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Organo transition metal initiated living polymerizations

H. Yasuda*

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshama 739-8527, Japan

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Abstract

This review article describes the recent advances of organo transition metal initiated polymerizations and copolymerizations of polar and nonpolar monomers. The article deals with Group 3–6 and Group 8–10 metal initiated polymerizations, in addition to some main group metal initiated polymerizations of ethylene. Group 3 rare earth metal complexes are by themselves very active in the absence of cocatalysts such as methylalumoxane or phenyl borates for both polar monomers such as alkyl (meth)acrylates, lactones, and cyclic carbonates, and also nonpolar monomers such as ethylene, 1-alkenes and 1,5-hexadiene. Group 4–5 complexes exhibit high catalytic activities toward the polymerizations of olefins only in the presence of methylalumoxane or phenyl borates. Group 5-6 metal carbene complexes are useful especially for polymerization of cyclic olefins and cyclic acetylenes. New catalyst systems composed of Group 8–10 metal imides and methylalumoxane or phenyl borates, show high catalytic activities for the polymerization of ethylene and olefins. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Organo transition metal initiator; Living polymerizations; Polar monomers; Nonpolar monomers

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* Fax: +81-824-22-7191.

E-mail address: yasuda@hiroshima-u.ac.jp (H. Yasuda).

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1. Introduction

The predominance of conventional heterogeneous multi-site Ziegler-Natta systems has been overturned by the advent of the Kaminsky catalyst, a homogeneous single-site catalyst composed of metallocene complexes involving zirconium, titanium and hafnium complexes combined with either methylalumoxane (AlMe–O–)_n or phenyl borates $B(Ar)_4$. These initiators exhibit many advantages, for example, the capability for the random copolymerization of ethylene with propylene in sharp contrast to the conventional Ziegler-Natta catalytic system, which typically produces only block copolymers between ethylene and propylene. Resulting polymer films have good mechanical properties and good heat-stabilities. Synthesis of syndiotactic polypropylene has been realized using these types of zirconium complexes. Furthermore, highly syndiotactic poly(styrene) can be obtained using a range of homogeneous Ti complexes. More recently, Brookhart developed the synthesis of polyethylene or polypropylenes having extensive branching along the main polymer chains using dimide complexes of Pd, Ni, Fe, or Co. Branching can be controlled by choosing an appropriate ligand. Novel homogeneous Cr complexes have also emerged in this decade, in place of the heterogeneous Phyllipse catalyst. On the other hand, polymerizations of cyclic monomers such as norbornene and norbonadiene have been effected as ROMP polymerizations using homogeneous Ta, Ti, Mo and W carbene complexes. Living polymerization proceeds frequently using these initiators. The living polymerizations of nonpolar monomers such as ethylene and propylene in addition to the living polymerizations of polar monomers such as alkyl (meth)acrylates, lactones, lactide, and cyclic carbonates have been accomplished by the use of rare earth metal complexes composed of metallocene type or non-metallocene type complexes. In these systems, high catalytic activity was observed without the use of cocatalyst such as methylalumoxane or metal oxides. This article reviews recent advances with homogeneous organometallic initiators including Group 3–10 metal complexes and details the effectiveness of these complexes toward the polymerization of polar and nonpolar monomers.

2. Group 3 metal initiated polymerization

In previous papers, we have reviewed the recent advances of the Group 3 rare earth metal initiated living polymerizations of polar and nonpolar monomers [1–5]. The accounts of these papers can be summarized as follows: (1) the preparation of highly syndiotactic (>95%) polymers of methyl methacrylate (MMA) was effected using $[Sm(C_5Me_5)_2H]_2$ **1**, $Sm(C_5Me_5)_2Me(THF)$ **2**, $Yb(C_5Me_5)_2CH(SiMe_3)_2$ **3**, $Sm(C_5Me_5)_2(\mu-Me)_2AIMe_2$ **4**, $Y(C_5Me_5)_2Me(THF)$ **5** (Fig. 1), and $Lu(C_5Me_5)_2Me(THF)$ in high



Fig. 1. Typical examples of organolanthanide initiators.

