Chem 466

lecture # 22

04/15/2014

* Exam III $\bar{x} = 53$, S.D. = 26

A	≥ 66	(36)
B	40 – 65	(38)
C	14 – 39	(15)
D	< 14	(11)

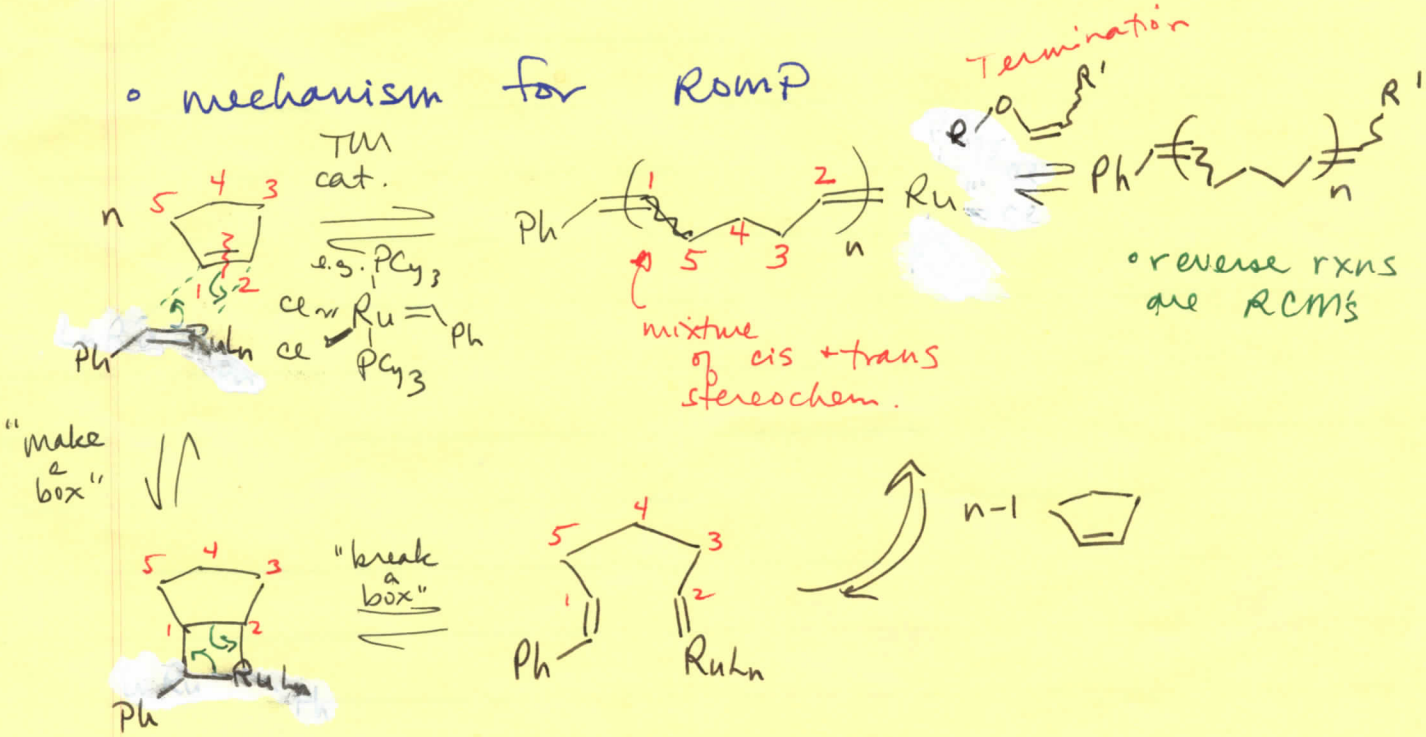
* Pre-final grades will be calculated tomorrow — come to office hours to obtain grade information (no email of grades)

VI Transition metal-mediated polyms + stereoregularity

(A) Ring-opening metathesis polym. (ROMP)

- 2005 Nobel prize to Yves Chauvin, Robert H. Grubbs + Richard R. Schrock
  "for the developement of the metathesis method in organic synthesis"
  - ROMP + RCM (ring closing metathesis) — opposites
  - metathesis involves exchange rxns of TM=C + C=C where TM = Ru, W, Rh, Mo
- show animation
  http://nobelprize.org/chemistry/laureates/2005/animation.html

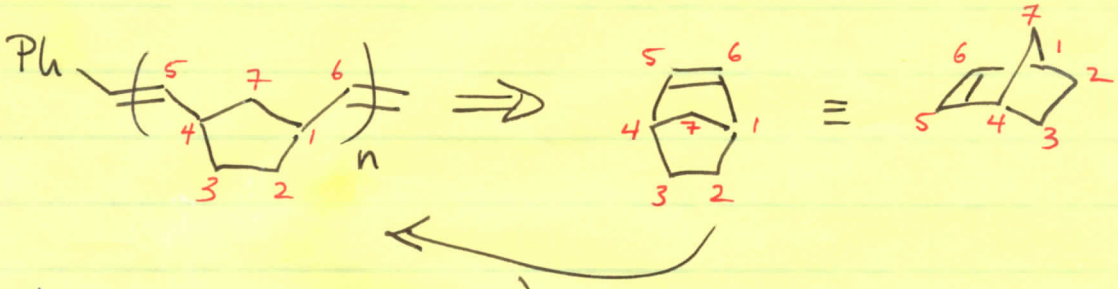
- mechanism for ROMP



- reverse rxns are RCM's

(already discussed polydicyclopentadiene xlinked materials on 03/04/14, lecture #14)

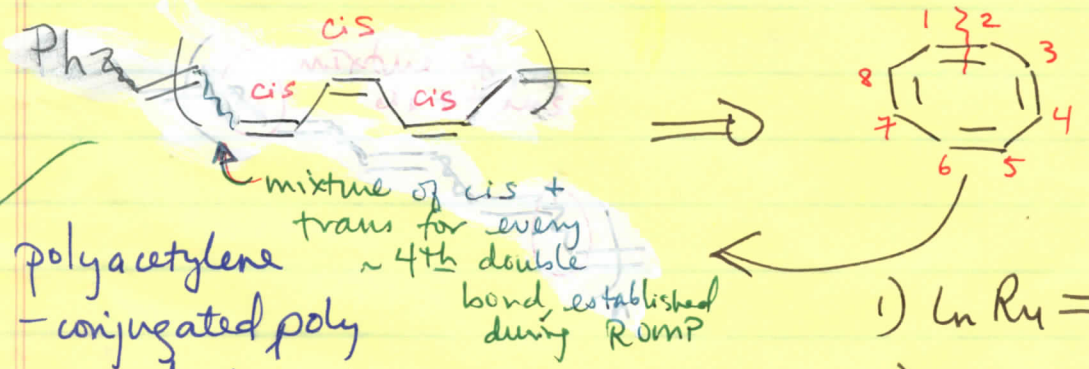
- useful polys from ROMP



polynorbornene
tradename Norsorex
- high tear strength
- high dynamic damping props.

⟹ noise control + vibration damping applications, e.g. in autos

cyclooctatetraene



polyacetylene
- conjugated poly
- conducting when doped (e.g. w/ iodine)

(H. Shirakana, A.J. Heeger, A.G. MacDiarmid Nobel Prize 2000)

H_2, Pd/C

linear polyethylene

possible incorporation of func groups via initiator + terminator

⊛ ROMP to produce conjugated polys w/ interesting optical + optoelectronic properties } substituted PPVs

⊛ sufficient ring strain is required for ROMP

ACS Macro Letters

Letter

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[2.2.2]Paracyclophane-Trienes—Attractive Monomers for ROMP

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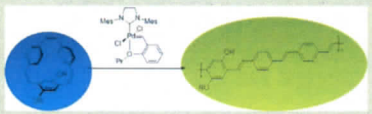
Supporting Information

ABSTRACT: Three derivatives of 4,7-substituted [2.2.2]-paracyclophane-trienes were synthesized and used in ring-opening metathesis polymerization (ROMP), resulting in well-soluble poly(*para*-phenylenevinylene)s (PPV). The paracyclophane-trienes were prepared using an iterative buildup of a phenylene–ethynylene backbone, followed by a cis selective Grignard reduction and an intramolecular McMurry reaction. The monomers were applied in ROMP to result in well-soluble PPV derivatives with an unusual substituent pattern. The PPVs were spin-coated into amorphous, highly fluorescent films. To the best of our knowledge, we are the first to synthesize 4,7-substituted [2.2.2]paracyclophane-trienes and use them as ROMP monomers.



