics and have included articles that illustrate the potential for catalysis to influence polymer properties.

Diversity in Polymer Chemistry. The natural diversity of polymerization catalysts and polymer chemistries is seemingly boundless, including catalysts for alkene coordination polymerizations, controlled radical polymerizations, polycondensations and group-transfer polymerization, ring-opening metathesis polymerization, and ionic ring-opening polymerization. These methods are by no means an exhaustive list of possible polymer syntheses, but as the tip of the iceberg they do reflect both large-scale processes in use and newer methods that allow for control over composition, architecture, stereochemistry, and, even, monomer sequence. A common theme for all the new catalysts reflected in this Virtual Issue is that, despite the maturity of some fields, such as alkene coordination polymerization, high innovation potential remains and we have a continued need for greater diversity in catalyst structures and increased activity.

The Renaissance of Oxygen-Containing Polymers. The largest group of articles in our selection addresses improvements in the synthesis of oxygen-containing polymers, notably polyesters and polycarbonates. These polymers are already well-known in industry for the commodity plastics, polyol, and specialty markets. These articles reflect a renewed interest in polyesters and polycarbonates as sustainable and, potentially, degradable materials, where the oxygen functionality may facilitate chain cleavage. Advances in catalysis will be critical to improving manufacturing efficiency and moderating properties in future generations of these polymers.

Depolymerization catalysis is another area experiencing a renaissance, and in this context polyester and carbonate backbones may show more favorable depolymerization thermodynamics—that is, lower polymer ceiling temperatures.³ Catalysts for ring-opening polymerization of cyclic monomers may also prove useful in lowering activation barriers to chemical recycling, and for these equilibrium polymerizations the same catalysts are applied

for both forward (polymerization) and reverse (depolymerization) reactions ([DOI: 10.1021/acs.macromol.9b00817](https://doi.org/10.1021/acs.macromol.9b00817)).

Polyesters were observed by polymer pioneer Wallace Hume Carothers and colleagues in the early 20th century as being able to thermally equilibrate between polymer and lactone, and this property is being reexplored as researchers and industrial ecologists dig deeper into the “circular economies” of plastics.⁴ Polylactide, for example, is the leading biobased polymer produced at ~1-2 million tons/year.² There is still significant opportunity for innovation, understanding, and improvement of the needed catalysts. Our selection includes research optimizing catalytic stereoselectivity so as to produce high-molecular-mass semicrystalline PLA from racemic raw materials ([DOI: 10.1021/acs.macromol.8b00924](https://doi.org/10.1021/acs.macromol.8b00924)). It also includes detailed insight into how to understand, both experimentally and theoretically, the balance of active-site Lewis acidity in catalysis ([DOI: 10.1021/acs.inorgchem.6b02433](https://doi.org/10.1021/acs.inorgchem.6b02433)). These articles also focus on how to improve lactone ring-opening polymerization catalytic activity and selectivity while also providing better understanding of the (de)polymerization mechanism. Most of the catalysts feature metals drawn from main-group or lanthanide metals, but where transition metals are applied, it's also apparent that both the oxidation state and spin state mediate catalytic performances ([DOI: 10.1021/acs.inorgchem.7b02964](https://doi.org/10.1021/acs.inorgchem.7b02964)).

Several of the articles feature collaboration between experimentalists and experts in computational methods or theory, which exemplifies the opportunities to use computational methods in catalyst design. The ability to recycle carbon dioxide via copolymerization with epoxides to produce aliphatic polycarbonates inspires research into improving and understanding the parameters for the catalysis. This selection includes research focused on the use of earth-abundant iron catalysts ([DOI: 10.1021/acs.inorgchem.9b01909](https://doi.org/10.1021/acs.inorgchem.9b01909)).

Challenges in Olefin Polymerization Catalysis. Despite more than 70 years of intense research into polyolefins, and with production volumes exceeding 100 million tons/year, important research questions still surround olefin polymerization catalysis. This Virtual Issue selection includes seven articles highlighting some of the challenges and providing solutions. For example, discovering how to improve Group 4 and lanthanide catalysts remains an ongoing research topic and is illustrated by detailed investigations of the influence of catalyst nuclearity and activity ([DOI: 10.1021/acs.macromol.8b00181](https://doi.org/10.1021/acs.macromol.8b00181)). There is also an opportunity for highly selective catalysis to deliver high-performing multiblock polyolefins ([DOI: 10.1021/acs.macromol.8b01907](https://doi.org/10.1021/acs.macromol.8b01907)). These multiblock polyolefins improve blend compatibilization of polyethylene and isotactic polypropylene, research that may be relevant to enabling mixed plastic waste recycling.

Understanding and characterizing the catalysts used industrially to produce polyethylene remains an active topic as well, as described by research into the mechanism exhibited by the Cr(III) Phillips catalyst class ([DOI: 10.1021/acs.macromol.9b00588](https://doi.org/10.1021/acs.macromol.9b00588)). Designing catalysts to enable olefin copolymerization, particularly with polar monomers, continues to inspire research as a means to control polyolefin grades, properties, and applications. Late transition metals, notably Ni(II), are important in enabling copolymerization with polar monomers ([DOI: 10.1021/acs.macromol.7b01947](https://doi.org/10.1021/acs.macromol.7b01947) and [DOI: 10.1021/acs.inorgchem.8b02687](https://doi.org/10.1021/acs.inorgchem.8b02687)).

