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Polar vinyl monomer polymerization and copolymerization with olefins promoted by organometallic catalysts*)

Summary — Polymerization of polar vinyl monomers and their copolymerization with olefins in the presence of organometallic catalysts, in particular of the Ziegler-Natta type, including metallocene-based catalysts, has been reviewed in terms of the kind of monomer and catalyst and the reaction mechanism.

Ziegler-Natta catalysts are commonly known as unique catalysts for polymerization and copolymerization of ethylene and α-olefins [1, 2]. Although these catalysts, especially their new metallocene generations, greatly expand the range and versatility of technically feasible types of polyolefin materials [3], relatively little attention has been paid to homopolymers and copolymers of olefins with polar vinyl monomers which could be obtained by using organometallic catalysts.

As with poly(α-olefin)s, the properties of polymers derived from polar monomers may be highly dependent on the stereoregularity of the polymer backbone. Moreover, copolymers of polar monomers with olefins can exhibit some advantageous properties with respect to those characteristic of non-polar polyolefins. The lack of reactive groups in polyolefins significantly limits many of their end uses, especially where adhesion, paintability, printability, or compatibility is required.

In general, there are two ways to functionalize polyolefins: direct copolymerization of olefin with a polar monomer [4] and chemical modification of preformed polymers [5—10].

In view of the importance of functionalized polyolefins, organometallic-catalyzed polymerizations and copolymerizations of polar monomers with olefins have been reviewed including author's own reults.

INSERTION POLYMERIZATION OF ETHYLENE AND α-OLEFINS

After the discovery of the „metallorganische Mischkatalysatoren" for low-pressure polymerization of ethylene by Ziegler in 1953 [1] and application of the new catalysts for stereospecific polymerization of α-olefins by Natta in 1954 [2], polymerization of alkenes underwent a very rapid development which resulted in an enormous growth of the polyethylene production and in starting the large-scale production of stereoregular poly(α-olefin)s, especially isotactic polypropylene [3].

It was Kaminsky who in the 1980s gave a new impetus to the progress of olefin polymerization and made a major contribution towards a breakthrough in the field of polyolefins, by introducing extraordinarily active metallocene—methylaluminoxane catalysts [11—13]. Metallocene catalysts, which are capable of producing polyethylene [12] and a variety of stereoregular poly(α-olefin)s [13—15] are focusing interest from both the academic and industrial point of view. These catalysts are uniquely suited to study subtle steric factors that govern the remarkably high various stereospecificities exhibited in polymerization of propylene and other α-olefins [16]. In contrast to heterogeneous Ziegler-Natta catalysts, polymerization by homogeneous metallocene catalysts occurs principally at a uniform type of metal center with a defined coordination environment. This makes it possible to correlate metallocene structures with poly(α-olefin) properties such as molecular weight, stereochemical microstructure, crystallization behavior, and mechanical properties. Homogeneous metallocene catalysts now afford efficient control of regio- and stereoregularities, molecular weights and molecular weight distributions, and comonomer incorporation. By providing a means for the homo- and copolymerization of cyclic olefins, cyclopolymerization of dienes and access even to functionalized polyolefins, these catalysts greatly expand the range and versatility of technically feasible types of polyolefin materials [17]. Therefore, homogeneous metallocene catalysts are very promising for the future development of the polyolefins technology. It has to be emphasized that various companies already have metallocene-based polymers on the market. Some

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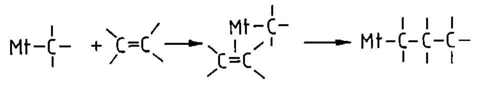
of them went into production with polyethylene, stereoregular (isotactic and syndiotactic) polypropylene, and polyolefin elastomers [18].

A general feature of the olefin polymerization with heterogeneous and homogeneous Ziegler-Natta catalysts is the insertion reaction of the coordinating monomer into the metal-carbon (Mt-C) bond. A vacant coordination site at the metal atom allows the monomer to approach the metal atom and to form an intermediate π-complex. The metal-carbon bond in the catalyst is stable in the uncomplexed state; however, coordination of an olefin molecule results in a mixing of *d* orbitals of the metal with π^* antibonding orbitals of the olefin. The resulting hybridized orbital is sufficiently lower in energy relative to the original metal *d* orbitals so that an electron can easily be excited into it from the Mt-C bond, the resultant alkyl radical attaches itself in a concerted way to the nearest C atom of the bound olefin which is the essence of the matter in the insertion polymerization of olefins (Eqn. 1) [19—21].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INSERTION POLYMERIZATION OF FUNCTIONALIZED α-OLEFINS AND THEIR COPOLYMERIZATION WITH α-OLEFINS BY ZIEGLER-NATTA CATALYSTS

