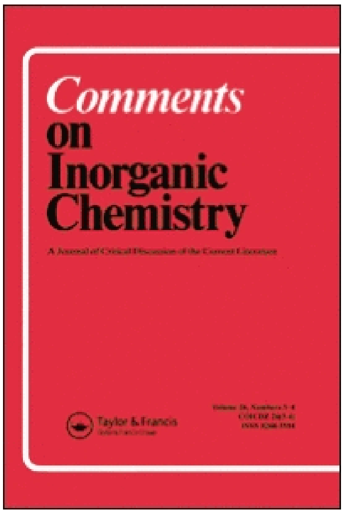

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

ION-PAIRING POLYMERIZATION

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To cite this Article Chen, Eugene Y. -X.(2009) 'ION-PAIRING POLYMERIZATION', Comments on Inorganic Chemistry, 30: 1, 7 — 27
To link to this Article: DOI: 10.1080/02603590902744280
URL: http://dx.doi.org/10.1080/02603590902744280

Comments on Inorganic Chemistry, 30: 7–27, 2009

ISSN: 0260-3594 print
DOI: 10.1080/02603590902744280

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ION-PAIRING POLYMERIZATION

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This account describes the development of a new type of polymerization catalysis termed ion-pairing polymerization (IPP). IPP utilizes compatible and dually active transition-metal cation–main-group anion ion pairs in which *both* the cation and the anion can independently catalyze the polymer chain growth in a single polymerization reaction. Furthermore, cations and anions of ion pairs can exhibit different stereoselectivity and growing chains at the cationic and anionic sites can undergo infrequent exchange between the two sites, thereby covalently linking the polymer chains produced at both sites to afford functionalized vinyl polymers with unique stereomultiblock microstructures.

Keywords: ion-pairing polymerization, living polymerization, metallocene catalysts, stereomicrostructure, stereospecific polymerization

Abbreviations: *at* (*it*, *sb*, *st*)-, atactic (isotactic, stereoblock, syndiotactic); BHT, butylated hydroxytoluene; BMA, *n*-butyl methacrylate; CD, circular dichroism; CGC, $Me_2Si(\eta^5\text{-}Me_4C_5)(t\text{-}BuN)$; Cp, η^5-cyclopentadienyl; DMAA, *N*,*N*-dimethyl acrylamide; DPAA, *N*,*N*-diphenyl acrylamide; DSC, differential scanning calorimetry; EBI, $C_2H_4(\eta^5\text{-Ind})_2$; FG, functional group; Flu, η^5-fluorenyl; GPC, gel-permeation chromatography; *mm* (*rr*, *mr*), isotactic (syndiotactic, heterotactic) triad; MMA, methyl methacrylate; M_n (M_w), number (weight) average molecular weight; MWD, molecular weight distribution; P, growing polymer chain; PDI, polydispersity index (M_w/M_n); PMMA, poly(MMA); RT, room temperature; SBI, $Me_2Si(\eta^5\text{-Ind})_2$; T_g (T_m), glass (melting) transition temperature.

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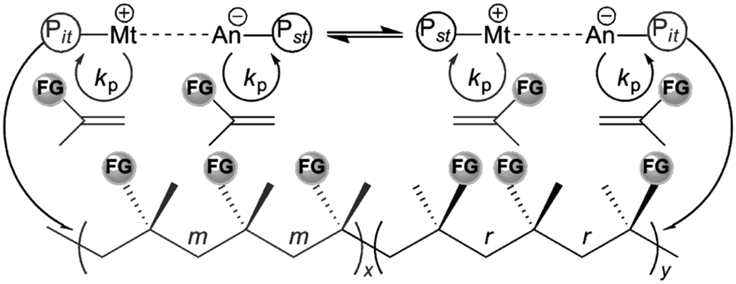
INTRODUCTION

Ion-pairing polymerization (IPP) is termed by us as a polymerization reaction that utilizes both the cation and the anion of compatible and dually active ion pairs, $\mathrm{Mt}^{\oplus}$—$\mathrm{An}^{\ominus}$, for simultaneous constructions of polymer chains at both sites, and that the growing chains can also undergo occasional exchanges between the two sites, thereby producing covalently linked (rather than physically blended) polymer products. IPP fundamentally departs from conventional ionic polymerization processes because both the cation and the anion of the ion pairs in the IPP system serve as active centers for the same polymerization reaction, each bringing different reactivity and/or stereoselectivity to the polymer products. If the cations and the anions of such a system exhibit different stereospecificity (e.g., isospecificity and syndiospecificity for the cationic and anionic sites, respectively), diastereospecific ion-pairing polymerization (DIPP) is created, producing polymers with unique isotactic-*b*-syndiotactic stereomultiblock microstructures.[1] Scheme 1 shows three key events involved in an exemplary DIPP polymerization reaction: isospecific polymerization by the cation, syndiospecific polymerization by the anion, and switching of the growing polymer chains between the cationic and anionic sites.

This account is divided into three major sections: (a) stereospecific polymerization by *ansa*-metallocene cations, (b) stereospecific polymerization by enolaluminate anions, and (c) ion paring polymerization by dually active ion pairs. In each section, a concise summary of key findings or examples is described, without elaborating the details of such findings or examples.



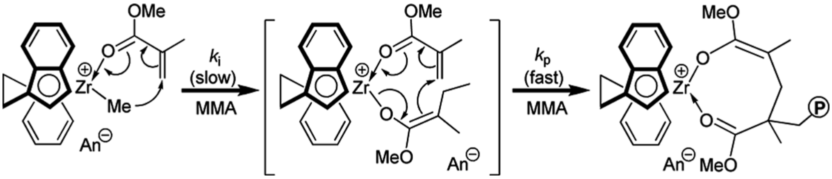
Scheme 1. A pictorial illustration of DIPP. Reproduced with permission from Chen and Cooney.[1]

STEREOSPECIFIC POLYMERIZATION BY *ANSA*-METALLOCENE CATIONS

We began this research by seeking for chiral transition-metal cations that can polymerize functionalized vinyl monomers such as MMA in a stereospecific *and* controlled/living fashion. A coupling of a high degree of stereospecificity with livingness of a polymerization system will render this system highly useful for precise control of polymer chain structures and stereoconfigurations.