Due to their spectacular optical and optoelectronic properties, conjugated polymers such as polyfluorene,[1] polythiophene,[2] poly(phenyleneethynylene) (PPE),[3] or poly-(*para*-phenylenevinylene) (PPV)[4] have been studied intensely.[5] Their potential as semiconductors in applications such as organic field-effect transistors (OFET),[6] organic photovoltaics (OPV),[7] or organic light-emitting diodes (OLEDs)[8] is significant.

PPV might be the most examined semiconducting polymer. Unsubstituted PPV has successfully been exploited for OLEDs[9] and OPVs.[10] Due to the parents' poor solubility, it is processed out of a precursor polymer by extrusion of leaving groups, as studied by Wessling et al., which gives the parent PPV.[11] If solubilizing groups are attached to the PPV backbone, processable PPVs with controlled morphology are accessible.[12] Dozens of different side chains were attached to the PPV backbone, highlighting relationships between polymer structure, photoluminescence yield, and efficiency of electroluminescence.[13,14]

Substituted and soluble PPVs are synthesized by Gilch-type, Pd-catalyzed, and other methods.[15−18] Acyclic diene metathesis (ADMET) or ring-opening metathesis polymerization (ROMP) of suitable precursors is an attractive alternative for defect-free PPVs.[19] After Bazan et al. studied the ROMP of paracyclophenes into PPV precursor polymers,[20] Turner et al. elegantly developed a direct ROMP-approach of substituted [2.2]paracyclophane-dienes giving PPV-homo-[21] and -*block*-copolymers.[22,23] However, the paracyclophane-diene monomers are difficult to synthesize, yet ROMP is a suitable and powerful method for the *direct* synthesis of soluble PPV derivatives with low polydispersities.

Inspired by Müllen et al.[24] and Oda et al.[25] we contended that larger cyclophenes might have enough strain energy to give ROMP-able monomers. We found that unsubstituted [2.2.2]-paracyclophane-triene follows ROMP into insoluble PPV. The (*E*,*Z*,*E*,*Z*)-isomer[25] of [2.2.2.2]paracyclophane-tetraene is also ring-opened into PPV, whereas the (*Z*,*Z*,*Z*,*Z*)-isomer does not have enough strain energy to be active (Figure 1).[25]

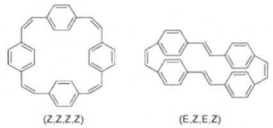


Figure 1. Structures of the [2.2.2.2]paracyclophane-tetraenes.

Herein we report the synthesis of dodecyl-, dodecyloxy-, and 2-ethylhexyloxy substituted [2.2.2]paracyclophane-trienes **4a−c** as monomers of well-soluble PPVs with an unusual substituent pattern. We developed a new synthetic route for these [2.2.2]paracyclophane-trienes and applied them in ROMP to give the PPVs **5a−c**.

Scheme 1 shows the key synthetic steps. In the original synthesis of the parent **4**, Tanner et al. used a Wittig reaction building up the cis double bonds. Trying the same with para-substituted benzene derivatives led to a mixture of cis and trans isomers, hardly separable. Consequently, we developed an alternative route. Sonogashira-Hagihara coupling gives **1a−c**, which are easily and cis selectively transformed into **2a−c** through a Grignard reduction.[26]

For cyclization we used the McMurry reaction but encountered several problems. Deprotection of acetals **2a−c** with hydrochloric acid in THF yields crude dialdehydes **3a−c**, which can be purified by column chromatography. Unfortunately, when dissolved, **3a−c** isomerize rapidly. The yield of the desired all-cis isomers drop. Nevertheless, **3a−c** can be coupled

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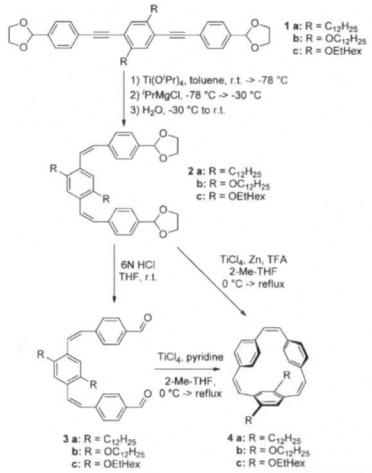
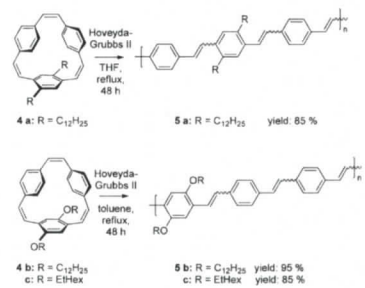
Scheme 1. Synthesis of 4,7-Substituted [2.2.2]Paracyclophane-Trienes 4a−c



Scheme 2. Polymerization of Monomers 4a−c to PPV Derivatives 5a−c



in an intramolecular McMurry reaction, yielding the 4,7-substituted [2.2.2]paracyclophane-trienes **4a−c**.

To avoid the problem of isomerization of **3a−c**, we employed the configurationally stable acetals **2a−c** in the intramolecular McMurry reaction.[27] Acceptable yields are obtained (100 mg ∼40%) on small scales but yields drop upon scale-up, and the competing intermolecular polymerization becomes prevalent. Reductive ring closure, yielding a single instead of a double bond, is another side reaction when using **2a−c**, complicating purification.

The solution to the problem of isomerization and low yields during scale-up is the simple omission of the purification of the dialdehydes **3a−c**. Dioxolanes **2a−c** are deprotected by diluted

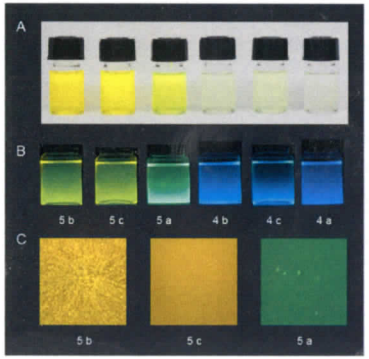


Figure 2. Photographs of (A) absorption and (B) emission under ultraviolet illumination (365 nm) of polymer and monomer solutions in $CHCl_3$. (C) Photographs of spin-coated films out of C_6H_5Cl under ultraviolet illumination (365 nm).

hydrochloric acid, overnight in the dark. Phase separation, filtration through a plug of silica, and evaporation of the solvent under light exclusion give **3a−c** with a nearly complete all-cis configuration according to ^{1}H NMR. The dialdehydes **3a−c** were directly applied in the pseudo high dilution McMurry cyclization using a syringe pump, protected with aluminum foil. The [2.2.2]paracyclophane-trienes **4a−c** are obtained in good yields (55−64%) after scaling up. This is higher than the yields published for similar systems.[24,28,29] **4a−c** were isolated as pale yellow-colored oils which show weak fluorescence in their pure and dissolved states.[30]

Aromatic proton signals in ^{1}H NMR spectra are high-field shifted, overlapping with vinylic signals, reflecting the electronic interaction within the system. Surprisingly cyclophanes **4a−c** are oils, in contrast to their unsubstituted parent molecule[31] or their ortho substituted derivatives.[29]

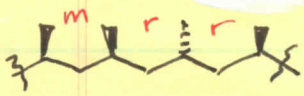
In Scheme 2, ROMP of **4a−c** into PPVs **5a−c** is shown; Table 1 summarizes the properties of the resulting PPVs. Polymerization of **4a** at room temperature yields PPV **5a** with a polydispersity of 2.8. Increasing the temperature lowers the polydispersity of **5a** to 1.9, assuming that higher temperatures improves the initiation of ROMP of **4a**. The alkoxy substituted derivatives **4b** and **4c** do not show any reaction at room temperature or in refluxing THF. A change to the higher boiling solvent toluene (110 °C reaction temperature) produces PPVs **5b** and **5c** with polydispersities of 1.4 and 1.7.