Polymerization of monomers containing heteroatoms in the presence of Ziegler-Natta catalysts has been less investigated than insertion polymerization of unsaturated hydrocarbons. Because of the very high reactivity of organometallic complexes that polymerize olefins, heteroatoms usually hinder the insertion reaction of C=C bonds into Mt-C bonds. However, some monomers containing heteroatoms have been homopolymerized and/or copolymerized with olefins according to the insertion mechanism, by using typical Ziegler-Natta catalysts, by minimizing the interaction between the monomer's heteroatom and the catalyst. This has been accomplished by various methods allowing active sites to remain susceptible to the insertion reaction: the heteroatom in the monomer is separated from the C=C bond by more than one methylene group, the heteroatom in the monomer and the Mt-C bond in the catalyst are sterically shielded, the electron-donating ability of the heteroatom in the monomer is lowered by particular groups attached to it, the heteroatom has low reactivity, the heteroatom is complexed with the catalyst activator, and the labile hydrogen atom, like the one in the hydroxyl group, is made to react with the catalyst activator or other compound. An interesting new approach concerning the last-mentioned aspect involves the copolymerization of borane-containing monomers with olefins, the resulting copolymers are then converted into various functional polymers in postpolymerization processes [22—25]. Therefore, monomers capable of undergoing the insertion polymerization with Ziegler-Natta catalysts are, in principle, monomers in which the heteroatom (X) is not electronically interacting with the double bond to be polymerized [CH_2=CH-$(CH_2)_x$-X]. Representative examples of insertion polymerization of functionalized α-olefins and their copolymerization with α-olefins are shown in Table 1.

Insertion polymerizations of Si- and Sn-containing α-

T a b l e 1. INSERTION POLYMERIZATION OF FUNCTIONALIZED α-OLEFINS AND THEIR COPOLYMERIZATION WITH α-OLEFINS IN THE PRESENCE OF CONVENTIONAL ZIEGLER—NATTA CATALYSTS$^{a)}$

Monomer	Catalyst	Ref.
CH_2=CH-CH_2-SiH_3	$TiCl_4$—$AlEt_3$	26, 27
CH_2=CH-CH_2-$SiMe_3$	$TiCl_4$—$AlEt_3$	26, 27
CH_2=CH-$(CH_2)_x$-N(*i*-Pr)$_2$; x = 1,2,3,5,9	δ-$TiCl_3$·1/3 $AlCl_3$—Al(*i*-Bu)$_2$Cl	28
CH_2=CH-$(CH_2)_3$-$NMe_2$$^{b)}$	δ-$TiCl_3$—$AlEt_2Cl$	28
CH_2=CH-$(CH_2)_3$-$NEt_2$$^{b)}$	δ-$TiCl_3$—$AlEt_2Cl$	28
CH_2=CH-$(CH_2)_3$-O-$SiMe_3$	δ-$TiCl_3$·1/3 $AlCl_3$—Al(*i*-Bu)$_2$Cl	28
CH_2=CH-SiH_2Et	VCl_3—$AlEt_3$	29
CH_2=CH-CH_2-$SiMe_3$	$TiCl_4$—$AlEt_3$	30
CH_2=CH-$(CH_2)_9$-I	$TiCl_3$—$AlEt_2Cl$	31
CH_2=CH-C_6H_4-F$^{c)}$	$TiCl_4$—$AlEt_3$	32, 33
CH_2=CH-C_6H_4-Cl$^{c)}$	$TiCl_4$—$AlEt_3$	32, 33
CH_2=CH-C_6H_4-Br$^{d)}$	$TiCl_4$—$AlEt_3$	32, 33
CH_2=CH-C_6H_4-I$^{d)}$	$TiCl_4$—$AlEt_3$	32, 33
CH_2=CH-$(CH_2)_4$-B(C_8H_{15})/CH_2=CH-R$^{e)}$	$TiCl_3$—$AlEt_2Cl$	25
CH_2=CH-$(CH_2)_x$-C_6H_2(O-*t*-Bu)$_2$-$OAlEt_2$/ /CH_2=CH-CH_3; x = 2—5$^{f)}$	$MgCl_2$/$TiCl_4$—$AlEt_3$/$Ph_2Si(OMe)_2$	34