Highly isotactic PMMA ($mm > 93\%$) can be conveniently produced at RT with chiral *ansa*-zirconocene dimethyl complexes incorporating C_2-symmetric ligands, such as *rac*-(EBI)$ZrMe_2$ and *rac*-(SBI)$ZrMe_2$, upon activation with suitable activators including $B(C_6F_5)_3$[2] and $Ph_3CB(C_6F_5)_4/Et_2Zn$ (excess),[3] or with the isolated zirconocenium cations.[4] The tetrahydroindenyl derivative *rac*-$[C_2H_4(H_4Ind)_2]ZrMe_2$, once activated with $[^nBu_3NH][BPh_4]$ at 0°C, also affords highly isotactic PMMA.[5] The metallocenium cations intercalated inside layered silicate nano-galleries can control both the stereochemistry of the MMA polymerization in the galleries and the morphology of the silicate filler, affording stereochemically controlled PMMA–exfoliated silicate nanocomposites by *in situ* polymerization approach.[6,7] However, such alkyl-based cationic catalysts are inefficient (low initiator efficiency) in MMA polymerization and cannot control this polymerization, thus yielding the polymer with much higher M_n than that calculated with broad MWD, presumably due to slow initiation by the methyl ligand with respect to fast propagation by the more reactive ester enolate ligand (Scheme 2).

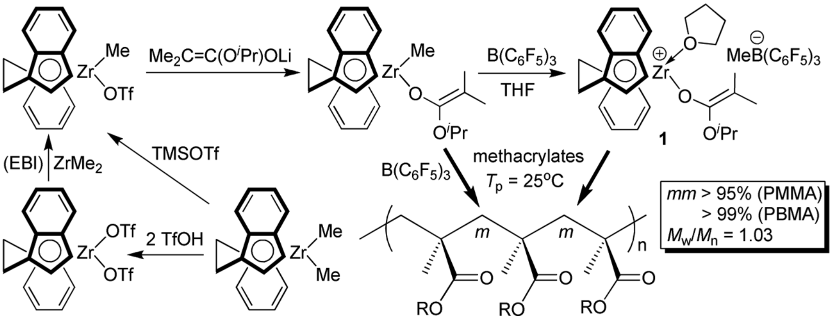
On the basis of the above observation and hypothesis we synthesized a preformed cationic zirconocenium ester enolate catalyst, *rac*-(EBI)Zr^+(THF)$[OC(O^iPr){=}CMe_2][MeB(C_6F_5)_3]^-$ (**1**, Scheme 3).[8] The structure of **1** simulates the proposed active propagating species (Scheme 2), thus in essence bypassing the slow chain-initiation step, and therefore it not only significantly enhances the polymerization activity but also renders a living polymerization process. Accordingly, this catalyst polymerizes $\geq$400 equiv of MMA with quantitative monomer conversions in less than 10 min (vs. hours with the methyl catalyst) at ambient temperature, producing PMMA with high isotacticity ($mm = 95\%$) and narrow MWD ($PDI = 1.03$). This polymerization is enantiomorphic-site controlled (as a methyl triad test using $2[rr]/[mr]$ gave 1.0) and of living



Scheme 2. Slow initiation and fast propagation steps by the C_2-ligated chiral Zr methyl cation.

nature with initiator efficiency typically $\geq$80%. The MMA polymerization activity and initiator efficiency as well as the resulting polymer MWD and isotacticity with the isolated cationic ester enolate catalyst **1** are nearly identical to those of the polymerization with premixing the activator $B(C_6F_5)_3$ with MMA followed by addition of the precursory neutral methyl ester enolate complex *rac*-(EBI)ZrMe[OC(O^{i}Pr)=CMe$_2$] (Scheme 3); this convenient polymerization procedure employs directly the neutral ester enolate precursor (which is much easier to handle than the corresponding cationic species) via in-reactor activation. Polymerization of BMA by this catalyst system produces PBMA with nearly perfect isotacticity (*mm* > 99%), narrow MWD ($M_w/M_n = 1.03$), and high initiator efficiency (95%).[8]

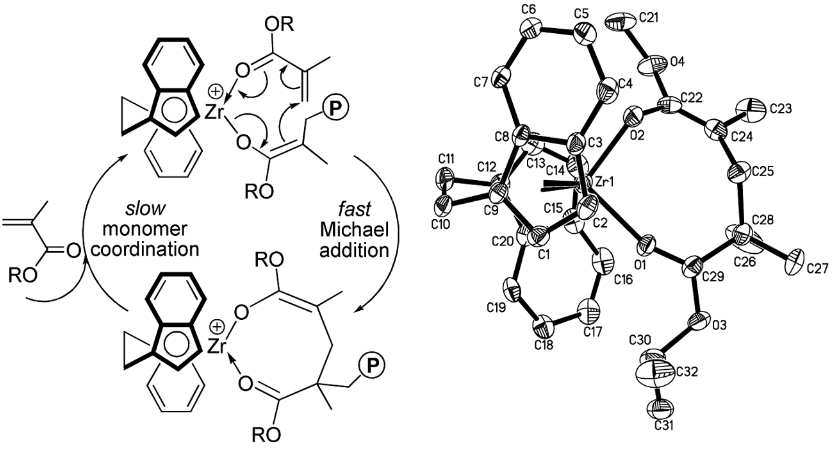
Kinetic and mechanistic studies show that the isospecific methacrylate polymerization catalyzed by the preformed ester enolate cation **1** is site controlled and proceeds in a monometallic, intramolecular conjugate addition mechanism.[9] In a propagation "catalysis" cycle, the fast intramolecular Michael addition produces the eight-membered-ring



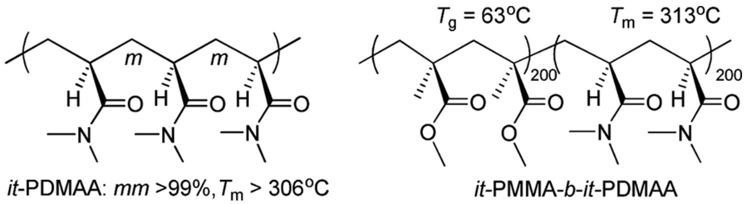
Scheme 3. Synthesis of cationic zirconocenium ester enolate **1** and its MMA polymerization characteristics.

cyclic ester enolate chelate as the resting intermediate, followed by the rate-limiting step of the associative displacement of the coordinated penultimate ester group by incoming methacrylate monomer (ring-opening of the chelate) to regenerate the active species (Scheme 4). The molecular structure of the resting intermediate was confirmed by the successful isolation of the single-monomer addition product[9] and its structural characterization by X-ray diffraction analysis.[10] This structure resembles the eight-membered ring intermediate involved in the MMA polymerization with the single-component lanthanocene catalyst.[11]

