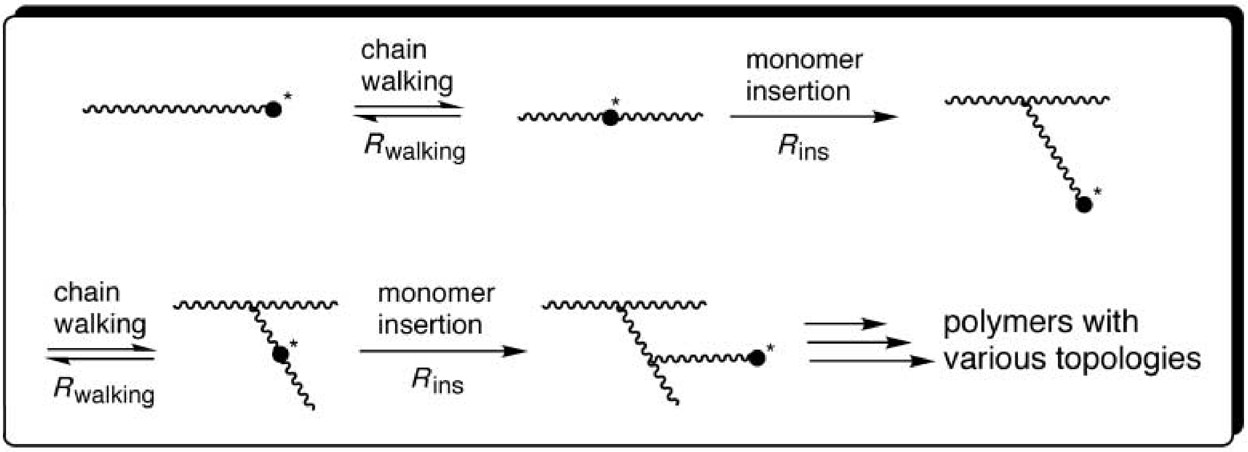

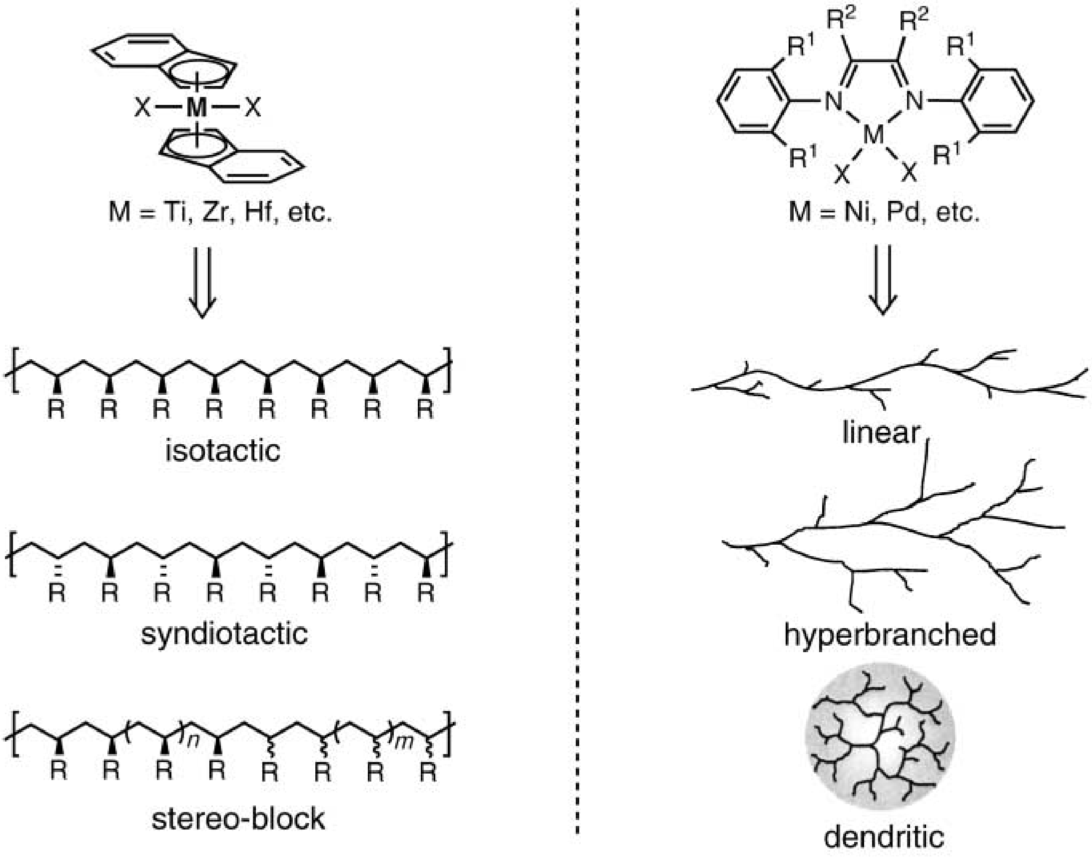

If the most striking feature of early transition metal polymerization catalysts is their capability in controlling polymer tacticity, one of the most amazing features of late transition metal catalysts is their versatility in controlling polymer branching topology.

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Control of Polymer Topology by Chain-Walking Catalysts

Zhibin Guan*[a]

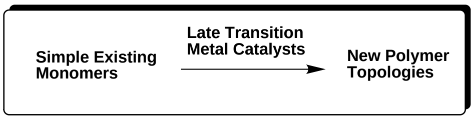
Abstract: Chain-walking catalysts are demonstrated to control the branching topology of polyethylene by tuning the competition between monomer insertion and chain isomerization (walking). The topology of the polyethylene was controlled from linear with moderate branching to hyperbranched to dendritic. Although overall branching number and distribution of short chain branching are relatively constant, the topology of the polyethylene changes from linear polyethylene with moderate branches at high ethylene pressures to a dendritic polyethylene at low pressures. This provides a straightforward one-pot process for making polymers with a full range of tunable topologies.

Keywords: catalysts · dendrimers · palladium · polymerization · polymers · polyolefins

Introduction

The topology[1] of a macromolecule is an important molecular parameter that determines its physical properties and applications.[2] To control macromolecular topology and architecture accurately is currently a central theme in polymer science with the aim to prepare polymeric materials with new properties.[3] Many concepts and synthetic approaches have been developed to prepare macromolecules with various architectures and topologies, including dendrimers[4] and hyperbranched polymers,[5] supramolecular polymers,[6] cylindrical and spherical polymers,[7] polymers having folded structures,[8] molecular wires,[9] metal core polymers,[10] and polymeric nanostructures.[11] Despite the elegance and success of these approaches, most of them involve multi-step organic syntheses and usually require specially designed monomers to suit each particular synthesis. It is highly desirable to develop methods that can directly polymerize existing simple monomers to give controllable topology. One attractive approach is transition metal catalyzed polymerization of simple monomers to obtain polymers with controlled topologies.