[a)] Me — CH_3, Et — CH_3CH_2, *i*-Pr — $(CH_3)_2CH$, *i*-Bu — $(CH_3)_2CHCH_2$, *t*-Bu — $(CH_3)_3C$, Hx — $CH_3(CH_2)_5$, B(C_8H_{15}) — 9-borabicyclo[3.3.1]nonane. [b)] Complexed with stoichiometric amount of $AlEt_2Cl$. [c)] *o*-, *m*-, and *p*-Isomers. [d)] *p*-Isomer. [e)] Copolymerization; R = H, Me, Et, Hx; in order to recover the OH functionality in the copolymer, the protecting borane-containing group was removed by the NaOH/H_2O_2 treatment. [f)] Copolymerization; functionalized α-olefin was derived from the reaction of 4-(ω-alkenyl)-2,6-di-*t*-butylphenol with triethylaluminum (1:1 by mole); in order to recover the OH functionality in the copolymer, the protecting $AlEt_2$ group was removed by the HCl/ethanol treatment.

olefins are well known [26—30]. Among the N-containing olefins, only tertiary amines have been polymerized and copolymerized (involving the insertion mechanism), with the exception of allyl amines [28, 30]. ω-N,N-Dimethylamino-substituted and ω-N,N-diethylamino-substituted α-olefins could be polymerized by using Ziegler-Natta catalysts after having been complexed with the Lewis acid [28, 30]. Among the unsaturated O-containing compounds, alkoxystyrenes deserve attention [35]. Olefinic monomers containing -OSi and -NSi groupings undergo insertion polymerization [28, 30, 36]. Halogen (F, Cl, Br, or I)-containing monomers can undergo insertion polymerization only when the halogen atom is situated far away from the C=C bond; this concerns ω-halo-α-olefins [31] and halostyrenes [32, 33, 37, 38].

RADICAL POLYMERIZATION OF POLAR VINYL MONOMERS

In the case of monomers in which heteroatoms are directly bound to ($CH_2{=}CH{-}X$) or are conjugated with the double bond ($CH_2{=}CH{-}\underset{|}{C}{=}X$, $CH_2{=}CH{-}C{\equiv}X$), polymerization promoted by Ziegler-Natta catalysts takes place, but in principle no insertion mechanism operates in this case. Active sites of Ziegler-Natta catalysts, which may be capable of promoting the radical polymerization and/or copolymerization of heteroatom-containing monomers with olefins, are formed in some systems, depending on the kind of monomers and catalysts used.

Monomers in which the heteroatom is directly bound to be olefinic carbon atom ($CH_2{=}CH{-}X$) such as vinyl chloride can be polymerized with modified Ziegler-Natta catalysts by the radical mechanism [39—43]. Dehydrochlorination is a problem in this case [44], although it can be reduced by using a modified activator such as dialkylaluminum alkoxide or substituted dialkylaluminum alkoxide like $AlEt_2OCH_2CH_2NR_2$ [39], or by addition of the Lewis base such as tetrahydrofuran to the polymerization system [40—43]. But the essential role of the Lewis base present in the polymerization system with the Ziegler-Natta catalysts, *e.g.*, $VOCl_3$-$AlEt_3$ (or $AlEt_2Cl$), is the acceleration of generating free radicals capable of initiating the vinyl chloride polymerization (Eqn. 2) [43].

$$VOCl_3 + THF\cdot AlEt_3 \longrightarrow VOCl_2 + THF\cdot AlEt_2Cl + Et^{\cdot} \qquad (2)$$

It is to be emphasized in this connection that alkyl radicals normally formed during the reduction of the transition metal compound in Ziegler-Natta catalyst systems do not initiate the radical polymerization of olefins, in cotrast to that of polar monomers. Most of the modified Ziegler-Natta catalysts for polar monomer polymerization are characterized by low activities and the lack of stereospecificity, producing polymers with properties which are very similar to those of polymers obtained by more conventional producers [45].

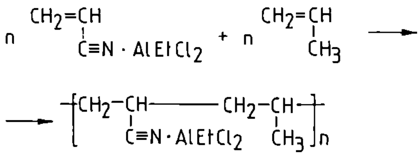
RADICAL COPOLYMERIZATION OF POLAR VINYL MONOMERS WITH OLEFINS AND CONJUGATED DIOLEFINS

Polar monomers in which the heteroatom is conjugated with the olefinic double bond undergo copolymerization with olefins [46, 47] or conjugated diolefins [48—52] when initiated with Ziegler-Natta catalysts. One of the possible reaction schemes of the formation of initiating radicals is presented in Eqn. (3) in which PM denotes a polar monomer acting as the Lewis base against the organoaluminum compound [52].