The higher reaction temperature is necessary due to the oxygen in the side chains of **4b,c**, which works as anchor group for the catalyst, inducing an energy barrier for ROMP. ^{1}H NMR spectroscopy of polymers **5a−c** (see Supporting Information) shows a trans/cis ratio about 59−70%, respectively, indicating that the double bonds formed during ROMP are mostly trans-configured and those that are not opened by ROMP tend to isomerize easily (calculated trans/cis ratio: 33%).[32] Thermogravimetric analysis of the polymers indicates no weight loss up to 300 °C. As metathesis is quite sensitive to steric effects, we assume that the double bond

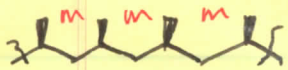
(B) Other T.M.-mediated Polyms, which give stereochemical control

- not referring to cis- vs. trans- stereochem
- stereo ~~chem.~~ regularity of aliphatic carbon-based poly backbone
- tacticity describes the stereochem. struc. of the poly chain

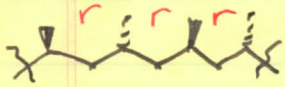
e.g. for polypropylene



— atactic = no stereoregularity



— isotactic = all substituents branch from the backbone in the same direction (all meso diads)



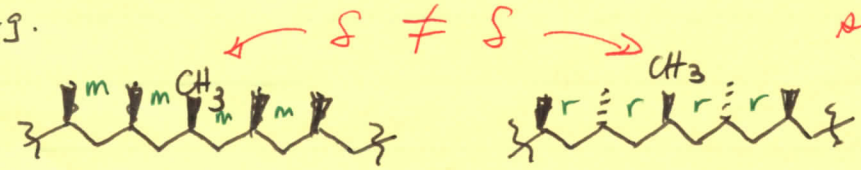
— syndiotactic = all substituents alternate in directions from backbone (all racemic diads, i.e. alternating stereocenters)

m = meso diad (superimposable on mirror image)
r = racemic diad (1 each R+S isomer)

see text sections 1.6.2 + 5.7–5.9 + Fig 1.3

- tacticity is det'md by NMR spectroscopy b/c ^{13}C resonance frequencies are dependent on tetrads

e.g.



see Fig 5.9 for full spectral differentiation of 9 diff tetrads

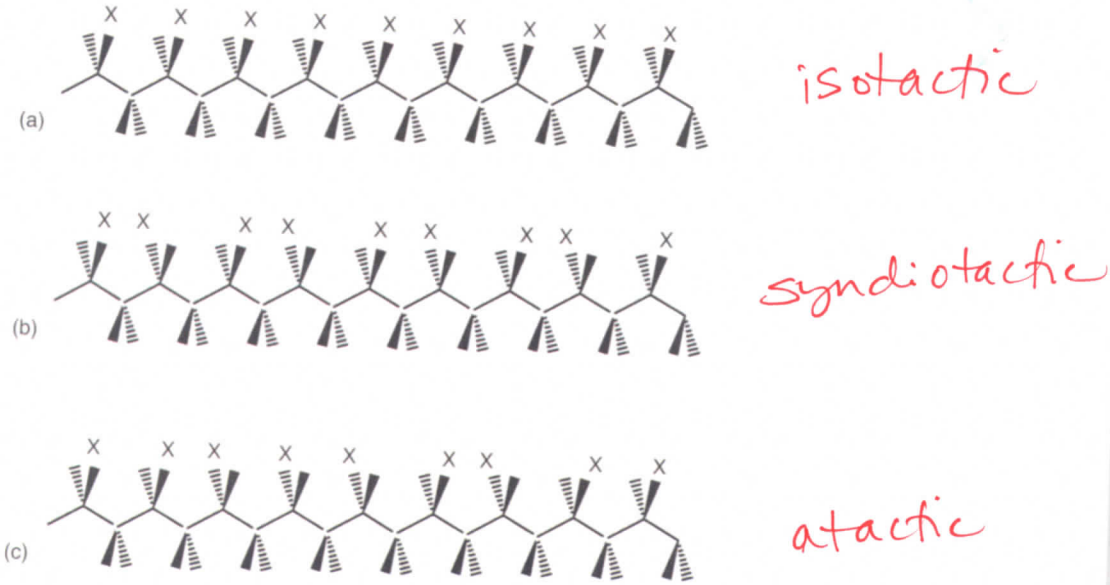


Figure 1.3 Sections of "polyvinyl X" chains of differing tacticity: (a) isotactic, (b) syndiotactic, and (c) atactic.

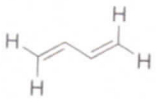
Chapter 5 is devoted to a discussion of their preparation and characterization. For now, only the terminology involved in their description concerns us. Three different situations can be distinguished along a chain containing pseudoasymmetric carbons:

1. *Isotactic*. All substituents lie on the same side of the extended chain. Alternatively, the stereoconfiguration at the asymmetric centers is the same, say, –DDDDDDDDD–.
2. *Syndiotactic*. Substituents on the fully extended chain lie on alternating sides of the backbone. This alternation of configuration can be represented as –DLDLDLDLDLDL–.
3. *Atactic*. Substituents are distributed at random along the chain, for example, DDLDLLLDLDLL–.

Figure 1.3 shows sections of polymer chains of these three types; the substituent X equals phenyl for polystyrene and methyl for polypropylene. The general term for this stereoregularity is *tacticity*, a term derived from the Greek word meaning "to put in order." Polymers of different tacticity have quite different properties, especially in the solid state. As we will see in Chapter 13, one of the requirements for polymer crystallinity is a high degree of microstructural regularity to enable the chains to pack in an orderly manner. Thus atactic polypropylene is a soft, tacky substance, whereas both isotactic and syndiotactic polypropylene are highly crystalline.

1.6.3 Geometrical Isomerism

The final type of isomerism we take up in this section is nicely illustrated by the various possible structures that result from the polymerization of 1,3-dienes. Three important monomers of this type are 1,3-butadiene, 1,3-isoprene, and 1,3-chloroprene, Structure (1.X) through Structure (1.XII), respectively:



(1.X)

Solution

Since the total numbers of dyads and triads always occur as ratios in Equation 5.9.3 and Equation 5.9.4, both the numerators and denominators of these ratios can be divided by the total number of dyads or triads to convert these total numbers into fractions, i.e.,

$$\nu_i/\nu_s = (\nu_i/\nu_{tot})/(\nu_s/\nu_{tot}) = p_i/p_s$$

Thus the fractions in Table 5.7 can be substituted for the ν's in Equation 5.9.3 and Equation 5.9.4. The values of $\bar{n}_i$ and $\bar{n}_s$ so calculated for the three polymers are:

	$\bar{n}_i$	$\bar{n}_s$
Atactic	1.59	5.64
Syndiotactic	1.32	6.45
Isotactic	9.14	1.37

This analysis adds nothing new to the picture already presented by the dyad and triad probabilities. It is somewhat easier to visualize an average sequence, however, although it must be remembered that the latter implies nothing about the distribution of sequence lengths.

We conclude this section via Figure 5.9, which introduces the use of ^{13}C-NMR obtained at 100 MHz for the analysis of stereoregularity in polypropylene. This spectrum shows the carbons on the pendant methyl groups for an atactic polymer. Individual peaks are resolved for all the possible pentad sequences. Polypropylene also serves as an excellent starting point for the next section, in which we examine some of the catalysts that are able to control stereoregularity in such polymers.