Inspired by the recent progress in late transition metal polymerization catalysis[12–15] and the increasing interest in designing macromolecules with new topologies,[3] I have been exploring the concept of controlling polymer topology using late transition metal catalysts with the goal of creating polymers with new topologies from simple existing monomers.[16, 17] Instead of designing new monomers, I was attempting to achieve new polymer topologies by controlling the covalent assembly of simple monomers through catalysis (Scheme 1).



Scheme 1. Concept of designing new polymer topology from simple existing monomers by using late transition metal catalysts.

I have succeeded in a few approaches demonstrating this concept.[16, 17] In one strategy, hyperbranched polymers were prepared via direct free-radical polymerization of divinyl monomers by controlling the competition between propagation and chain transfer using a cobalt chain transfer catalyst.[16] In another strategy,[17] polyethylene (PE) topology was successfully controlled by regulating the competition between propagation and "chain walking" for ethylene polymerization using a Pd^{II}-α-bisimine catalyst.[12] Concurrent to my studies, others have reported different transition-metal catalysts that polymerize ethylene to give branched to hyperbranched architectures. Bazan and co-workers have developed an elegant approach for the synthesis of polyolefins having controlled short-chain branches through a tandem action of two well-defined homogeneous catalysts, one for olefin oligomerization and the other one for polymerization.[18] Sen and co-workers have reported the synthesis of hyperbranched PEs having low molecular weights using different nickel or palladium catalysts.[19]

Discussion

This article will highlight the use of a chain-walking catalyst to control polyolefin topology.[17] These olefin polymerization studies using a chain walking catalyst, the catalytic site (active