Highly isospecific polymerization of acrylamides such as DMAA is also achieved using the ester enolate cation **1** under ambient conditions. The PDMAA produced has a quantitative isotacticity of *mm* of >99%, a controlled M_n, a narrow MWD of 1.07, and a high T_m of >306°C (Scheme 5).[12] This polymerization is also rapid (0.25 mol% catalyst, 25 min, 96% conversion) and proceeds in a living fashion, enabling the synthesis of the well-defined isotactic PMMA-*b*-PDMAA stereodiblock copolymer (Scheme 5).[13] The kinetic and mechanistic studies show that, as in the methacrylate polymerization with this catalyst, the propagation is first order in both concentrations of the monomer and the active species and proceeds via a monometallic, conjugate-addition mechanism through cyclic amide enolate intermediates. The resting state



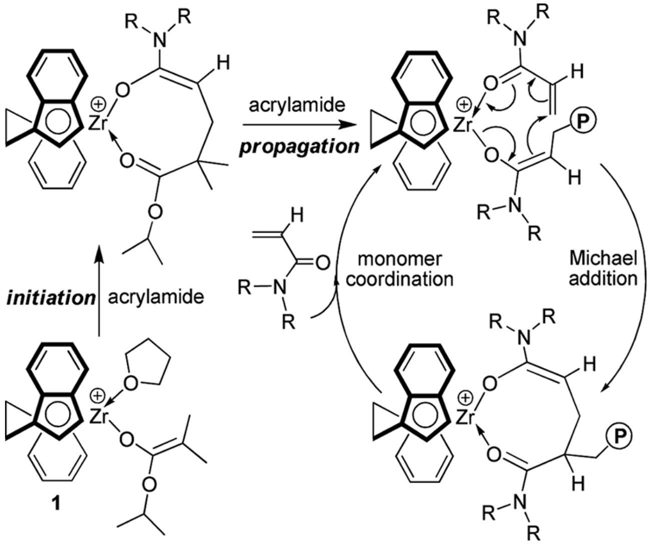
Scheme 4. Mechanism of the propagation "catalysis" cycle and the X-ray structure of the cyclic catalyst resting intermediate. Reproduced with permission from Rodriguez-Delgado and Chen[9] and Ning and Chen.[10]



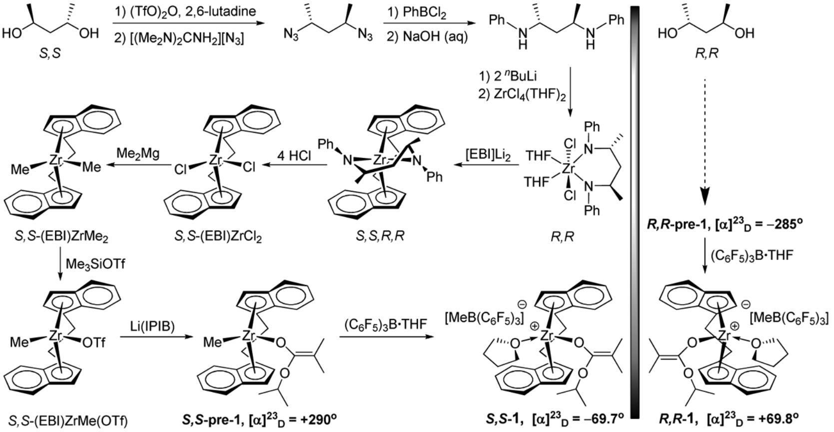
Scheme 5. Highly isotactic acrylamide DMAA polymer and its copolymer with methacrylate MMA.

during a "catalytic" propagation cycle is the cyclic amide enolate and associative displacement of the coordinated penultimate amide group by incoming acrylamide monomer to regenerate the active species is the rate-determining step (Scheme 6).[13]

The racemic *ansa*-zirconocenium ester enolate catalyst **1** also catalyzes the rapid polymerization of bulky *N*,*N*-diaryl acrylamides such as DPAA under ambient conditions in a living fashion, leading to rigid-rod-like, helical poly(*N*,*N*-diaryl acrylamide)s.[14] To render asymmetric coordination polymerization of *N*,*N*-diaryl acrylamides, we subsequently



Scheme 6. Initiation and propagation mechanisms for the coordination polymerization of acrylamides using zirconocenium ester enolate cation **1**. Adapted with permission from Marriott and Chen.[13]



Scheme 7. Outlined synthesis of enantiomeric catalysts (*S*,*S*)-**1** and (*R*,*R*)-**1**. Reproduced with permission from Miyake et al.[14]

synthesized enantiomeric *ansa*-zirconocenium ester enolate chiral catalysts by two mirror-image syntheses of 11 steps (Scheme 7)[14] starting from enantiomeric 2,4-pentanediol to two key precursors (*R*,*R*)- and (*S*,*S*)-(EBI)$ZrCl_2$ using Jordan's chelate-controlled synthesis.[15] Indeed, enantiomeric (*S*,*S*)-**1** and (*R*,*R*)-**1** afford optically active, rigid one-handed helical poly(*N*,*N*-diaryl acrylamide)s and their block copolymers with random-coil MMA blocks (Figure 1).[14] The optical activity of the resulting polymers hinges on the nature of the catalyst; while *rac*-**1** affords the optically inactive polymers, (*S*,*S*)-**1** and (*R*,*R*)-**1** lead to the polymers of opposite optical rotations (specific rotation values up to 185°). These results were further confirmed by their CD spectra, which show, respectively, no, positively signed, and negatively signed Cotton effects for the polymers produced by *rac*-**1**, (*S*,*S*)-**1**, and (*R*,*R*)-**1**; the latter 2 spectra are near mirror images of each other (Figure 1).[14]

The C_s-ligated cationic (CGC)Ti alkyl complex, (CGC)$TiMe^+$ $MeB(C_6F_5)_3^-$ (**2**, Scheme 8), effects ***living and syndioselective*** polymerization of methacrylates at ambient[16,17] or higher (up to 100°C)[18] temperatures via an apparent chain-end control mechanism. The living and syndioselective features of this catalyst system allowed for the highly efficient (>80% initiator efficiency) synthesis of syndiotactic PMMA (up to 80% *rr*) with controlled MW and narrow MWD (PDI = 1.09) as well as the well-defined, syndiotactic diblock or random copolymers of methacrylates.[16] The corresponding chiral cationic (CGC)Ti ester