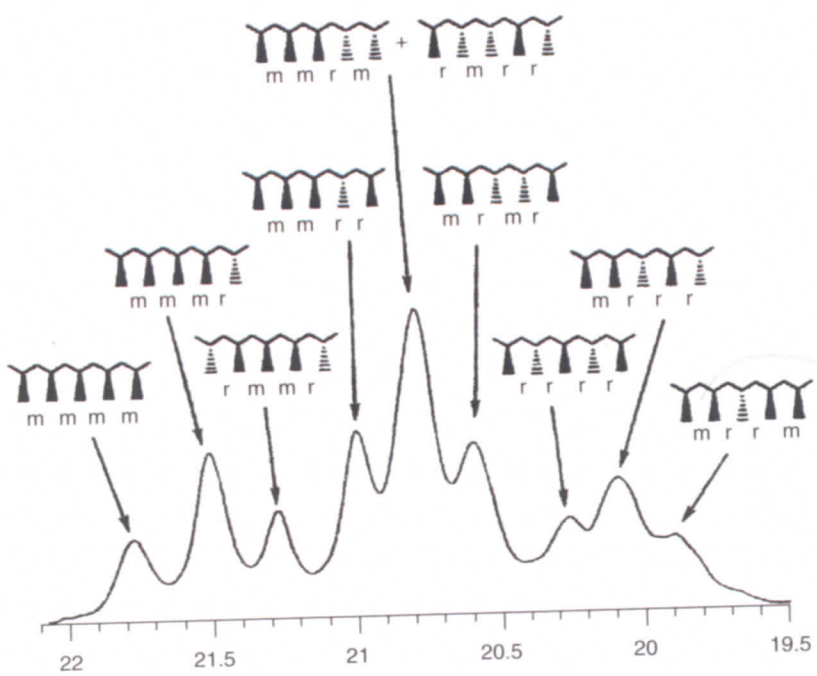


Figure 5.9 ^{13}C-NMR assignments for polypropylene. (From Bruce, M.D. and Waymouth, R.M., *Macromolecules*, 31, 2707, 1998. With permission.)

(1) Ziegler-Natta Polym.

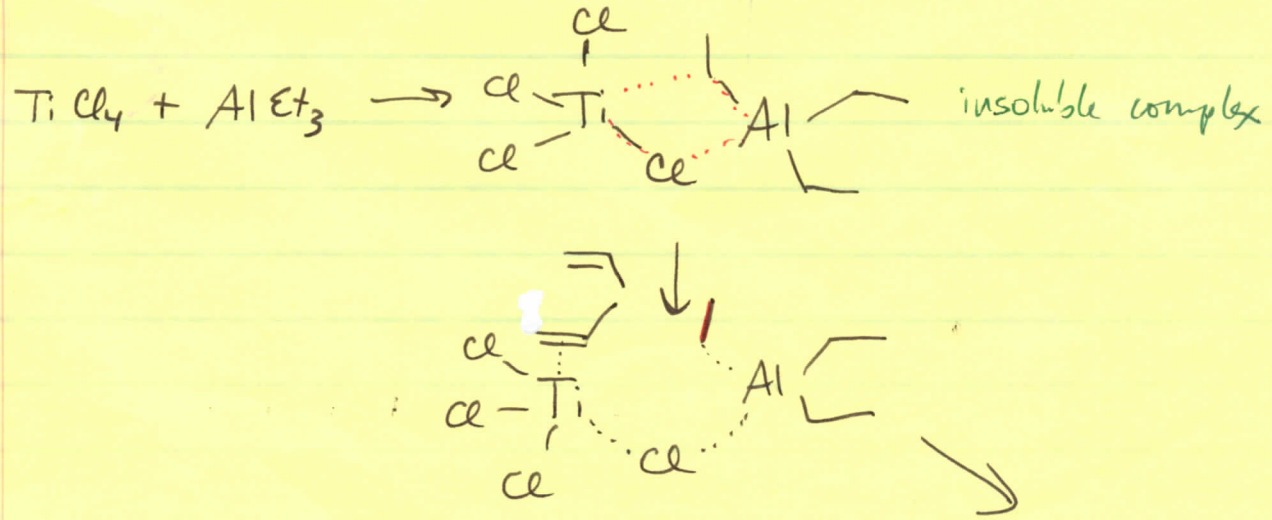
- Karl Ziegler (German) + Giulio Natta (Italian) 1963 Nobel Prize for Ti-based catalysts development for polym of ethylene + stereoregular polys

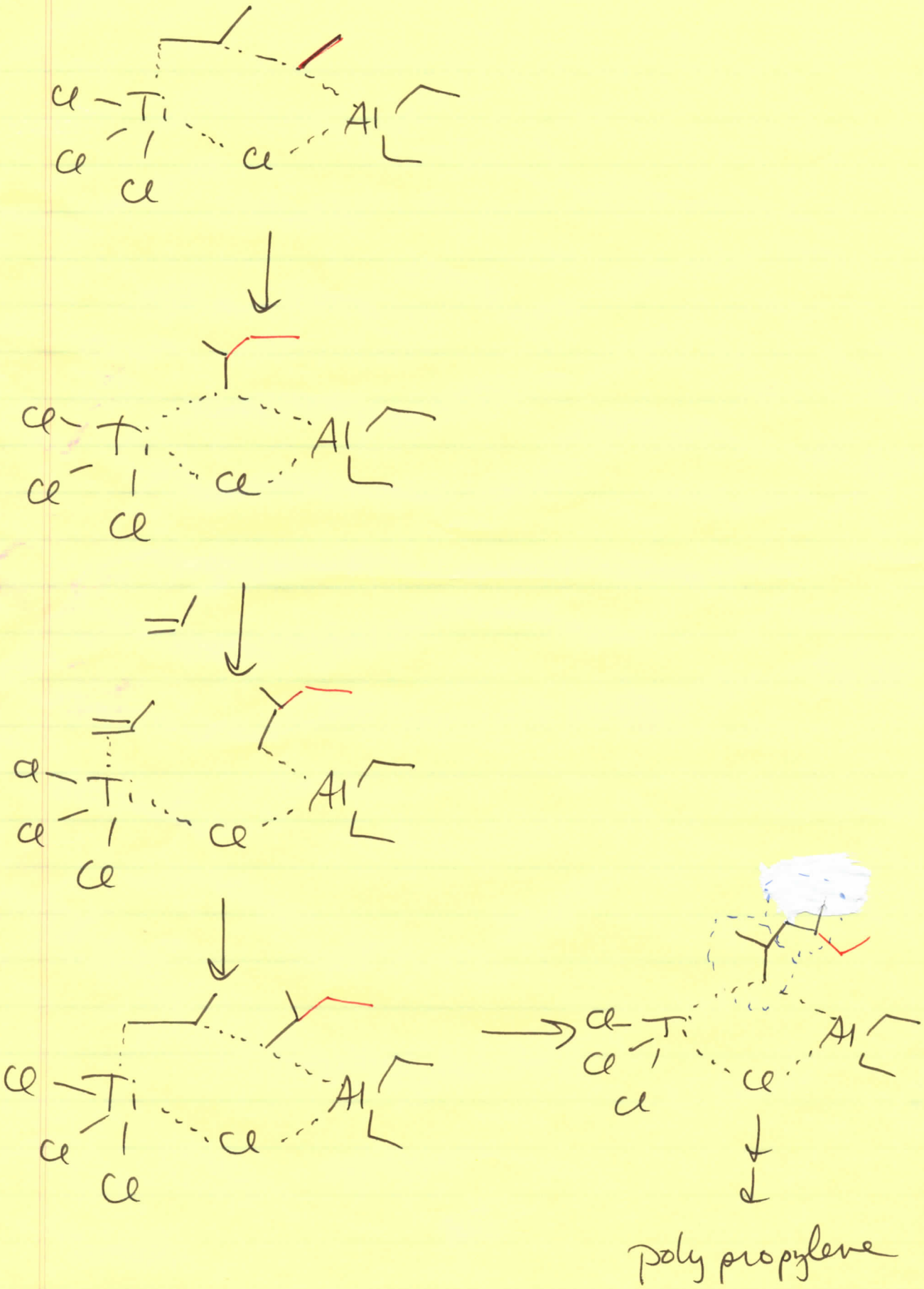
- even today ca. 100 M metric tons of poly produced via Ziegler-Natta cats.
  e.g. polyethylene (HDPE) or polypropylene