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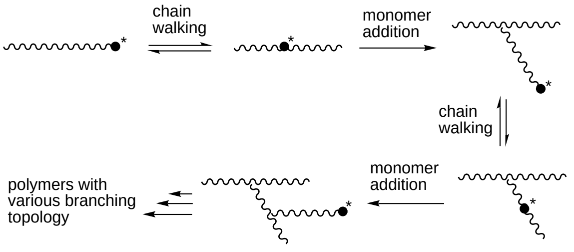
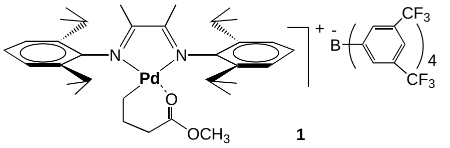
growing site) isomerizes or walks on polymer chain during propagation, so that the next monomer unit is assembled onto any part of the polymer backbone instead of at the end (Scheme 2).[17] Instead of introducing branching by monomer structure, here the branching is introduced by a catalyst that can control the position for the next monomer addition. This nonlinear fashion of chain propagation leads to the formation of polymers with various branching topologies.



Scheme 2. Chain walking as a new strategy for controlling polymer branching topology.

The catalyst used in the study is a Pd^{II}-α-bisimine complex, **1**, a catalyst which was discovered by Brookhart and co-workers[12] (Scheme 3).



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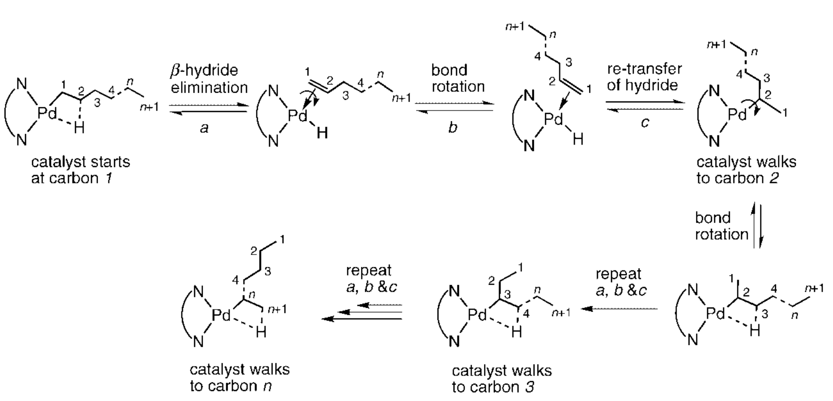
Scheme 3. The chemical structure of the Brookhart Pd^{II}-α-bisimine chain walking catalyst.

Brookhart[12] and Fink[20] discovered that when certain Ni^{II} and Pd^{II} catalysts were used for ethylene polymerization, branched instead of linear PEs were obtained. They proposed that the branching was introduced by catalyst isomerization or "walking" along the PE backbone during the migratory insertion polymerization. The chain walking of the catalysts is facilitated by a process involving β-hydride elimination, bond rotation and re-transfer of the hydride as depicted in Scheme 4.[12, 20, 21]



Scheme 4. The proposed mechanism for chain walking.[12a, 20]

From fine mechanistic studies, Brookhart and co-workers have shown that the Pd^{II}-α-bisimine catalyst can walk through a secondary or tertiary carbon but not a quaternary carbon center.[21] ^{13}C NMR spectroscopic analysis of the PEs produced by these catalysts provided information on the local-scale microstructure such as the total branching density, the distribution of short-chain branches, and the shortest branch-on-branches, isobutyl group.[22] Nevertheless, the global branching topology of these polymers was not clear and there was no attempt to control the PE topology using the chain-walking catalyst prior to our report in 1999.[17]

Following the discovery of the Ni^{II} and Pd^{II}-α-bisimine catalysts by Brookhart and co-workers at the University of North Carolina at Chapel Hill, a collaborative effort on developing this polymerization catalyst system was initiated at the DuPont Central Research and Development where I was working as a Senior Research Chemist at that time. I was intrigued by the chain-walking mechanism and conceived that it could be used to control PE topology if the competition between chain walking and insertion could be regulated.[17] I proposed that at polymerization conditions that favor insertion more than chain walking, the catalyst cannot walk too far after each insertion, therefore, PE with a relatively linear topology will be formed. On the other hand, if chain walking is very competitive, the catalyst will walk extensively on polymer chain after each insertion, which will result in a hyperbranched or dendritic polymer. Whereas this concept seems to be obvious in retrospect, my proposal was not accepted initially until it was proven experimentally.