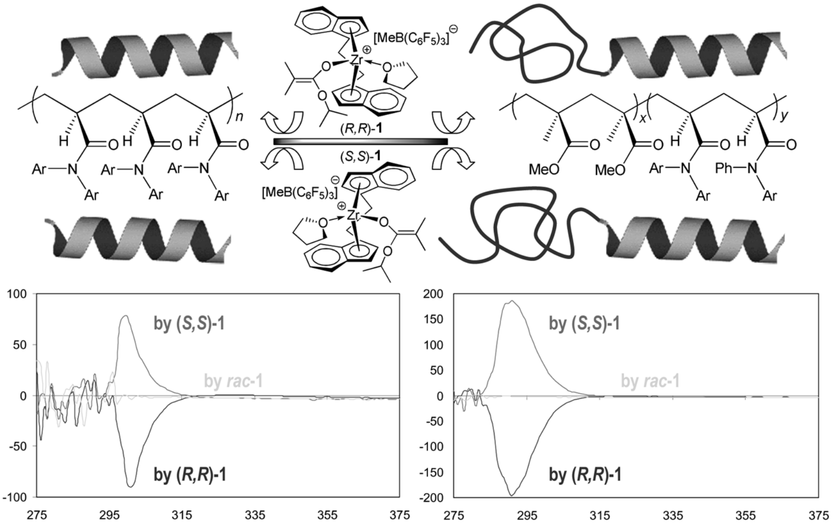
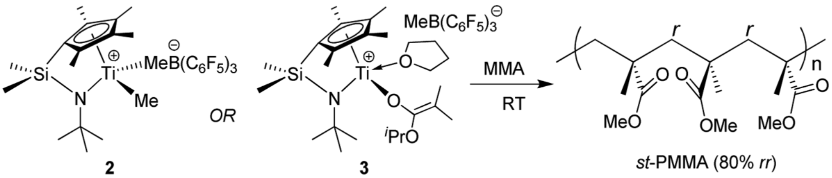


Figure 1. Asymmetric polymerization by enantiomeric catalysts **1** for the synthesis of chiroptical isotactic polymers. Shown on the bottom are the CD spectra of homo- and block copolymers by (*S*,*S*)-**1** (red), *rac*-**1** (green), and (*R*,*R*)-**1** (blue). Adapted with permission from Miyake et al.[14]

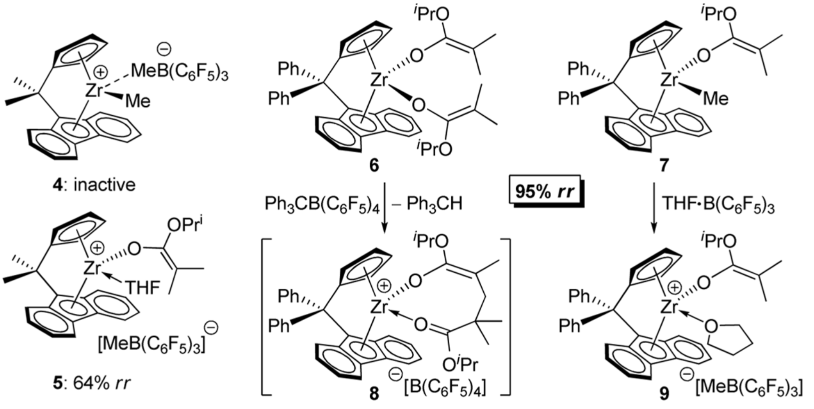
enolate complex, $\{(CGC)Ti(THF)[OC(O^iPr)=CMe_2]\}^+[MeB(C_6F_5)_3]^-$ (**3**, Scheme 8), which simulates the structure of the active propagating species, behaves similarly to that of the (CGC)Ti alkyl complex,[16] producing syndiotactic PMMA (80% *rr*, 18% *mr*, 2.0% *mm*) at ambient temperature with predominately isolated *m* stereoerrors (confirmed by the stereomicrostructure analysis at the pentad level) and again pointing to the apparent chain-end control nature of the (CGC)Ti catalysts. A combined experimental and theoretical study shows the stereoselectivity for the monomer addition is actually determined by the chiral catalyst site, while MMA- or counterion-assisted catalyst site-epimerization after a stereomistake, the process of which converts the kinetic product after a



Scheme 8. Syndiotactic PMMA produced by C_s-ligated (CGC)Ti catalysts.

stereomistake into a thermodynamically more stable resting chelating intermediate, accounts for the formation of the predominately isolated *m* stereoerrors.[19]

The C_s-ligated cationic zirconocene methyl complex, $[Me_2C(Cp)(Flu)ZrMe]^+$ (**4**, Scheme 9), which is known for its ability to catalyze the syndiospecific polymerization of propylene, is however inactive for MMA polymerization. Although we solved this inactivity issue using an ester enolate derivative, $\{Me_2C(Cp)(Flu)Zr(THF)[OC(O^iPr){=}CMe_2]\}^+$ (**5**),[20] the resulting PMMA is essentially a syndio-biased atactic polymer (64% *rr*, 32% *mr*, 4.0% *mm*) via a chain-end control mechanism. Intriguingly, $Ph_2C<$ bridged analogous C_s-ligated *ansa*-zirconocene bis(ester enolate) **6** and mono(ester enolate) **7**—which, upon activation with appropriate activators, generate the corresponding chiral cationic catalysts **8** and **9** (Scheme 9)—produce highly syndiotactic PMMA (up to 95% *rr*) at ambient temperature via a predominately site-controlled mechanism.[21] It is currently unclear why the profound differences in reactivity and stereoselectivity are observed between the $Me_2C<$ and $Ph_2C<$ bridged C_s-ligated *ansa*-zirconocene catalysts, but may be tentatively explained by their different Thorpe–Ingold effect in terms of relative rates of ring-closing (Michael addition step) and ring-opening (monomer coordination step) as compared to the rate of MMA-assisted site epimerization.