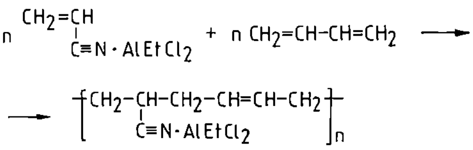
$$VOCl_3 + PM\cdot AlEtCl_2 \longrightarrow VOCl_2 + PM\cdot AlCl_3 + Et^{\cdot} \qquad (3)$$

However, the copolymerization of polar vinyl monomers and olefins or conjugated diolefins can proceed also in systems without a transition metal compound, *i.e.*, in the presence of the organoaluminum compound alone. Organoaluminum compounds catalyze the free-radical copolymerization of polar monomers with electron-donating monomers [53, 54]. Formation of a complex between a polar monomer, *e.g.*, acrylonitrile, and organoaluminum compound, *e.g.* $AlEtCl_2$ (Eqn. 4) [55, 56], causes an increase in the electron-accepting properties of the monomer and hence an increase in its susceptibility to the copolymerization with the olefin (Eqn. 5) or the conjugated diolefin (Eqn. 6) as the electron-donating monomer; the copolymerization tends to produce an alternating copolymer.

$$CH_2{=}CH{-}C{\equiv}N + AlEtCl_2 \longrightarrow CH_2{=}CH{-}C{\equiv}N\cdot AlEICl_2 \qquad (4)$$



$$n\,\underset{C\equiv N\cdot AlEtCl_2}{CH_2{=}\underset{|}{CH}} + n\,\underset{CH_3}{CH_2{=}\underset{|}{CH}} \longrightarrow \left[CH_2{-}\underset{C\equiv N\cdot AlEtCl_2}{\underset{|}{CH}}{-}CH_2{-}\underset{CH_3}{\underset{|}{CH}}\right]_n \qquad (5)$$



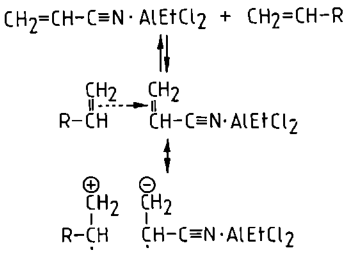
$$n\,\underset{C\equiv N\cdot AlEtCl_2}{CH_2{=}\underset{|}{CH}} + n\,CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \left[CH_2{-}\underset{C\equiv N\cdot AlEtCl_2}{\underset{|}{CH}}{-}CH_2{-}CH{=}CH{-}CH_2\right]_n \qquad (6)$$

Organoaluminum compounds produce also free radicals by homolytic cleavage of the Al-C bond in the complexed polar monomer (Eqn. 7).

$$CH_2{=}CH{-}C{\equiv}N\cdot AlEtCl_2 \longrightarrow CH_2{=}CH{-}C{\equiv}N\cdot \dot{A}lCl_2 + Et^{\cdot} \qquad (7)$$

These radicals initiate a spontaneous copolymerization presented by Eqn. (5) [57, 58] and Eqn. (6) [59—62]. The presence of the transition metal compound in the system results in acceleration of the copolymerization rate, since initiating radicals are more readily formed according to Eqn. (3) rather than Eqn. (7).

Attempts to copolymerize polar vinyl monomers, complexed with organoaluminum compounds, with olefins in the presence of Ziegler-Natta catalysts were made [63] prior to the disclosures of the spontaneous alternating copolymerizations of acrylonitrile, complexed by organoaluminum compound, with propylene [64—66] and vinyl chloride [66]. The latter studies [67, 68] have revealed a formation of respective charge-transfer complexes between the polar monomer, complexed with organoaluminum compound, and olefin (Eqn. 8) which are susceptible to radical propagation.



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CATIONIC POLYMERIZATION OF POLAR VINYL MONOMERS

Vinyl ethers have been polymerized in the presence of Ziegler-Natta catalysts of the $TiCl_4$—AlR_3 type (with AlR_3 used in a lower amount than that of the transition metal compound) [69] and of the VCl_4—AlR_3—AlR_3·THF type [70] to yield highly isotactic polymers. Cationic mechanism has been proved to operate in these polymerizations which involves Friedel-Crafts catalyst's species. Also N-vinylcarbazole has been cationically polymerized using $TiCl_4$—AlR_3 and $TiCl_3$—AlR_2Cl catalysts [71].

It is worth noting in this connection that also hydrocarbon monomers which are capable of forming relatively stable carbo-cations, *e.g.* acenaphthylene, undergo easily cationic polymerization with Ziegler-Natta catalysts [72].

METALLOCENE-CATALYZED INSERTION POLYMERIZATION OF FUNCTIONALIZED α-OLEFINS AND THEIR COPOLYMERIZATION WITH α-OLEFINS

Advances toward polymerizing polar monomers by Ziegler-Natta catalysts have recently been made with cationic metallocene catalysts without an organometallic activator. The catalysts appeared to be considerably more tolerant of functional groups than either heterogeneous Ziegler-Natta catalysts or homogeneous metallocene catalysts activated by methylaluminoxane [17]. Hence, a variety of functionalized α-olefins and diolefins have been polymerized successfully *via* the insertion mechanism in the presence of borane-activated zirconocene catalysts. Some examples of such polymerization are given in Table 2 [73].