To test my hypothesis, I designed a series of experiments in which the ethylene pressure (P_E) was varied systematically. It was expected that at high P_E ethylene has high concentration in the polymerization solution and hence insertion would be relatively fast. At low P_E the chain walking will be competitive to the insertion so the catalyst can walk extensively on polymer chain between two consecutive insertions.

The initial characterization by quantitative ^{13}C NMR spectroscopy and regular gel-permeation chromatography (GPC) of the PEs made at different P_E showed surprisingly that they were very similar as characterized by these methods. The GPC results showed that they have similar molecular weights and the NMR spectra showed that they have similar total branching density and the distribution of short chain branches. A representative quantitative ^{13}C NMR spectrum of PE made with catalyst **1** is shown in Figure 1 with the short-chain branches assigned.[23]

The distribution of short-chain branches as represented by the number of branches in 1000 methylenes for a series of PEs made with catalyst **1** at different P_Es is plotted in Figure 2. Without further analysis, we would have fortuitously concluded that these polymers made at different pressures were about the same.

However, since the experiments were purposely designed

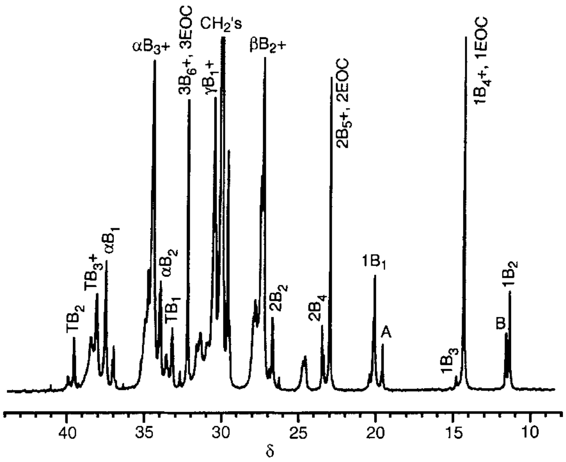


Figure 1. A representative ^{13}C NMR spectrum of the branched PE made with the Pd^{II}-α-bisimine catalyst. Note on labels: In xBy B$_y$ is a branch of length y carbons and x is the carbon being discussed with the methyl at the end of the branch being numbered 1. For example, the second carbon from the end of a butyl branch is 2B$_4$. xB$_y$+ refers to branches of length y and longer. When x in xB$_y$ is replaced by a T, the methine carbon of that branch is denoted. Greek letters indicate the position of the methylenes in the backbone. For example, γB$_1$+ refers to methylenes γ from a branch of length 1 or longer. EOC is the end of the chain; 2EOC is the second carbon from the end of the chain. A and B are the methyl groups of the methyl and ethyl branches, respectively, in the *sec*-butyl branches.

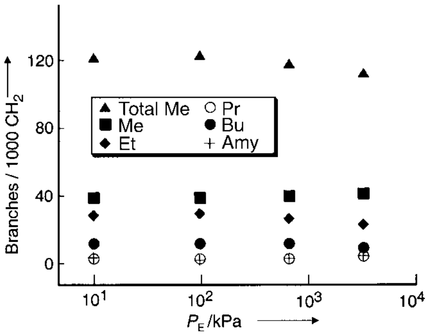


Figure 2. ^{13}C NMR data on total number of branches and the distribution of short chain branches for PEs made at different P_Es. Integrals of characteristic carbons in each branch were measured and reported as number of branches per 1000 methylenes (including methylenes in the backbone and branches).

to examine the polymer topology change with polymerization conditions, we resorted to more sophisticated analytical tools to reveal the global topology of the polymers. Specifically, we combined static and dynamic light scattering, solution viscosity, neutron scattering and atomic force microscopy (AFM) to investigate the global topology of the PEs made at different pressures.

Firstly, size-exclusion chromatography (SEC) equipped with an online multi-angle light scattering (MALS) detector provided clear evidence that the PEs made at different pressures have different topologies.[17, 23] Because the online MALS detector measures both molecular weight (M) and size of polymer (radius of gyration, R_g) for every fraction of polymers eluted from the SEC column, we can compare the R_g at the same M for different samples. In Figure 3 we compare the angular dependence of the fraction of PE at M of 400000 g mol^{-1} for the three samples that were made at 0.1, 1.0, and 34 atm, respectively. A large difference in the slope was observed, indicating that at the same M the R_g values are different. The R_g at $M = 400000$ g mol^{-1} was 30.0, 18.5, and 10.5 nm for the samples polymerized at 34, 1.0, and 0.1 atm, respectively (a factor of 3 range in R_g). The separation of the polymer by SEC provides R_g as a function of M and as shown in Figure 4, R_g consistently shifts upwards as P_E increases.