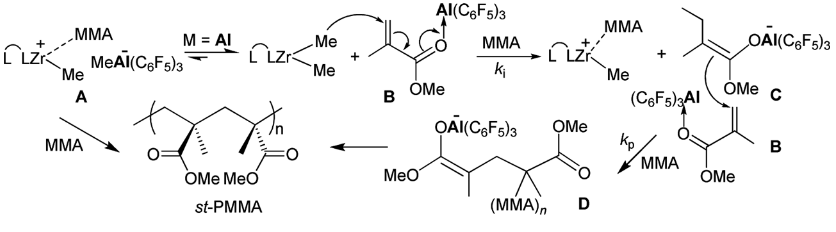


Scheme 9. C_s-Ligated *ansa*-zirconocene catalysts for the synthesis of syndiotactic PMMA with low to high syndiotacticity. Adapted with permission from Ning and Chen.[21]

STEREOSPECIFIC POLYMERIZATION BY ENOLALUMINATE ANIONS

While investigating potential effects of the anion on the stereoselectivity of MMA polymerization by C_2-ligated *ansa*-zirconocene cations, we found that chiral *ansa*-zirconocenium methyl aluminate complexes, unlike analogous methyl borate complexes, which yield highly isotactic PMMA, produce, unexpectedly, syndiotactic PMMA.[4] Scheme 10 outlines the mechanism for the MMA polymerization by the zirconocenium aluminates, which satisfactorily explains the formation of the syndiotactic PMMA, the observed spectroscopic changes while monitoring the polymerization reaction, as well as the observed nearly constant polymer syndiotacticity upon varying the cation symmetry.[4] Owing to the Lewis acidity and oxophilicity of $Al(C_6F_5)_3$ toward MMA exceeding those of the zirconocenium cation, a MMA-separated ion-pair **A**, formed spontaneously upon mixing a zirconocenium aluminate and MMA, is converted to the neutral zirconocene dimethyl and the MMA • $Al(C_6F_5)_3$ adduct (**B**). Initiation involves methyl transfer to **B** forming enolaluminate **C** that participates in rapid propagation via intermolecular Michael addition to **B** producing *st*-PMMA. Hence, this polymerization is bimetallic and chain-end controlled through enolaluminate **D**, typically leading to *st*-PMMA.

In the above polymerization, uniquely regulated by the anion, the zirconocene species participates only in the initiation step, a postulate further supported by experiments with the zirconocene being replaced with anionic initiators such as ^{t}BuLi and $Me_2C{=}C(OMe)OLi$.[4] For example, MMA polymerizations initiated by ^{t}BuLi or $Me_2C{=}C(OMe)OLi$ in toluene have low activity and produce *isotactic* polymer with broad MWDs ($M_w/M_n = 14–22$), whereas the addition of two equiv



Scheme 10. Initiation and propagation pathways involving enolaluminate anions for the formation of syndiotactic PMMA. Adapted with permission from Bolig and Chen.[4]

of $Al(C_6F_5)_3$ to MMA before introducing either anionic initiator to start the polymerization (one equiv for generating enolaluminates and the second for activating monomer) brings about much faster and more controlled polymerizations, producing *syndiotactic* PMMA with tacticity ranging from moderate 76% *rr* to high 95% *rr*, T_g from moderate 127 to high 140°C, and PDI from moderate 1.35 to low 1.08, depending on polymerization temperature. In the case of the polymerization initiated by ^{t}BuLi in combination with $Al(C_6F_5)_3$, if ^{t}BuLi and $Al(C_6F_5)_3$ are premixed for 10 min before addition of MMA to start the polymerization, then the actual initiator is not ^{t}BuLi, rather a hydride-bridged aluminate dimer $[(C_6F_5)_3Al–H–Al(C_6F_5)_3]^-$, which is formed via hydride abstraction with concomitant elimination of isobutylene.[22] Nevertheless, this polymerization procedure is also highly efficient and well controlled, as indicated by its high activity and low PDI values of the resulting polymer.

MMA polymerization using stable alkyl lithioisobutyrates (e.g., $Me_2C{=}C(O^iPr)OLi$) in combination with $Al(C_6F_5)_3$ is more controlled at RT than that using $Me_2C{=}C(OMe)OLi$, producing PMMA with a syndiotacticity of 80% *rr* and a narrow MWD of 1.04. Polymerization of BMA using this initiator system is likewise syndioselective and well controlled. Thus, at a polymerization temperature of 23°C, syndiotactic PBMA (79% *rr*) with a narrow MWD (1.07 PDI) was produced in 96% yield within 30 min. Lowering the polymerization temperature to 0°C achieved higher syndiotacticity (84% *rr*) with a narrow MWD of 1.05.[22] There are dramatic effects of Lewis acids $E(C_6F_5)_3$ ($E = Al, B$) on polymerization of MMA and DMAA mediated by $Me_2C{=}C(O^iPr)OLi$. While the $Me_2C{=}C(O^iPr)OLi/2Al(C_6F_5)_3$ system is *highly active* for MMA polymerization, the seemingly analogous $Me_2C{=}C(O^iPr)OLi/2B(C_6F_5)_3$ system is *inactive*.[23] Structural analyses of the resulting lithium enolaluminate and enolborate adducts, $Li^+[Me_2C{=}C(O^iPr)\text{-}OE(C_6F_5)_3]^-$ (Figure 2), coupled with polymerization studies, show that the remarkable differences observed for Al vs. B are due to the inability of the lithium enolborate/borane pair to effect the bimolecular, activated-monomer anionic polymerization as does the lithium enolaluminate/alane pair.

Polymerization by the alane $Al(C_6F_5)_3$ and group 4 metallocenes containing an ester enolate initiating group, such as $Cp_2ZrMe[OC(O^iPr){=}CMe_2]$, is also highly effective. For example, in a ratio of $[MMA]_0/[Al(C_6F_5)_3]_0/[Zr]_0 = 200{:}2{:}1$, a quantitative monomer conversion was achieved in just 5 min at room temperature, producing PMMA with a syndiotacticity of 69% *rr*, a close-to-the theoretical M_n value of 2.39×10^4,