Nevertheless, methylaluminoxane-activated metallocene-based Ziegler-Natta catalysts have also been successfully applied to promote the copolymerization of functionalized α-olefins with ethylene, propylene and higher α-olefins. Examples concerning the copolymerization of functionalized α-olefins with α-olefins are presented in Table 2 [25, 74, 75].

GROUP-TRANSFER POLYMERIZATION OF POLAR VINYL MONOMERS WITH METALLOCENE CATALYSTS

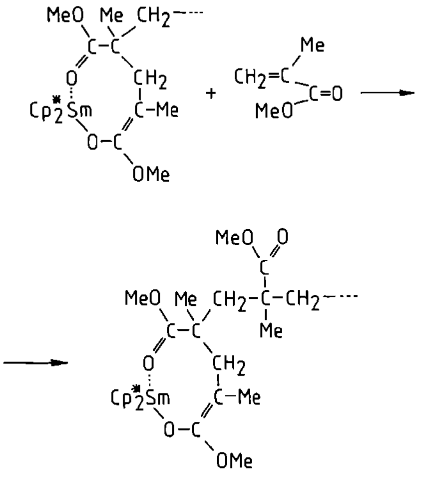
Neutral organolanthanide metallocenes [76—80] and cationic zirconocene organic derivatives [81] proved to be excellent catalysts for polymerization of polar vinyl monomers in which the heteroatom is conjugated with the double bond, such as acrylates and methacrylates.

An achiral organolanthanide such as bis(pentamethylcyclopentadienyl)samarium hydride dimer $[(Cp^*_2SmH)_2]$ was shown to efficiently catalyze the living, highly syndiospecific polymerization of methyl methacrylate [76—80]. Complexation of the catalyst with the monomer has been proposed, involving its carbonyl group, followed by 1,4-addition of the Ln-R functionality to generate an enolate [76]. Futhermore, an eight-membered-ring intermediate has been postulated to form which should stabilize the enol chain end, also allowing enchainment of the monomer. The chain end binds to the metal in an enol form, while the penultimate methyl methacrylate unit complexes with the metal at its carbonyl group (Eqn. 9) [76].

Table 2. INSERTION POLYMERIZATION OF FUNCTIONALIZED α-OLEFINS AND THEIR COPOLYMERIZATION WITH α-OLEFINS IN THE PRESENCE OF METALLOCENE CATALYSTS[a]

Monomer	Catalyst	Ref.
$CH_2=CH-CH_2-C[O-SiMe_2(t\text{-}Bu)]_2CH_3$	$[Cp^*_2ZrMe]^+[B(C_6F_5)_4]^-$	73
$CH_2=CH-(CH_2)_3-N(i\text{-}Pr)_2$	$[Cp^*_2ZrMe]^+[B(C_6F_5)_4]^-$	73
$(CH_2=CH-CH_2)_2CH-O-SiMe_3$	$[Cp^*_2ZrMe]^+[B(C_6F_5)_4]^-$	73
$CH_2=CH-(CH_2)_4-B(C_8H_{15})$[b]	Cp_2ZrCl_2—$[Al(Me)-O]_x$	25
$CH_2=CH-(CH_2)_4-B(C_8H_{15})$[b]	$En(Ind)_2ZrCl_2$—$[Al(Me)-O]_x$	25
$CH_2=CH-(CH_2)_9-OAl<$[b,c]	$(BuCp)_2ZrCl_2$—$[Al(Me)-O]_x$	74
$CH_2=CH-(CH_2)_9-OAl<$[b,c]	$Et(Ind)_2ZrCl_2$—$[Al(Me)-O]_x$	74
$CH_2=CH-(CH_2)_9-OAl<$[b,c]	$Me_2Si(Ind)_2ZrCl_2$—$[Al(Me)-O]_x$	75

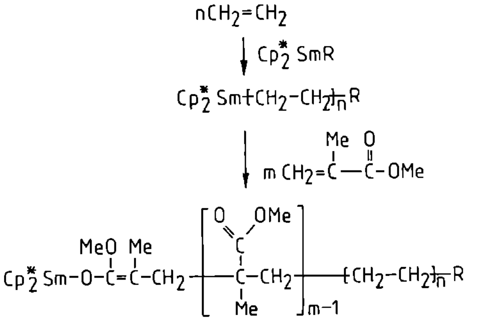
[a] Me — CH_3, *i*-Pr — $(CH_3)_2CH$, *t*-Bu — $(CH_3)_3C$, Bu — $CH_3(CH_2)_3$, En — $-CH_2CH_2-$, Cp — C_5H_5, Cp* — C_5Me_5, Ind — C_9H_7(1-indenyl), $B(C_8H_{15})$ — 9-borabicyclo[3.3.1]nonane. [b] Copolymerization with ethylene or α-olefin. [c] $CH_2=CH-(CH_2)_9-OH$ pretreated with $[Al(Me)-O]_x$.