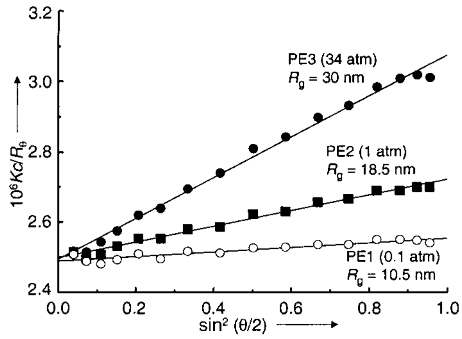


Figure 3. Comparison of Debye plots for the fraction of polymer at $M = 400000$ g mol^{-1} for the three PE samples made at 0.1, 1.0, and 34 atm, respectively.

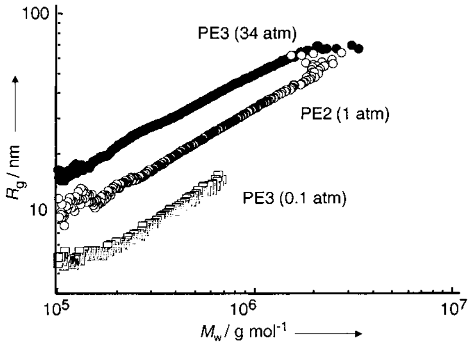


Figure 4. Correlation of R_g with molecular weight for the three PE samples made at 0.1, 1.0, and 34 atm, respectively.

For a linear flexible polymer forming a random coil, R_g scales as $M^{1/2}$.[24] So, a radius change of a factor of 3 requires nearly an order of magnitude change in M. The dramatic difference in R_g for PE samples of the same M could in principle be caused by either a change of the branching density or a change of the branching topology with P_E. However, because the branching density stays relatively constant as shown by ^{13}C NMR spectrum (Figure 2), this large change in R_g can only be attributed to a change in branching topology. This leads to an unambiguous conclusion that the PE topology changes with the P_E: As the P_E was decreased, the PE topology was becoming more and more hyperbranched (Figure 5).

Our further investigation of the polymers by dynamic light scattering, solution viscosity, neutron scattering and AFM have revealed more information on the PE topology.[17, 23, 25, 26] The hydrodynamic radius (R_H) was measured by dynamic light scattering. Combining static and dynamic light scattering, the ratio R_g/R_H was obtained which reflects polymer chain topology and segment density.[27] In general, linear flexible polymers exhibit values of R_g/R_H around 1.5–1.7 in good

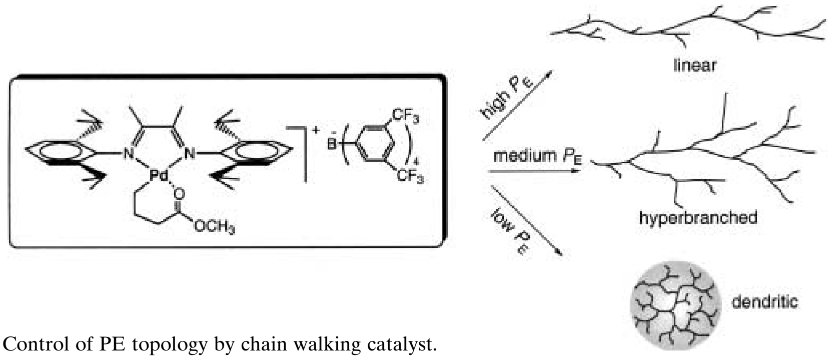


Figure 5. Control of PE topology by chain walking catalyst.

solvents. A value less than unity, 0.78, is predicted for a hard sphere. Experimental results of less than unity have been reported for multi-arm stars,[28] micro-gels,[29] and dendritic polymers.[30] Whereas our high-pressure polymer has a ratio of 1.7, for the lowest pressure sample, this ratio is only, 0.8, indicating that the PE made at the lowest pressure has a compact and globular topology resembling dendrimers.