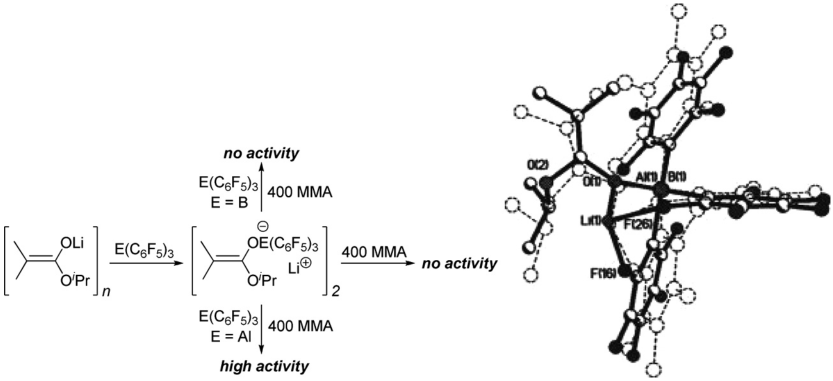
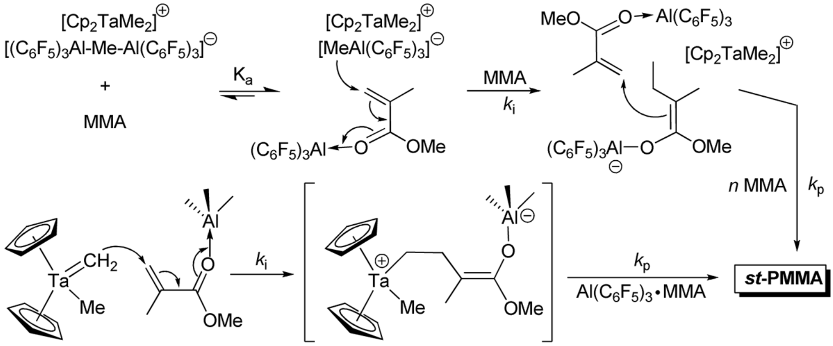


Figure 2. Remarkable Lewis acids effects on the MMA polymerization with lithium ester enolates and structural overlay of enolaluminate and enolborate anions. Adapted with permission from Ning et al.[23]

and a narrow MWD of 1.05. Group 5 metallocene initiators such as Cp_2TaMe_3 and $Cp_2Ta(=CH_2)Me$ in combination with $Al(C_6F_5)_3$ were also shown to form *st*-PMMA through the bimetallic mechanism involving the enolaluminate propagating species (Scheme 11).[24,25] It is apparently general for such a bimetallic pathway involving the enolaluminate active species when combining an initiating molecule with 2 equiv of $Al(C_6F_5)_3$, extending to metallocene imido complexes[26,27] and main-group alkyl complexes.[28]

Anionic active species derived from conventional initiators such as alkyllithium reagents and lithium ester enolates exist as aggregates, both



Scheme 11. Initiation and propagation pathways involving enolaluminate anions for the formation of *st*-PMMA.

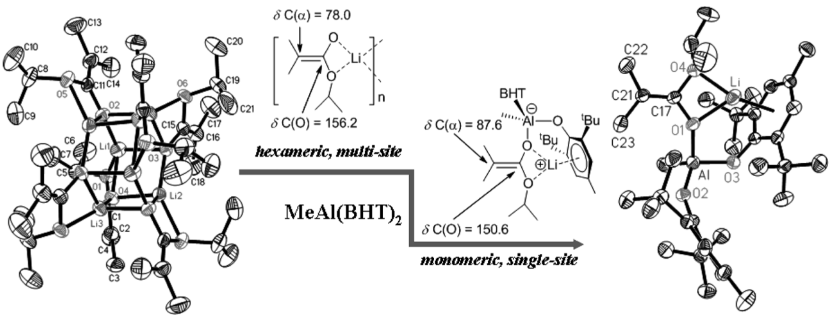
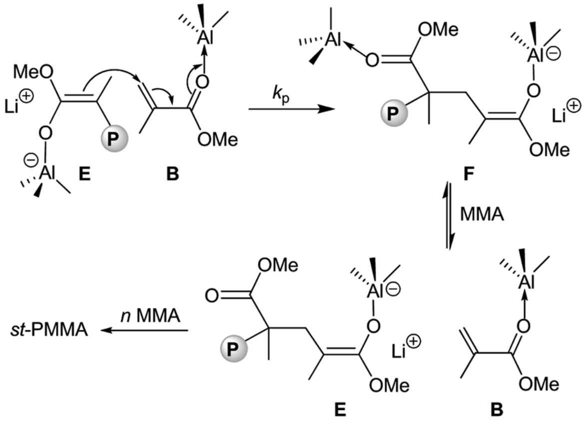


Figure 3. Generation of single-site enolaluminate active propagating species via deaggregation of lithium enolate aggregates with, and subsequent stabilization by, $MeAl(BHT)_2$. Adapted with permission from Rodriguez-Delgado and Chen.[29]

in solid state and in solution. Such anionic active species cannot control the polymer MW and MWD due to the coexistence of various aggregated species that exhibit different reactivity and exchange comparably to, or more slowly than, the polymerization time scale. Thus, they can be characterized as *multi-site* anionic active species and produce polymers with ill-defined chain structures. We found that certain bulky aluminum alkyl compounds such as $MeAl(BHT)_2$, when added to the anionic polymerization system initiated by lithium ester enolates, serve as both catalyst for monomer activation *and* deaggregator for converting the oligomeric, multi-site active species to monomeric, single-site active species (i.e., ester enolaluminate anions, Figure 3).[29] The end result is a promotion of *single-site anionic polymerization* that propagates in a syndioselective, bimetallic fashion (derived from studies by kinetics and NMR). Specifically, the bimolecular chain propagation for the MMA polymerization by the lithium ester enolaluminate and organoaluminum catalyst combination involves Michael addition of monomeric enolaluminate active species **E** to Al-activated monomer **B**, followed by the release of the coordinated aluminum catalyst to the ester group of the polymer chain in intermediate **F** by MMA to regenerate **E** and **B**. Repeated Michael additions of **E** to **B** produce the syndiotactic polymer in a living fashion (Scheme 12).

ION-PAIRING POLYMERIZATION BY DUALLY ACTIVE ION PAIRS

To effect IPP, the cations and anions in dually active ion pairs must be compatible with each other (chemically and kinetically) and the growing



Scheme 12. Single-site anionic polymerization effected by discrete lithium enolaluminate anions. Reproduced with permission from Rodriguez-Delgado and Chen.[29]

polymer chains must undergo infrequent exchange between the cationic and anionic sites. When two sites are diastereospecific, the IPP system becomes a DIPP system.