Radical Approaches to Controlled Radical Polymerizations. The controlled polymerization of vinyl, acrylate, and other alkene monomers is of central importance in polymerization catalysis. Our selection highlights an article describing miniemulsion approaches to controlled radical generation and polymerization at ppm and ppb levels of residual copper ([DOI: 10.1021/acs.macromol.7b01730](https://doi.org/10.1021/acs.macromol.7b01730)). Another article highlights the potential for flow chemistry and engineering of photoinduced atom-transfer radical

polymerization organocatalysts to deliver improved processes ([DOI: 10.1021/acs.macromol.6b02791](https://doi.org/10.1021/acs.macromol.6b02791)). One advantage of these controlled radical polymerizations is the ability to exert exquisite control over monomer enchainment rates and to produce different copolymer structures; the selection includes an article where strongly H-bonding functionalized polymer side-chain substituents are installed with in situ titanium-catalysed transesterification reactions ([DOI: 10.1021/acs.macromol.7b00070](https://doi.org/10.1021/acs.macromol.7b00070)).

Catalysis and Precision Polymers. Improving the control over polymer compositions, sequences, side-chain chemistries, and interchain interactions will be central to the delivery of better properties in tomorrow's polymers and materials. Our Virtual Issue picks up on this theme in polymerization catalysis and features articles in which catalysts are controlled or switched between different polymerization mechanisms ([DOI: 10.1021/acs.macromol.8b01719](https://doi.org/10.1021/acs.macromol.8b01719) and [DOI: 10.1021/acs.macromol.9b00676](https://doi.org/10.1021/acs.macromol.9b00676)). This chemistry allows for beautiful regulation and control over block sequence and even monomer placement in the polymer chains. Sequence control and monomer enchainment patterns recur in olefin ring-opening metathesis polymerization, with key contributions illustrating how to modify catalysts or monomer pairs to control polymer sequence or substituent regiochemistry ([DOI: 10.1021/acs.macromol.8b00562](https://doi.org/10.1021/acs.macromol.8b00562) and [DOI: 10.1021/acs.macromol.8b00969](https://doi.org/10.1021/acs.macromol.8b00969)).

Organocatalysts and Metal Catalysts: More in Common than Meets the Eye. As we alluded to earlier, our research interests lie in the fields of homogeneous metal polymerization catalysts, and the majority of our Virtual Issue selection features metals from the first-row transition metal, main-group, and rare-earth regions of the Periodic Table. But we recognize the long-standing importance of activated monomers, nonmetal salts, and organocatalysts for use in polymerization catalysis, and thus we also include articles where organocatalysts or salts are used as polymerization catalysts ([DOI: 10.1021/acs.macromol.8b00540](https://doi.org/10.1021/acs.macromol.8b00540) and [DOI: 10.1021/acs.macromol.9b00122](https://doi.org/10.1021/acs.macromol.9b00122)). In both examples, we are intrigued by the similarity of roles for metals and the organic molecules in catalysis. We note that in these reactions the polymerization catalysis occurs through cooperative acid/base interactions, most often delivered by Lewis acids. It's quite apparent that this acidic functionality does not have to be delivered by a metal, and that by using Brønsted acids it is perhaps appropriate to view the proton as the "lightest" and most abundant acidic site available.

The importance of acid/base cooperativity is also described in the context of the synthesis of poly(oxazolidine-2-ones) ([DOI: 10.1021/acs.macromol.8b02403](https://doi.org/10.1021/acs.macromol.8b02403)). One advantage for organocatalysts could be as tools for detailed polymerization mechanistic studies, which are essential to properly design future catalysts. And they may even help the communities focused on metal-catalyzed polymerizations to better understand subtleties of metal-based acid/base systems.

We hope this joint *Inorganic Chemistry-Macromolecules* Virtual Issue illustrates some of the scope, range, and diversity of polymerization catalysis research worldwide. The production of and applications for polymers continue to grow, making efficient catalysis enabling their cost-effective manufacturing essential for the future. Given the enormous breadth of different chemistries involved in creating, studying, and applying polymerization catalysts, it's rather difficult to make generalized predictions of future trends. Nonetheless, understanding how to design catalysts more effectively for activity, selectivity, and control is a key objective. Operando catalyst characterization methods and improvements to calculations and theoretical models will play key roles, together with the tools of kinetics and structure-activity relationship investigation, in providing data to underpin mechanistic hypotheses. Research

into catalysts prepared using earth-abundant elements and operable at low loadings is relevant to almost all sectors, and understanding how to moderate the active site to improve monomer selectivity, including stereo/regiochemical control, are also cross-cutting research challenges. The past decades have seen tremendous advances in efficient catalysis for the forward (monomer to polymer) reaction, but the drive to improve resource efficiency, increase polymer recycling, and ameliorate the environmental footprint of polymer production and use will power research into catalysis for the reverse (polymer to small-molecule) reaction. We foresee that research in the field of (de)polymerization catalysis will continue to grow, and we hope it will attract new generations of researchers focused on improving polymers' sustainability and allowing their application in completely new sectors and fields.

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Notes

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