In neutron scattering experiments,[25] the PE made at the lowest pressure shows a peak in the Kratky plot (Figure 6), further proving a densely packed globular topology for the polymer. To our knowledge, this phenomenon has only been observed for dendrimers[31] but not for hyperbranched polymers. The intrinsic viscosity of the PE made at 0.1 atm is only one eighth of the value for polypropylene of comparable molecular weight.[17] We have recently observed directly the different PE topologies by AFM (Figure 7).[26] All these studies indicate that the PE made at very low P_E has a very densely packed topology resembling a dendrimer. Recently Lutz and co-workers[32] have also investigated the structural changes of PEs with polymerization conditions using the chain walking catalyst, which confirmed our original observation.[17]

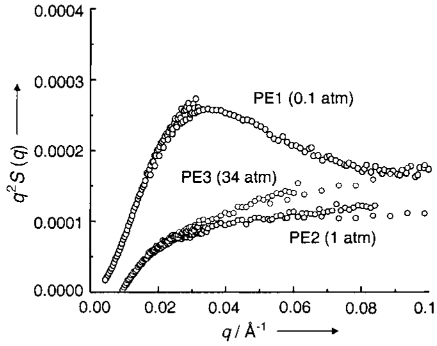


Figure 6. Comparison of Kratky plots obtained by small angle neutron scattering of the three PE samples made at 0.1, 1.0, and 34 atm, respectively.

Whereas hyperbranched vinyl polymers have been elegantly prepared by cationic,[33] radical,[34] and group-transfer[35] self-condensing polymerization of specially designed vinyl monomers, to our knowledge, our results showed the first time that a vinyl polymer having dendritic topology can be prepared by direct coordination polymerization of a simple vinyl monomer such as ethylene. This is also the first time to show that a polymer topology can be systematically tuned by simply changing an experimental parameter such as pressure. Although these polymers are not perfect dendrimers because of their polydisperse nature in molecular weight and branching length distribution, their cascade branch-on-branch topology, compact globular structure and characteristic solution behavior all resemble those of dendrimers.[4, 17] It is reasonable to expect that many physical properties of these dendritic polymers made by the chain walking catalyst should be similar to a perfect dendrimer made of the same building block. Whereas perfect dendrimers have beautiful structural precision and uniformity,[4] the multistep syntheses involved in their preparations indeed limit their general applications. Our approach offers a simple one-pot process for making tunable polymers with topologies ranging from linear to hyperbranched to dendritic starting with simple olefinic monomers. Due to the ease of synthesis and the availability of many olefinic monomers, these hyperbranched and imperfect dendrimers may find many general applications in which polymer structural precision and uniformity are not critical.

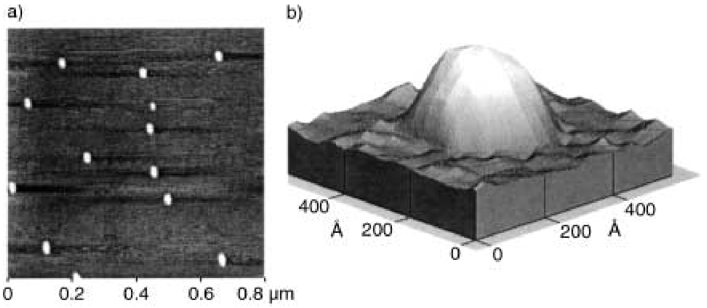


Figure 7. AFM study on topology of the dendritic PE made at very low P_E. a) An image showing separated individual PE molecules; b) a 3D image of one dendritic PE molecule.

To broaden the scope of our strategy, my group is currently extending the methodology to functional polymer synthesis through copolymerization of ethylene with polar monomers by taking advantage of the excellent functional group tolerance of the late transition metal polymerization catalysts.[12b, 13, 36] By copolymerizing ethylene with functional monomers at different P_E values, copolymers carrying a variety of functional groups with a spectrum of topologies can be obtained.[37] This offers a simple one-pot approach to design functional polymers with a broad range of topologies. Post-polymerization treatment of functional groups can further introduce more functional groups that cannot be tolerated by the chain walking catalysts.