The switching of a growing polymer chain from the isospecific, cationic zirconocenium site to the syndioselective, anionic aluminate site was demonstrated by the synthesis of highly stereoregular isotactic-*b*-syndiotactic *sb*-PMMA (Figure 4).[30] In this sequential polymerization, the first MMA feed was polymerized with *rac*-(EBI)ZrMe$^+$MeB(C$_6$F$_5$)$_3^-$ at RT to an isotactic block via living, isospecific cationic zirconocene enolate propagating species **G**. Next, the methyl zirconocenium aluminate complex *rac*-(EBI)ZrMe$^+$MeAl(C$_6$F$_5$)$_3^-$ was added to convert the cationic enolate **G** to the neutral methyl zirconocene enolate **H**. After cooling to –78°C, a second feed of MMA was then added, and the polymerization was reinitiated via Michael addition of the isotactic polymeric enolate ligand at Zr to the activated MMA at Al (**B**), starting the construction of a syndiotactic block via the syndioselective enolaluminate propagating species **D**. The resulting polymer is both highly isotactic and syndiotactic, as evidenced by the methyl triad distributions of $[mm]/[rr]/[mr] = 46.4/45.7/7.9$ derived from the ^{1}H NMR of the methyl triad region and by a pentad distribution of $[mmmm] = 42.8$ and $[rrrr] = 39.6$ derived from the ^{13}C NMR spectrum of the C=O pentad region. The molecular weight of the stereodiblock PMMA is approximately a double of the two PMMA homopolymers.[30]

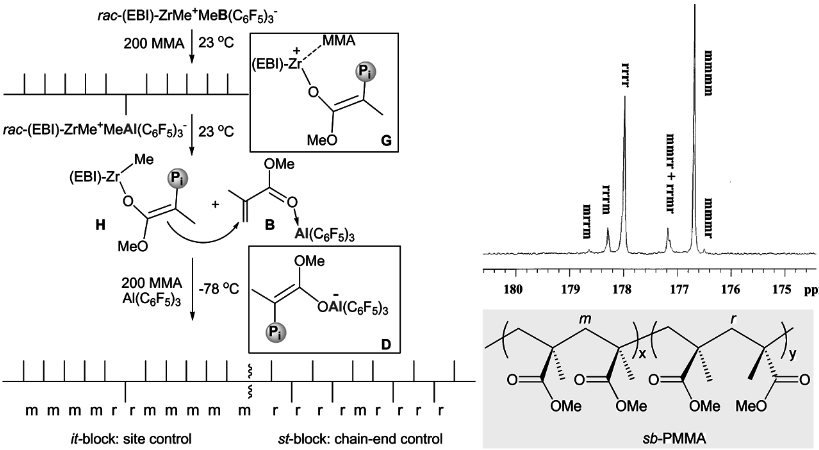
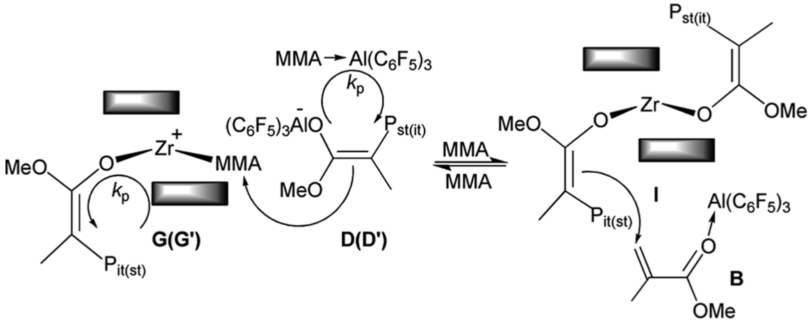


Figure 4. Stereoblock copolymerization reaction sequence (left column) and the resulting polymer microstructure (pentad distributions) shown by ^{13}C NMR spectrum of the C=O region (right column). Reproduced with permission from Bolig and Chen.[30]

The greater challenge was to switch the growing polymer chains back and forth between diastereospecific cation Mt$^{\oplus}$ and anion An$^{\ominus}$ centers in a one-pot polymerization, namely DIPP. We achieved the first-generation of such a system by employing a catalyst mixture containing chiral zirconocenium methyl cations paired with both methyl borate and methyl aluminate anions, e.g., *rac*-(EBI)ZrMe$^+$[MeB(C$_6$F$_5$)$_3^-$]$_{0.5}$[MeAl(C$_6$F$_5$)$_3^-$]$_{0.5}$, which is generated by activating *rac*-(EBI)ZrMe$_2$ with a 1:1 ratio of Lewis acids E(C$_6$F$_5$)$_3$ (E = B, Al).[1] The MMA polymerization by such a system was proposed to proceed in a diastereospecific ion-pairing fashion, in which the Zr$^+$/B$^-$ ion pair produces the *it*-block via the zirconium ester enolate cation and the Zr$^+$/Al$^-$ ion pair affords the *st*-block via the enolaluminate anion, whereas the exchange of growing diastereomeric polymer chains occurs via a neutral zirconocene bis(ester enolate) intermediate to yield *it-b-st* stereomultiblock PMMA, *sb*-PMMA. Scheme 13 illustrates how the diastereomeric polymer chains can be switched back and forth between the cationic and the anionic sites. In this proposed reaction sequence, the chiral zirconocenium cation renders isotactic blocks of *sb*-PMMA via a monometallic propagation, whereas the enolaluminate anion furnishes syndiotactic blocks of *sb*-PMMA via a bimetallic propagation. The polymer chain exchange occurs via intermolecular Michael addition

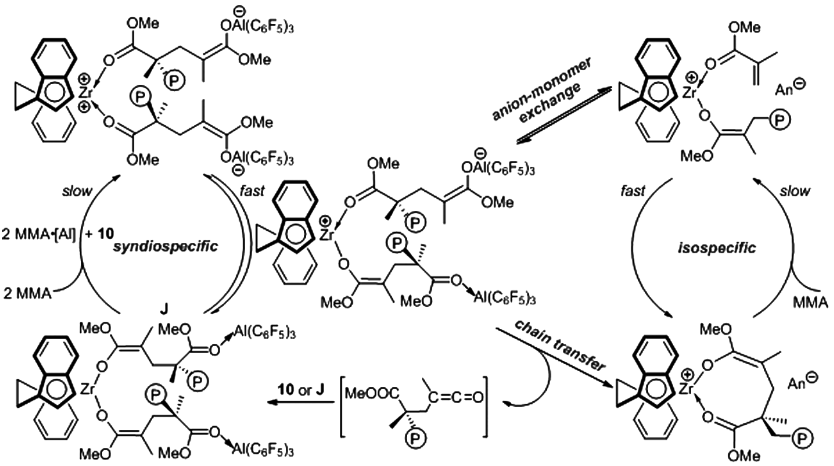


Scheme 13. Schematic presentation for switching of the growing diastereomeric polymer chains between cationic and anionic sites. Reproduced with permission from Chen and Cooney.[1]