- yet, still, the mechanism remains unknown / unconfirmed
  see text section 5.10

- catalysts + co-catalysts are involved
  e.g. $TiCl_4$ + $AlEt_3$

- to achieve stereochem control, most likely a bimetallic coordination chem. mechanism




Cl
Ti
Cl
Cl
Cl
Al
polypropylene

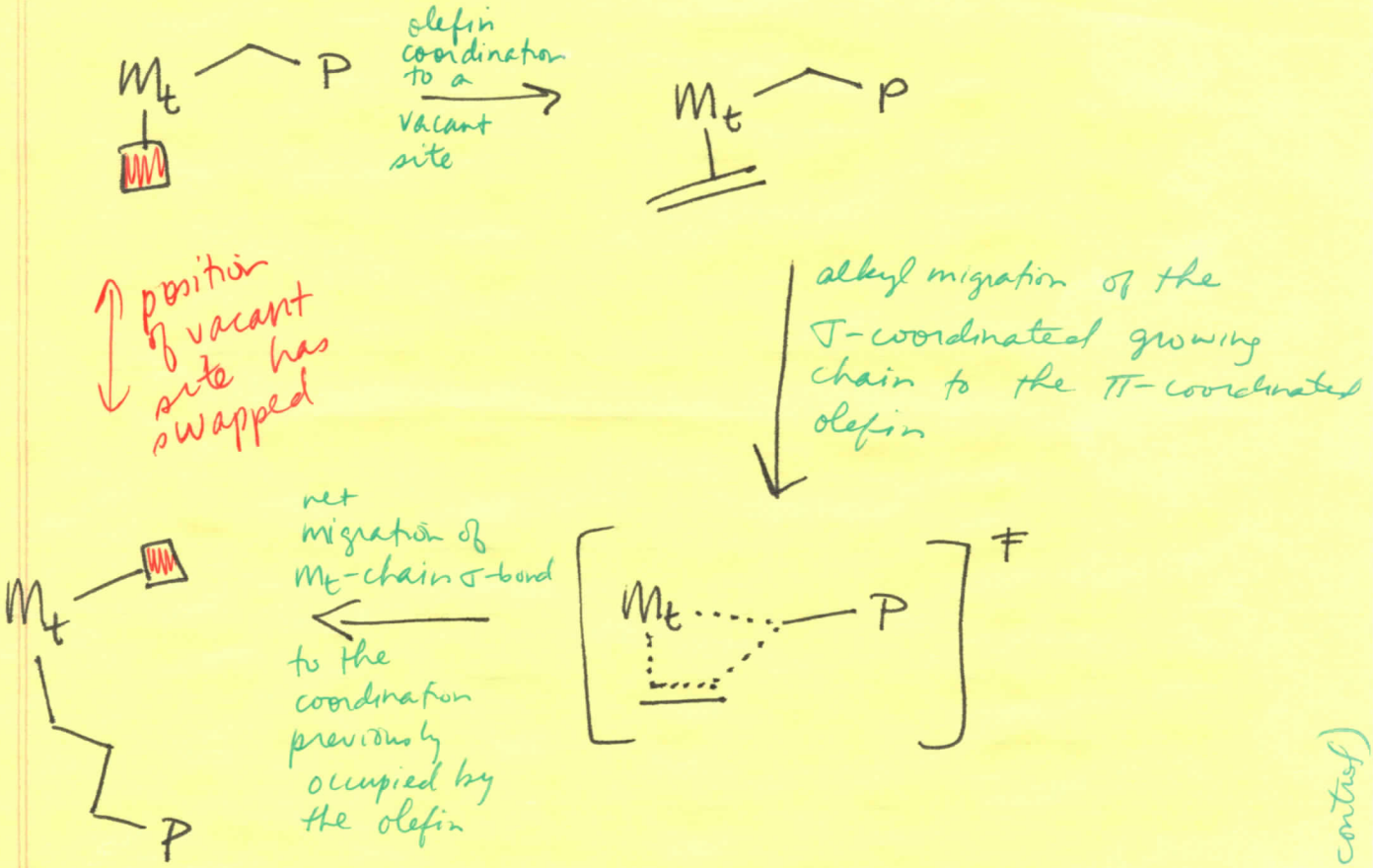
(2) Single-site T.M. catalysts

⊛ Show transparency from G.W. Coates Chem Rev. 2000, 100, 1223-1252

- coordination polyn
- multiple insertions of olefinic monomers into a metal-carbon bond
- cis opening of the double bond i.e., both new bonds are formed on the same side of the inserting olefin
- the growing chain migrates to the olefin ⇒ net exchange of the two available coordination positions on the metal center
- active metal center bearing the growing alkyl chain must have an available coordination site for the incoming monomer
- poly chain remains bound to the active metal center
- both the ligands on the metal & the attached poly chain influence the stereochem. of each ~~in~~ monomer insertion

for Group 3 and 4 Transition Metals; proposed mechanisms:

Cossee Mech. (Direct insertion)



and modified versions of this + other mechanisms

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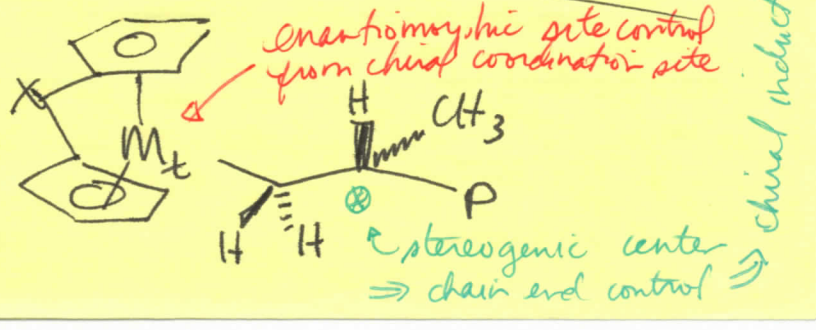
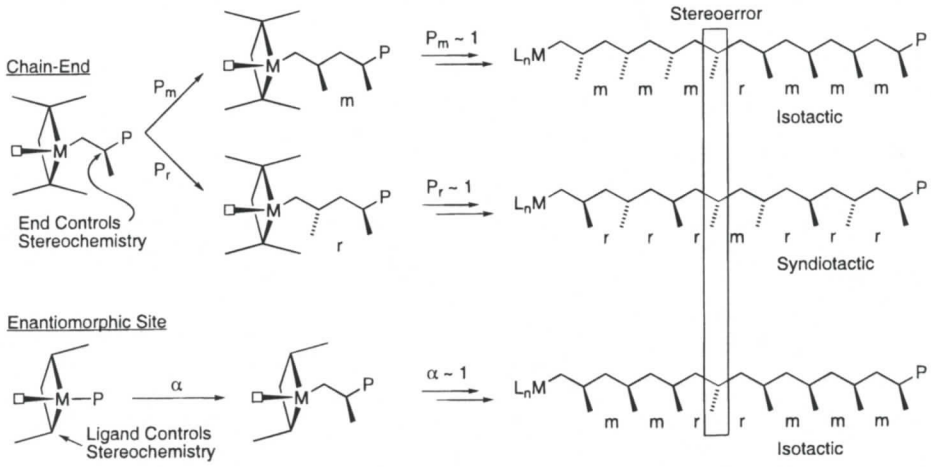
stereochem comes from:



Scheme 1. Chain-End and Enantiomorphic Site Mechanisms of Stereocontrol



are now available that can control the molecular weight, molecular weight distribution, comonomer incorporation, and both the relative and absolute stereochemistry of a polymer in a way that is often impossible using conventional hetereogeneous catalysts. Although their commercial implementation in the solution phase is often impractical, they can be heterogenized for efficient gas-phase or flow-through reaction by attaching them to a solid support. Perhaps most importantly, these defined molecular-based systems allow detailed structural and mechanistic studies. Thus, through theoretical and empirical studies scientists can rapidly evolve new and improved generations of catalysts.