(9)

By using chiral organolanthanide *ansa*-metallocenes for the methyl methacrylate polymerization, highly stereoregular poly(methyl methacrylate)s were obtained; a syndiotactic or an isotactic polymer could be obtained, depending on the architecture of the metallocene catalyst [80].

The applicability of organolanthanide metallocenes as polymerization catalysts can also be seen from the results of block copolymerization of ethylene and methyl methacrylate. The persistence of lanthanide-alkyl bond has been utilized to prepare ethylene copolymers with polar poly(methyl methacrylate) blocks. For this purpose, ethylene is being introduced as the first monomer to the polymerization system with a samarocene catalyst, and then methyl methacrylate is polymerized which leads to block copolymer formation (Eqn. 10) [76—78].



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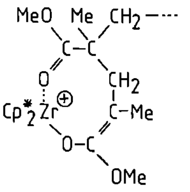
The application of achiral cationic zirconocene compounds to the methyl methacrylate polymerization, *e.g.* a mixture $[Cp^*_2ZrMe(THF)]^+[BPh_4]^-$ and $Cp^*_2ZrMe_2$ in methylene chloride solution, has led to the formation of syndiotactic poly(methyl methacrylate) [81]. The species responsible for propagation are believed to be the bimetallic ones, involving cationic zirconium enolate and neutral zirconocene which facilitates the process. Propagation is postulated to occur *via* the Michael reaction between the coordinating monomer and the cationic enolate [81]:



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CONCLUDING REMARKS

Ziegler-Natta and related coordination catalysts which are commonly considered to be olefin polymerization catalysts can be used for promoting the polymerization of polar vinyl monomers of various types.

Monomers containing a heteroatom which is not electronically interacting with the double bond to be polymerized $[CH_2=CH-(CH_2)_x-X]$ can undergo polymerization in the presence of Ziegler-Natta catalysts, including metallocene-based catalysts, involving an insertion mechanism, characteristic of that operating in olefin polymerization. This makes it possible to easily obtain block copolymers of olefins with polar vinyl monomers.

Monomers containing a heteroatom which is electronically interacting with the double bond to be polymerized, *via* direct bond ($CH_2=CH-X$) and *via* conjugated bond ($CH_2=CH-C=X$, $CH_2=CH-C\equiv X$), can be polymerized by Ziegler-Natta and related catalysts; however, no insertion mechanism but rather a radical propagation mechanism operates in this case. Moreover, the radical copolymerization of conjugated polar vinyl monomers with olefins can be carried out in the presence of Ziegler-Natta catalysts. Some monomers with the vinyl group directly bound to the heteroatom ($CH_2=CH-X$), which are capable of forming relatively stable carbo-cations, can be polymerized cationically.

Conjugated polar monomers like acrylates and methacrylates can be polymerized with metallocene catalysts *via* the group-transfer mechanism. In the case of application of the lanthanide metallocene catalysts which contain the relatively stable Ln-C bond block copolymerization of ethylene (propagation *via* insertion mechanism) and methyl methacrylate (propagation *via* group-transfer mechanism) is possible.

Recent progress in the polymerization of heteroatom-containing monomers with the aid of metallocene catalysts shows new perspectives for the polar vinyl monomer enchainment involving its vinyl group in copolymerization systems with olefins.

REFERENCES

[1] Ziegler K., Holzkamp E., Breil H., Martin H.: *Angew. Chem.* 1955, **67**, 541. [2] Natta G., Pino P., Corradini P., Danusso F., Mantica E., Mazzanti G., Moraglio G.: *J. Am. Chem. Soc.* 1955, **77**, 1708. [3] Whiteley K. S., Heggs T. G., Koch H., Mawer R. L., Goldbach G., Immel W.:

Ullmann's Encyclopedia of Industrial Chemistry, Vol. A21, VCH Publishers, Weinheim 1992, p. 487. [4] Deng H., Shiono T., Soga K.: *Macromolecules* 1995, **28**, 3067. [5] Mülhaupt R., Duschek T., Rieger B.: *Makromol. Chem., Macromol. Symp.* 1991, **48/49**, 317. [6] Shiono T., Kurosawa H., Ishida O., Soga K.: *Macromolecules* 1993, **26**, 2085. [7] Mogstad A., Waymouth R. M.: *Macromolecules* 1994, **27**, 2313. [8] Shiono T., Kurosawa H., Soga K.: *Macromolecules* 1994, **27**, 2635. [9] Chung T. C., Raate M., Berluche E., Schulz D. N.: *Macromolecules* 1988, **21**, 1903. [10] Chung T. C., Rhubright D.: *J. Polym. Sci., Pt. A* 1993, **31**, 2759.