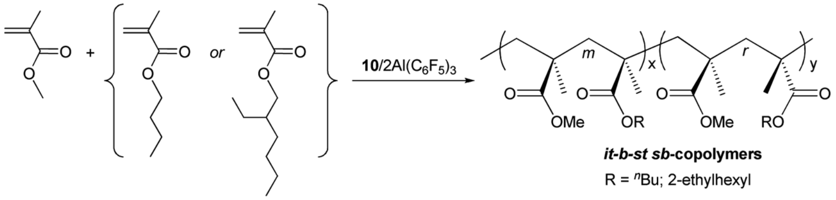
of the syndiotactic enolate chain in **D** to the Zr-activated MMA in **G**. Subsequently, the *it*-polymeric enolate ligand in the resulting neutral bis-enolate zirconocene intermediate **I** immediately attacks the MMA-alane adduct **B** to form back to the same propagating species (**G′** and **D′**), but each propagating species is now carrying a diastereomeric block (denoted as $P_{it(st)}$ or $P_{st(it)}$). If the propagation rates at both sites are compatible and the chain exchange rate is comparable with the propagation rates, well-defined *sb*-PMMA is formed. Noteworthy here is that no such *sb*-PMMA is produced using either cationic diastereospecific metallocene pairs or cationic diastereomeric *ansa*-metallocene mixtures, indicating growing polymer chains did not undergo exchange between such diastereospecific cationic sites.[31]

The slow initiation steps in our first-generation DIPP system involved transfers of methyl groups to the activated monomers by the Zr cation and by the Al Lewis acid to generate cationic zirconocenium ester enolate and anionic ester enolaluminate diastereospecific propagating species, respectively, for DIPP; these slow steps hampered our mechanistic studies and also resulted in the formation of ill-defined polymer products. On the basis of the hypothesis presented in Scheme 12, we employed directly zirconocene bis(ester enolate) complex *rac*-(EBI)Zr-$[OC(O^{i}Pr){=}CMe_2]_2$ (**10**), in combination with 2 equiv of $Al(C_6F_5)_3$, for DIPP of MMA. Indeed, the **10**/$2Al(C_6F_5)_3$ combination, in the presence of MMA, rapidly forms the diastereospecific ion-pairing propagating species, thereby eliminating those slow initiation steps. As a result, this *second-generation* DIPP system exhibits higher efficiency and enhanced control over the polymerization; equally important is the excellent opportunity offered by this controlled system to investigate the kinetics and mechanism of DIPP.

To this end, our detailed investigations (polymerization characteristics, kinetics, elementary reactions, characterization and behavior of the isolated key intermediates, as well as temperature and Lewis acid effects) have yielded a mechanism for the DIPP of MMA by the **10**/2Al(C_6F_5)$_3$ system (**10** denotes the starting bis-ester enolate **10** and its derived homologues in Scheme 14). This mechanism consists of four manifolds—an isospecific cycle by the metallocenium cation, a syndiospecific cycle by the enolaluminate anion, anion-monomer exchange, and then chain transfer, the latter two serving to interconvert diastereospecific propagating manifolds.[10] The proposed overall mechanism is consistent with all the evidence we collected and satisfactorily explains the formation of the various polymer stereomicrostructures formed under given conditions. This unique polymerization technique has also been applied to the copolymerization of MMA with methacrylates having longer alkyl chains, leading to functionalized polymeric materials with tunable properties controlled by their stereomicrostructures and nature of the comonomer (Scheme 15).[10] This IPP system has been extended to other catalysts such as Cp$_2$Zr



Scheme 14. Overall mechanism of DIPP by *rac*-(EBI)Zr[OC(O^{i}Pr)=CMe$_2$]$_2$ (**10**)/2Al(C_6F_5)$_3$ catalyst system. Reproduced with permission from Ning and Chen.[10]



Scheme 15. Stereomultiblock copolymerization of MMA and methacrylates using DIPP with the **10**/$2Al(C_6F_5)_3$ catalyst system. Reproduced with permission from Ning and Chen.[10]

$[OC(O^iPr){=}CMe_2]_2/2Al(C_6F_5)_3]$, which has been utilized for the synthesis of well-defined homopolymers as well as diblock and triblock copolymer of methacrylates.[23]

SUMMARY

The unique cation-anion cooperativity in IPP catalysis involves participation from both the cation and the anion as catalysts for the same reaction, each bringing different reactivity and stereoselectivity (in the case of DIPP) to the polymer products. From a fundamental perspective, this polymerization represents a novel polymerization catalysis concept that utilizes both the cation and the anion of ion pairs in the diastereomeric polymer chain growth as well as in the exchange of the growing polymer chains; the end result is the production of new functionalized vinyl polymers with unique stereomultiblock microstructures. From a technological point of view, the DIPP system presents two significant advantages over other polymerization systems: *first*, there is no need to remove inhibitors typically present in the functionalized vinyl monomers (as required for processes such as radical polymerization); and *second*, the DIPP system is a simple process, yet it offers diverse polymer products having variable unique stereomicrostructures. This approach is arguably desirable for an industrial process: one catalyst system, multiple materials as products. Lastly, from a polymeric materials point of view, the IPP technique allows for the production of technologically important polymeric materials, with unique stereomultiblock microstructures in a one-pot synthesis.

In closing, our contributions made to the development of IPP have introduced a new polymerization catalysis concept and produced polymers with unique stereomicrostructures. Future research in this area will design more effective IPP catalysts and apply them to polymerization of other functionalized vinyl monomers, especially biorenewable vinyl monomers. New stereomicrostructures incorporated into these polymers by IPP will undoubtedly lead to new polymer properties and, thereby, new or expanded materials applications.

ACKNOWLEDGMENTS

The author is indebted to his students and co-workers whose names appear in the cited references for their invaluable contributions to the research described in this account. Acknowledgment is made to National Science Foundation, Petroleum Research Fund, Alfred P. Sloan Foundation, and Colorado State University for support of this research.

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