Conclusion

In conclusion, it has been shown that late transition metal polymerization catalysts are excellent for controlling polymer topology. PE topology was successfully controlled by regulating the competition between propagation and chain walking by using the Brookhart Pd^{II}-α-bisimine catalyst.[17] PEs with a full spectrum of topologies could be obtained by simply changing P_E. Although the total branching density and the distribution of short chain branches are relatively constant, the branching topology changes dramatically with polymerization pressure, varying from predominantly linear with many short branches at high P_E to a densely branched, arborescent globular structure at very low P_E. Polymers synthesized at the lowest P_E exhibited similar properties of dendrimers. Our ability to produce polymers with continuum topologies without changing the chemical structure provides a unique opportunity for many fundamental studies, such as the investigation of topological effects on polymer physical properties.

Transition-metal catalysts have played and will continue to play crucial roles in making important polymeric materials.[38] Whereas early transition metal catalysts such as Ziegler–Natta and zirconocene catalysts remain as the workhorse in olefin polymerization industry, significant advances have been made recently in late transition metal polymerization catalysts.[15] Two most important attributes of late transition polymerization catalysts distinguish them from early transition metal systems as they are versatile for controlling polymer topology[17] and have good functional group tolerance.[12b, 13, 36] If the most striking feature of early transition metal olefin polymerization catalysts is their capability of controlling the stereochemistry of polymerization of α-olefin,[39] one most amazing nature of late transition metal polymerization catalysts would be their versatility for controlling polymer topology[17, 19] (Figure 8).

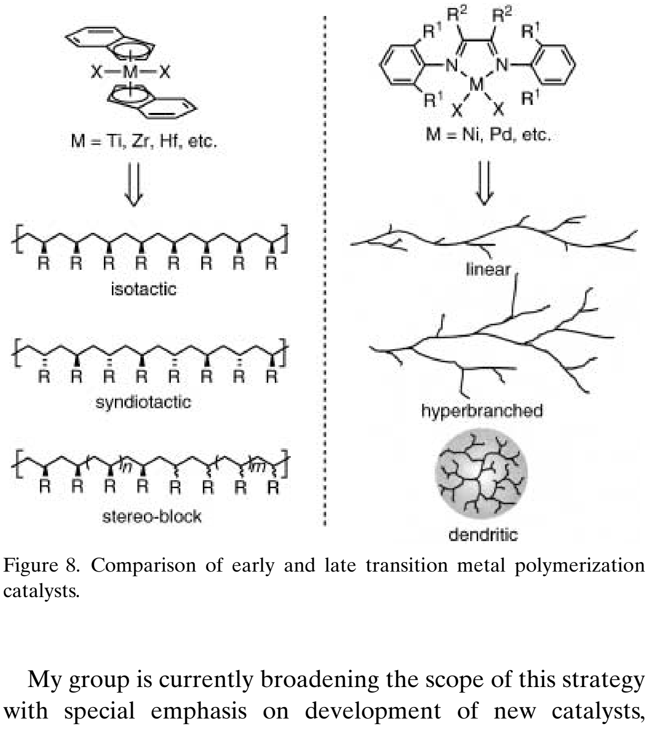


Figure 8. Comparison of early and late transition metal polymerization catalysts.

My group is currently broadening the scope of this strategy with special emphasis on development of new catalysts, synthesis of new functional materials, and design of polymers with unconventional topologies by using late transition metal catalysts. Given the unique features of late transition metal polymerization catalysts and the recent resurrection of great interest in them,[15] the future of designing new functional polymers with late transition metal catalysts is very promising.

Acknowledgements

I would like to thank the DuPont Company, the ACS Petroleum Research Fund, the US Army Research Office, and the University of California at Irvine for generous financial support. I would also like to thank many colleagues and co-workers, whose names appear in those references cited, for their important contribution to this research. ZG gratefully acknowledges a Beckman Young Investigator Award, a DuPont Young Faculty Award, and a NSF CAREER Award and a 3M Non-Tenured Faculty Award and a 3M Non-Tenured Faculty Award.

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[1] Polymer topology here refers to the geometric arrangement of monomeric units on a macromolecule, such as linear, hyperbranched and dendritic. Other terms, such as microstructure and architecture, are also used frequently in literature to describe polymers with different structures. Microstructure is usually used to describe polymer local structures which is not sufficient for characterizing macromolecular global topology. The term "polymer architecture" has been used very broadly to describe many types of polymer structures including star, block and graft polymers, polymers with various branching forms, and polymers with different tacticity. In this review, the term topology is chosen to describe polymers that are made of the same building blocks but in different geometric arrangements.

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