[11] Sinn H., Kaminsky W., Vollmer H. J., Woldt H. J.: *Angew. Chem.* 1980, **92**, 396. [12] Kaminsky W., Miri M., Sinn H., Woldt R.: *Makromol. Chem., Rapid Commun.* 1983, **4**, 417. [13] Kaminsky W., Külper K., Brintzinger H. H., Wild F. R. W. P.: *Angew. Chem., Int. Ed. Engl.* 1985, **24**, 507. [14] Ewen J. A.: *J. Am. Chem. Soc.* 1984, **106**, 6355. [15] Ewen J. A., Jones R. L., Razavi A., Ferrara J. D.: *J. Am. Chem. Soc.* 1988, **110**, 6255. [16] Küran W.: *Polimery* 1994, **39**, 570. [17] Brintzinger H. H., Fischer D., Mülhaupt R., Rieger B., Waymouth R. M.: *Angew. Chem., Int. Ed. Engl.* 1995, **34**, 1143. [18] Richardson K.: *Chem. Britain* **1994**, 87. [19] Arlman E. J., Cossee P.: *J. Catal.* 1964, **3**, 99. [20] Arlman E. J.: *J. Catal.* 1964, **3**, 89.

[21] Cossee P.: *J. Catal.* 1964, **3**, 80. [22] Chung T. C.: *Macromolecules* 1988, **21**, 865. [23] Ramakrishnan S., Berluche E., Chung T. C.: *Macromolecules* 1990, **23**, 378. [24] Chung T. C., Lu H. L., Li C. L.: *Macromolecules* 1994, **27**, 7533. [25] Chung T. C.: *Macromol. Symp.* 1995, **89**, 151. [26] Natta G., Mazzanti G., Longi P., Bernardini F.: *J. Polym. Sci.* 1958, **31**, 181. [27] Natta G., Mazzanti G., Longi P., Bernardini F.: *Chim. Ind. (Milan)* 1958, **40**, 813. [28] Giannini U., Brückner G., Pellino E., Cassata A.: *J. Polym. Sci., Pt. C* 1968, **22**, 157. [29] Carbonaro A., Greco A., Bassi I. W.: *Eur. Polym. J.* 1968, **4**, 445. [30] Giannini U., Brückner G., Pellino E., Cassata A.: *J. Polym. Sci., Pt. B* 1967, **5**, 527.

[31] Clark K. J., Powell T.: *Polymer* 1965, **6**, 531. [32] Natta G., Danusso F., Sianesi D.: *Makromol. Chem.* 1958, **28**, 253. [33] Danusso F., Sianesi D.: *Makromol. Chem.* 1959, **30**, 238. [34] Wilén C.-E., Auer M., Näsman J. H.: *Polymer* 1992, **33**, 5049. [35] Nocci R., Chiellini E., Carlini C.: *Chim. Ind. (Milan)* 1977, **59**, 329. [36] Pino P., Giannini U., Porri L.: *Encyclopedia of Polymer Science and Engineering* Vol. 8, Wiley-Interscience, New York 1987, p. 147. [37] Danusso F., Sianesi D., Calcagno B.: *Chim. Ind. (Milan)* 1958, **40**, 628. [38] Natta G.: *Makromol. Chem.* 1960, **35**, 93. [39] Higashi H., Watabe K., Namikawa S.: *J. Polym. Sci., Pt. B* 1967, **5**, 1125. [40] Mazurek V. V., Nesterchuk G. T., Merkureva A. V.: *Vysokomol. Soed.* 1969, **3**, 611.

[41] Suzuki Y., Saito M.: *J. Polym. Sci., Pt. A-1* 1971, **9**, 3639. [42] Chesworth A. G., Haszeldine R. L., Tait P. J. T.: *J. Polym. Sci., Pt. A-1* 1974, **12**, 1703. [43] Florjańczyk Z., Kuran W., Sitkowska J., Ziółkowski A.: *J. Polym. Sci., Pt. A* 1987, **25**, 343. [44] Pasynkiewicz A., Kuran W.: *J. Organometal. Chem.* 1968, **15**, 307. [45] Tait P. J. T.: Comprehensive Polymer Science, Vol. 4, Pergamon Press, Oxford 1989, p. 1. [46] Florjańczyk Z., Kuran W., Pasynkiewicz S., Langwald N.: *Makromol. Chem.* 1978, **179**, 287. [47] Florjańczyk Z., Kuran W., Langwald N., Sitkowska J.: *Makromol. Chem.* 1983, **184**, 2457. [48] Taniguchi M., Kawasaki A., Furukawa J.: *J. Polym. Sci., Pt. B* 1969, **7**, 411. [49] Furukawa J., Iseda Y., Haga K., Kataoka N., Yoshimoto T., Imamura T., Shido Y., Miyagi A.: *J. Polym. Sci., Pt. B* 1969, **7**, 561. [50] Furukawa J., Kobayashi E., Iseda Y.: *Polym. J.* 1970, **1**, 155.