B. Scope of Review

This review covers the scientific literature from the mid-1980s to the present concerning stereoselective polymerization by single-site transition metal and f-block metal complexes. Strategies for controlling the relative configuration of main-chain stereogenic centers of chain-growth polyolefins are included; since the emphasis is on stereochemical control of polymerization by the homogeneous catalyst, the polymerization of optically active monomers will not be covered. The review will concentrate on examining state-of-the-art stereoselective polymerization catalysts and will focus on proposed mechanisms of stereocontrol. Although the emphasis will be on stereochemical control by the catalyst, other important characteristics such as polymerization activity and polymer properties will be included.

C. Mechanisms, Nomenclature, and Quantification of Stereoregularity

Both the ligand set of a single-site catalyst and the growing polymer chain influence the stereochemistry of the polymerization reaction.[13] It is interesting to note that, unlike the catalytic synthesis of small molecules, during a chain-growth polymerization reaction a polymer chain remains bound to the active metal center during monomer enchainment. Thus, the stereogenic center from the last enchained monomer unit will have an influence on the stereochemistry of monomer addition; if this influence is significant, the mode of stereochemical regulation is referred to as "polymer chain-end control". It should be noted that in rare instances more than one stereogenic center of the polymer can play a significant role in stereoregulation. If the ligand set is chiral and overrides the influence of the polymer chain end, the mechanism of stereochemical direction is termed "enantiomorphic-site control" (Scheme 1). In the former mechanism, a stereochemical error is propagated, while in the latter a correction occurs since the ligands direct the stereochemical events.

Scheme 1 introduces the parameters that are used to describe the stereoselectivity of the monomer enchainment process. For chain-end control, the parameters P_m and P_r refer to the probability of *meso* and *racemic* placements, respectively (the Bovey formalism is a convenient way to describe polymer tacticity, with a small "*m*" for *meso*, and a small "*r*" for *racemic* relationships between adjacent stereogenic centers). A P_m equal to unity indicates isotacticity, while a P_r equal to unity signifies syndiotacticity. For site-control mechanisms, the parameter α represents the degree of enantiotopic selectivity of the enchainment. When α is either 1 or 0 an isotactic polymer forms, while an α parameter of 0.5 produces an atactic polymer. Polymer architectures relevant to this review are shown in Figure 1.

There are several techniques for determining the type of tacticity and degree of stereoregularity of a polymer sample. Commonly used methods include solubility, X-ray diffraction, IR spectroscopy, and thermal properties (melting point and glass-transition temperature). In the case of chiral polymers, optical rotation can be used to determine the absolute configuration as well as degree of enantiomeric purity when the optically pure polymer is available. However the most useful method for determining a polymer's tacticity classification as well as quantifying its stereochemical purity is nuclear magnetic resonance (NMR).[14,15] In many cases the shifts for the various polymer nuclei are sensitive to adjacent stereogenic centers, resulting in fine structure that can provide quantitative information about the polymer microstructure once the shifts identities are assigned. For example, the methyl region of a high-resolution ^{13}C NMR spectrum of atactic polypropyl-

(3) highly exciting chain shuttling polym — 2 catalysts + chain shuttling agent (C→A)

Catalytic Production of Olefin Block Copolymers via Chain Shuttling Polymerization

Daniel J. Arriola,[1*] Edmund M. Carnahan,[2*] Phillip D. Hustad,[2*] Roger L. Kuhlman,[2*] Timothy T. Wenzel[1*]

We report a catalytic system that produces olefin block copolymers with alternating semicrystalline and amorphous segments, achieved by varying the ratio of α-olefin to ethylene in the two types of blocks. The system uses a chain shuttling agent to transfer growing chains between two distinct catalysts with different monomer selectivities in a single polymerization reactor. The block copolymers simultaneously have high melting temperatures and low glass transition temperatures, and therefore they maintain excellent elastomeric properties at high temperatures. Furthermore, the materials are effectively produced in economically favorable, continuous polymerization processes.

During the past 50 years, polyolefins have become, by far, the highest volume commercial class of synthetic polymers. Olefin polymerization catalysts have evolved during this time from heterogeneous mixtures (*1*) to well-defined soluble molecules (*2*), allowing chemists to understand and control the effects of catalyst structure on polymer composition and microstructure. These advancements in catalysis have enabled the production of polyolefins with an exquisite degree of control over stereochemistry (*3*) and macromolecular branch architecture (*4*), leading to new classes of polymers with useful combinations of physical properties. However, the economical preparation of olefin block copolymers (*5*) having both "hard" (semicrystalline or high glass transition temperature) and "soft" (amorphous and low glass transition temperature) segments remains one of the major challenges in the field of polymerization catalysis. Here we report a method for the preparation of linear ethylene-based block copolymers with such properties by using chain shuttling polymerization.

A few strategies for preparation of stereoblock polyolefins have been reported in the recent literature (*6–9*). Despite the high melting temperatures exhibited by isotactic or syndiotactic polypropylenes (PPs), the relatively high glass transition temperatures of these materials ($T_g \sim 0°C$) limit their utility in elastomeric applications. More recently, olefin-based block copolymers have been made using living coordination polymerization catalysts (*10*). These catalysts, like living anionic (*11*), cationic (*12*), or radical (*13–15*) polymerization processes, can be used to achieve precise structural control in block copolymer synthesis through sequential monomer addition strategies. However, living polymerization processes are uneconomical because they produce only one polymer chain per catalyst molecule and operate in a batch polymerization process. In addition, the low reaction temperatures typically required to achieve living behavior with these systems inhibit the synthesis of materials containing more than one semicrystalline block because of premature precipitation of the polymer.

To circumvent the problems associated with previous strategies for the preparation of polyolefin block copolymers, we pursued the synthesis of these materials via a technique that we call "chain shuttling polymerization" (*16*). We define chain shuttling as the passing of a growing polymer chain between catalyst sites, such that portions of a single polymer molecule are synthesized by at least two different catalysts. Likewise, a chain shuttling agent (CSA) is a component such as a metal alkyl complex that facilitates this transfer. This approach can thus be used to prepare block copolymers from a common monomer environment by using a mixture of catalysts of different selectivities, namely stereoselectivity or monomer selectivity. Under the right conditions, efficient chain shuttling produces a linear multiblock copolymer that features alternating hard and soft blocks.

One key to forming differentiated block copolymers via chain shuttling is finding a monomer or combination of monomers that, on the basis of their arrangement in the polymer chain, can give rise to both hard and soft materials. Stereoblock PPs do not have the low glass transition temperatures required for most elastomeric applications. On the other hand, ethylene-based polymers that incorporate varying fractions of α-olefin fit this criterion. Polyethylenes (PE) with low co-monomer content are semicrystalline (hard) materials with melting temperatures (T_m) approaching 135°C, whereas PEs with high levels of comonomer are amorphous (soft) materials with very low glass transition temperatures (T_g < −40°C). We therefore focused on ethylene-based block copolymers with both hard and soft segments, with the hypothesis that the benefits of both the high T_m and low T_g would be retained. To this end, we required a mixed catalyst system capable of producing these different types of polymer in a common reaction environment. A further important requirement is that each of the catalysts undergoes chain shuttling with a common chain shuttling agent.