[51] Furukawa J., Iseda Y., Haga K., Kataoka N.: *J. Polym. Sci., Pt. A-1* 1970, **8**, 1147. [52] Florjańczyk Z., Kuran W., Pasynkiewicz S., Kasprzak E.: *Makromol. Chem.* 1977, **178**, 1915. [53] Gaylord N. G.: *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* 1970, **11**, 27. [54] Kuran W., Florjańczyk Z.: *Wiad. Chem.* 1976, **30**, 87. [55] Kuran W., Pasynkiewicz S.: *J. Organometal. Chem.* 1970, **23**, 343. [56] Kuran W., Pasynkiewicz S., Muszyński J.: *J. Organometal. Chem.* 1970, **25**, 23. [57] Kuran W., Pasynkiewicz S., Florjańczyk Z.: *Makromol. Chem.* 1973, **174**, 73. [58] Kuran W., Pasynkiewicz S., Florjańczyk Z., Kowalski A.: *Makromol. Chem.* 1974, **175**, 3411. [59] Kuran W., Pasynkiewicz S., Florjańczyk Z.: *Makromol. Chem.* 1972, **154**, 71. [60] Kuran W., Pasynkiewicz S., Nadir R., Kowalewska B.: *Makromol. Chem.* 1976, **177**, 1293.

[61] Kuran W., Pasynkiewicz S., Nadir R.: *Makromol. Chem.* 1977, **178**, 411. [62] Kuran W., Florjańczyk Z.: *J. Polym. Sci., Pt. A* 1978, **16**, 861. [63] Nowakowska M., Dahlig W., Pasynkiewicz S., Szewczyk H.: *Polimery* 1964, **9**, 516. [64] Hirooka M., Yabuuchi H., Morita S., Kawasumi S., Nakaguchi K.: *J. Polym. Sci., Pt. B* 1967, **5**, 47. [65] Hirooka M., Yabuuchi H., Iseki J., Nakai Y.: *J. Polym. Sci., Pt. A-1* 1968, **6**, 1381. [66] Pasynkiewicz S., Kuran W., Diem T.: *J. Polym. Sci., Pt. A-1* 1969, **7**, 2411. [67] Ikegami I., Hirai H.: *J. Polym. Sci., Pt. A-1* 1970, **8**, 195. [68] Kuran W., Pasynkiewicz S., Florjańczyk Z., Lusztyk E.: *Makromol. Chem.* 1976, **177**, 2627. [69] Natta G., Dall'Asta G., Mazzanti G., Giannini U., Cesca S.: *Angew. Chem.* 1959, **71**, 205. [70] Vandenberg E. J., Heck R. F., Breslow D. S.: *J. Polym. Sci.* 1959, **41**, 519.

[71] Heller J., Tieszen D. O., Parkinson D. D.: *J. Polym. Sci., Pt. A* 1963, **1**, 125. [72] Kuran W.: *Roczn. Chem.* 1967, **41**, 221. [73] Kesti M. R., Coates G. W., Waymouth R. M.: *J. Am. Chem. Soc.* 1992, **114**, 9679. [74] Aaltonen P., Lofgren B.: *Macromolecules* 1995, **28**, 5353. [75] Aaltonen P., Fink G., Lofgren B., Seppala J.: *Macromolecules* 1996, **29**, 5255. [76] Yasuda H., Yamamoto H., Yokota K., Miyake S., Nakamura A.: *J. Am. Chem. Soc.* 1992, **114**, 4908. [77] Yasuda H., Furo M., Yamamoto H., Nakamura A., Miyake S., Kibino N.: *Macromolecules* 1992, **25**, 5115. [78] Yasuda H., Yamamoto H., Yamashita M., Yokota K., Nakamura A., Miyake S., Kai Y., Tanehisa N.: *Macromolecules* 1993, **26**, 7134. [79] Jiang T., Shen Q., Lin Y., Lin S.: *J. Organomet. Chem.* 1993, **450**, 121. [80] Giardello M. A., Yamamoto Y., Brard L., Marks T. J.: *Macromolecules* 1993, **26**, 3276.

[81] Collins S., Ward D. G.: *J. Am. Chem. Soc.* 1992, **114**, 5460.