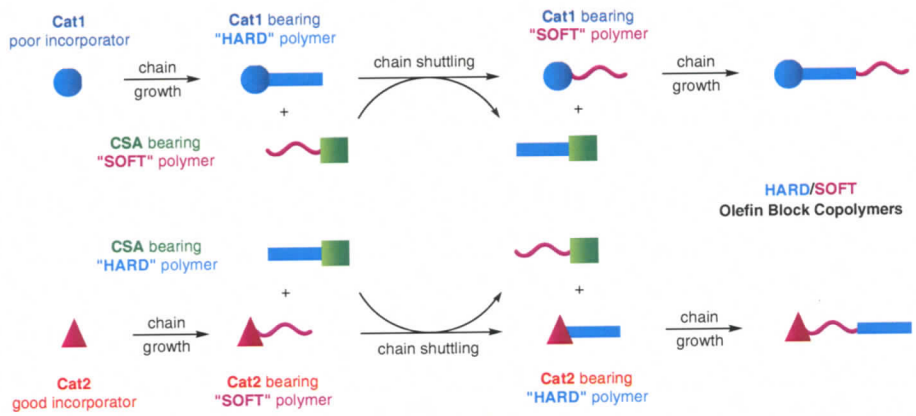


Fig. 1. Depiction of the likely chain shuttling mechanism in a single reactor, dual-catalyst approach. Cat1 (solid circles) and Cat2 (solid triangles) represent catalysts with high and low monomer selectivity, respectively, whereas the CSA (solid squares) facilitates the chain shuttling reaction. Cat1 produces a segment of hard polymer with low comonomer content. Shuttling occurs when this segment is exchanged with the CSA bearing a soft copolymer of higher comonomer content. Further chain growth at Cat1 then extends the soft copolymer chain with a hard segment, thus giving a block copolymer.

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This process (Fig. 1) requires one catalyst, Cat1, with high ethylene selectivity to form hard polymer chains. Meanwhile, a good incorporator of comonomer, Cat2, grows soft amorphous chains in the same reactor because of its dramatically different monomer selectivity. In the absence of chain shuttling, a polymer blend is produced with none of the advantageous properties of block copolymer architecture. In the presence of an effective CSA, however, polymer chains are swapped between catalysts before the chains terminate. To understand this swapping phenomenon, it is instructive to follow the lifetime of a representative polymer chain. The chain may begin growing on Cat1 as a hard polymer. The chain is then exchanged onto a CSA, where it is held for some period of time without growing. The dormant polymer chain may then return to another molecule of the same catalyst and lengthen the hard segment or it may shuttle to a molecule of Cat2, from which subsequent chain growth results in formation of a polymer chain with both soft and hard blocks. The process may be repeated any number of times during the lifetime of the chain before chain termination occurs via a usual mechanism such as hydrogenolysis. A statistical analysis of this chain shuttling phenomenon reveals multiblock copolymers with a most probable distribution of block lengths and number of blocks per chain. This microstructure is distinctly different from materials made with living polymerization techniques, which ideally have a Poisson distribution of block lengths and a precise number of blocks. Furthermore, the synthesis of these olefin block copolymers is not stoichiometrically limited by Cat1, Cat2, or CSA.

Furthermore, this approach enables precise control over polymer microstructure. Despite the differences in monomer selectivity between the two catalysts, fast rates of chain shuttling and judicious selection of process variables produce copolymers with homogeneous molecular weight and composition distributions. The overall composition, i.e., the hard-to-soft polymer ratio, can be easily controlled by the relative amount of the catalysts used. The comonomer content of the individual hard and soft blocks can be tailored by reactor feed or catalyst modifications. Finally, the average length of the blocks, which is a function of the relative rates of chain growth and shuttling, can be controlled simply by adjusting the ratio of concentrations of CSA and monomer ([CSA]/[C_2H_4]).

Selection of CSA and catalysts. It is well established in olefin polymerization that growing chains can be transferred from the catalyst to an added main-group metal in exchange for an alkyl group (i.e., chain transfer to metal) (*1*, *17*). This transfer is most often irreversible, leading to the termination of the growing chain and the initiation of a new polymer chain. However, the synthesis of block copolymers via chain shuttling requires this polymer chain transfer to be reversible. The main-group centers cannot act as a final repository for "dead" polymer chains; instead, they must serve as a reservoir of "live" chains that are intermittently reattached to catalyst centers for further growth. Chien (*7*) and Brintzinger (*8*) have independently claimed preparations of stereoblock PPs using reversible chain transfer between two catalyst centers with different stereoselectivities. However, polymer fractionation revealed that the samples were largely blends of isotactic and atactic PPs, with at most a small fraction of block copolymer. For single-catalyst systems, this process has been used to prepare long-chain metal alkyls (*18*–*22*) and has more recently been described as "catalyzed chain growth" (*23*, *24*). Gibson *et al.* have discussed the effects of catalyzed chain growth on molecular weight distribution, reporting that a Poisson distribution of molecular weights ($M_w/M_n = 1$, where M_w is the weight-average molecular weight and M_n is the number-average molecular weight) is expected under these conditions instead of the Schulz-Flory distribution ($M_w/M_n = 2$), observed when chain termination occurs (*24*). This behavior provides an easy means of probing the capabilities of a catalyst system for chain shuttling polymerization.

Given the multitude of olefin polymerization catalysts, it was daunting to identify a pair of catalysts with substantially different monomer selectivities that are also capable of chain shuttling. Furthermore, the chosen system also needs to operate at a high solution-reaction temperature ($T \geq 120°C$) to prevent undesired polymer precipitation. We therefore adopted a high-throughput method to expedite this discovery process. The technique uses a parallel screen of the effects of metal alkyl reagents on the molecular weight and molecular weight distributions of polyethylenes produced by catalyst/CSA combinations. These criteria provide a simple test for finding catalyst/CSA combinations suitable for use in our dual-catalyst system (Fig. 2).

To begin the selection process, we first selected representative examples from a broad variety of catalyst structure types known to have high polymerization rates. Two examples are shown in Fig. 2. Ethylene polymerizations were then carried out with these catalysts, in combi-

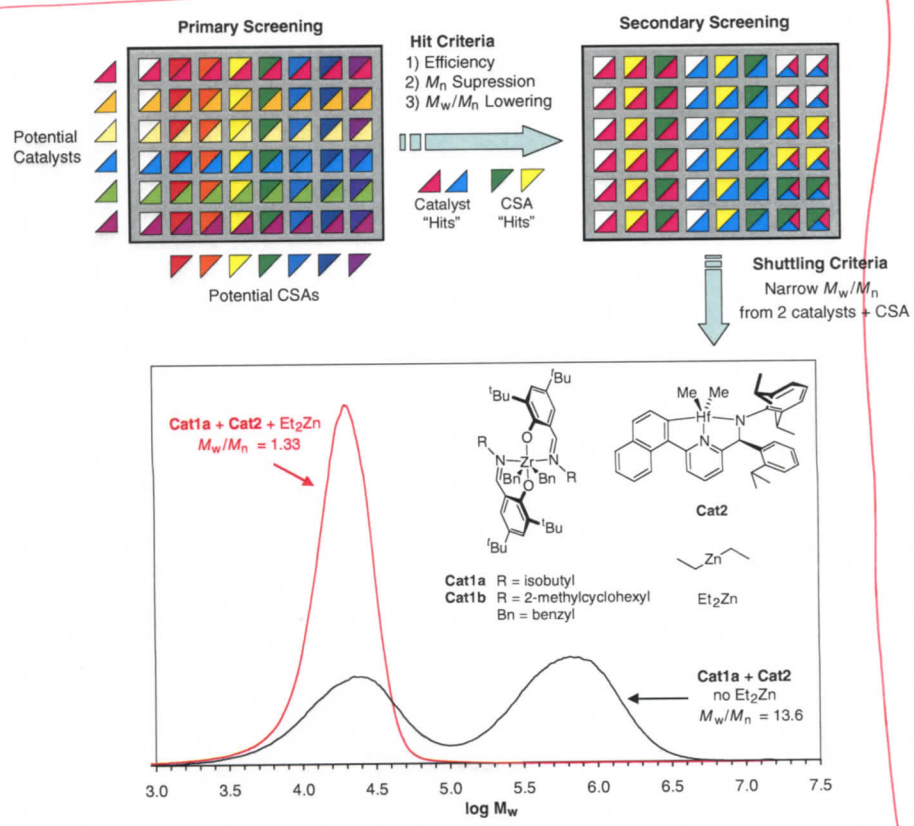

Fig. 2. High-throughput screening protocol and selected data from the chain shuttling screen. Polymerizations are conducted in a parallel grid of individual computer-controlled reactors with robotic addition of reagents and real-time monitoring, coupled with high-throughput characterization techniques. Primary screening involves a broad screen of several catalysts in combination with many potential shuttling agents. Combinations that result in good efficiency, lower molecular weight (M_n), and narrower molecular weight distribution (M_w/M_n), are considered hits. These hits are then subjected to a secondary screen, including individual catalyst and dual-catalyst/CSA combinations. Structures of **Cat1a**, **Cat1b**, **Cat2**, and the CSA are depicted. Shuttling for this trio is demonstrated by the coalescence of the bimodal molecular weight distribution by adding Et_2Zn to the dual-catalyst system.

systematically varied to study the effects of the ratio on polymer microstructure.

The set of experiments was begun with only **Cat2** to produce a copolymer with a density of 0.862 g/cm^3 by adjusting monomer feed rates and catalyst and cocatalyst flows (*26*). Molecular weight control was achieved with a mixture of Et_2Zn and hydrogen, which were adjusted to reach a M_w of 110,000 g/mol (sample 1). **Cat2** feed was then stopped, and **Cat1b** was introduced to the reactor under identical reactor conditions. The higher ethylene selectivity of this catalyst resulted in an increase in the measured polymer density to 0.936 g/cm^3. The large difference in comonomer content between these two copolymers, made under similar reaction conditions, demonstrates the substantial difference in the monomer selectivity of the two catalysts. The molecular weight of this hard comonomer–poor material was also much lower, indicative of faster chain termination (primarily by reaction with H_2) for this catalyst system. Et_2Zn feed was maintained, but some hydrogen was removed to give a polymer with M_w = 65,000 g/mol (sample 2).

These two baseline polymerizations provided an estimate of the catalyst ratio necessary to achieve the desired composition for the dual-catalyst product; an overall density of ~0.88 g/cm^3 was targeted to give the desired copolymer composed of 30% high-density material (*33*). As a control, a mixture of **Cat1b** and **Cat2** was added to the reactor under the same process conditions with no Et_2Zn, giving a reactor blend of the two component copolymers with an overall density of 0.89 g/cm^3. Hydrogen was added to give a polymer with M_w = 137,300 g/mol (sample 3), which was a simple blend of hard and soft PE made independently by the two catalysts. Et_2Zn was then added to induce chain shuttling between the two catalysts. Products were produced at three different levels of blockiness, controlled by the ratio of concentrations of Et_2Zn to ethylene ($[Zn]/[C_2H_4]$). Sample 6 was made with the highest Et_2Zn level possible, while still achieving the desired molecular weight.

Characterization of block copolymers. During this set of experiments, it was apparent by eye that this dual-catalyst chain shuttling system was producing desirable block copolymers at higher CSA levels. Physical blends of high-density and linear low-density PE are opaque because of the large high-density PE crystallites and the immiscibility of the two copolymers. However, the copolymers made at higher $[Zn]/[C_2H_4]$ ratios are surprisingly transparent, despite having essentially identical octene content (Fig. 3). This difference is a clear indication that the copolymers produced with Et_2Zn have a very different microstructure than the physical blend of sample 3. We attribute the enhanced clarity to a decrease in crystallite size of the high-density blocks when the average block length is shorter.

From gel permeation chromatography (GPC), we found that the copolymer prepared without Et_2Zn was clearly bimodal, with M_w/M_n = 13.8 (Fig. 4). The GPC trace was deconvoluted into components of M_w ~ 240,000 and ~9600 g/mol, with the high–molecular weight, low-density copolymer making up 64 wt % of the overall material. This large molecular weight split reflects the differing propensities for hydrogen-induced termination between the two catalysts. The molecular weight distribution narrows as Et_2Zn is added, as expected for an efficient chain shuttling polymerization. At the highest Et_2Zn level, a most probable molecular weight distribution (M_w/M_n = 1.97) is obtained (sample 6). This narrow molecular weight distribution is normally associated with a single catalytic species and is indicative of the multiblock nature of the copolymer, because several shuttling events are required to generate such a homogeneous molecular weight distribution.

This molecular weight response clearly indicates that chain-shuttled ethylene-octene block copolymers, rather than blends, are formed upon introduction of Et_2Zn. The M_n can also be used in conjunction with the Et_2Zn feed and polymerization rate to calculate the number of chains produced per Zn molecule. The low Et_2Zn level of sample 4 results in the production of approximately 12 chains per Zn. However, the reaction is practically stoichiometric at higher Et_2Zn (no H_2), with the production of sample 6 resulting in 1.9 chains per Zn (or ~1 chain per Zn-alkyl moiety). This result indicates that almost every polymer chain exits the reactor bound to the CSA with very little chain termination, demonstrating the efficiency of the chain shuttling reaction.

Despite the stoichiometric nature of the reaction with the CSA, a similar calculation of the number of chains per catalyst molecule reveals that the polymerization is highly catalytic in the hafnium and zirconium species. Block copolymers produced with living polymerization techniques are inherently expensive, because the living nature of the polymerization makes it necessary to use one molecule of catalyst for each chain produced. In contrast, the chain shuttling methodology is capable of generating hundreds to thousands of olefin block copolymer chains per catalyst. For example, the synthesis of sample 6 resulted in the formation of ~260 chains per total catalyst. This feature allows these olefin block copolymers to be produced far more cheaply than materials available from living polymerization techniques.

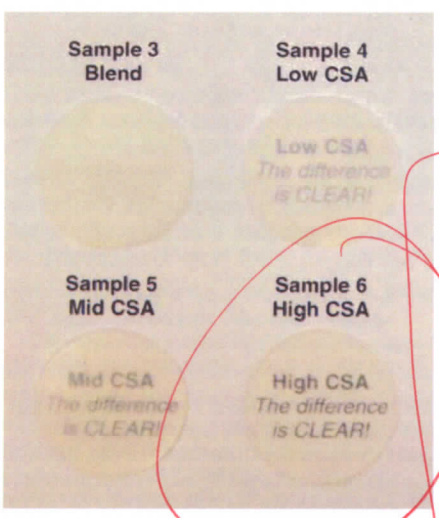

Fig. 3. Image of compression-molded samples (thickness = 0.35 mm), illustrating the effect of chain shuttling on clarity. Sample 3 is a physical blend of high- and low-density polymer and is opaque. Adding Et_2Zn during polymerization results in a block copolymer microstructure with intimately mixed interchain hard and soft segments, resulting in the increased transparency of samples 4 to 6.

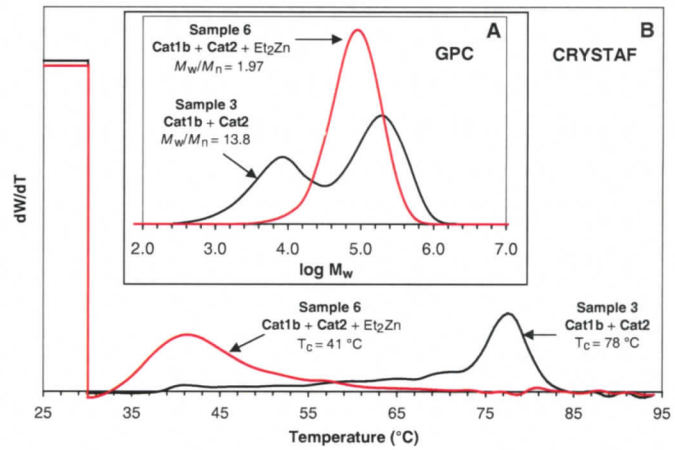

Fig. 4. Characterization of copolymers produced with the dual-catalyst chain shuttling system in a continuous process. Samples 3 (**Cat1b** + **Cat2**) and 6 (**Cat1b** + **Cat2** + CSA) are depicted. (**A**) GPC reveals a bimodal molecular weight distribution in the absence of CSA, whereas adding CSA homogenizes the copolymer to a most probable distribution (M_w/M_n = 2). (**B**) Crystallinity distributions as revealed by crystallization analysis fractionation (CRYSTAF). Sample 3, prepared in the absence of CSA, displays a bimodal composition distribution with a peak around 78°C from **Cat1b** and an amorphous soluble fraction from **Cat2**. Adding CSA gives a copolymer that crystallizes from solution at a much lower temperature, with no indication of highly crystalline material.