yields; (2) the rare earth metal initiated living polymerization of MMA provides high molecular weight polymers, $M_n > 1,500,000$, with very narrow molecular weight distributions, $M_w/M_n < 1.05.[6-8]$ More recently, the highly syndiotactic (syndiotacticity 88%) polymerization of MMA (Fig. 2) was carried out using (MeC₅H₄)₂YbNiPR₂(THF) as a catalyst, but the syndiotacticity is lower than the above noted initiators [8]; (3) living polymerizations of alkyl acrylates such as methyl, ethyl, and butyl acrylates were successful, yielding high molecular weight polymers of $M_n > 700,000$ with very narrow molecular weight distributions, $M_w/M_n < 1.05$ [9,10]; (4) living polymerizations of lactones such as β -propiolactone, δ -valerolactone, and ε -caprolactone resulted in high molecular weight polymers, $M_n > 70,000$, with narrow molecular weight distributions, $M_w/M_n = 1.07$ [11]; (5) rare earth metal initiated ethylene polymerization was reported using [LnH(C₅Me₅)₂]₂ (Ln = La, Nd, Lu) as a catalyst to give a polymer of molecular weight, $M_n = 2330-640 \times 10^3$, with molecular weight distribution of $M_w/M_n = 1.3-1.9$ [12].

2.1. Significance of Group 3 initiated living polymerizations

More recently, Nitto et al. found that a non-metallocene type Yb[C(SiMe₃)₃]₂ initiator can afford highly isotactic (isotacticity >97%) poly(MMA) with high molecular weight (M_n > 300,000) and narrow molecular weight distribution ($M_w/M_n = 1.1$) in quantitative yield [1,13,14]. Complex **6** also gives isotactic poly(MMA) (isotacticity, 73%) (Fig. 3) of $M_n = 54,000$ with a very low polydispersity (1.02) [14]. An eight membered cyclic intermediate **7** was proposed for the syndiotactic polymerization on the basis of X-ray analysis of the 1:2 adduct between SmH(C₅Me₅)₂ and MMA, while the non-cyclic intermediate **8** (Fig. 4) was proposed for the isotactic polymerization. Thus, a S_N2 type reaction is



Fig. 2. Cp_2^*LnR for syndiotactic poly(MMA).



Fig. 3. [(Me₃Si)₃C]₂Yb for isotactic poly(MMA).

conceivable for syndiotactic polymerization of MMA, while a $S_N 1$ type reaction is considered for isotactic polymerization. The significance of the living polymerization thus demonstrated was reflected in the following reactions.

(1) Stereo complexes between high molecular weight isotactic and syndiotactic poly(MMA) were obtained by mixing the acetone solutions of both polymers (Fig. 5). The highest yield (83%) was observed when the isotactic polymer ($M_n = 35.7 \times 10^4$, $M_w/M_n = 1.20$) was mixed with syndiotactic polymer ($M_n = 38.2 \times 10^4$, $M_w/M_n = 1.08$) in a 1:2 molar ratio, while the mixing of 1:1 and 2:1 ratios resulted in 57 and 2% yields, respectively. The physical properties of the stereo complex showed intermediate values between the homo polymers of isotactic and syndiotactic poly(MMA), i.e. elastic modulas of isotactic poly(MMA) 30.2 kgf/mm², syndiotactic poly(MMA) 116 kgf/mm², stereo complex 86.3 kgf/mm²; elongation/% of isotactic poly (MMA) 435, syndiotactic poly(MMA) 13.1, stereo complex 30.4; break stress of isotactic poly(MMA) 2 kgf/mm², syndiotactic poly(MMA) 10 kgf/mm², stereo complex 4.6 kgf/mm². T_g values of the stereo complex (79°C for the first heating and 115°C for the second heating) were in between the values for the isotactic (55°C) and syndiotactic polymers (133°C). When the stereo complex was dissolved in chloroform, the original two isomers were individually observed as evidenced by GPC using CHCl₃ as eluent. Although both isotactic and syndiotactic poly(MMA) show no clear $T_{\rm m}$ (melting point), the resulting stereo complex shows a high $T_{\rm m}$ (204°C), and annealing of the stereo complex at 200°C resulted in an increase of $T_{\rm m}$ (230°C). This is indicative that the crystallinity of the stereo complex increases as compared to the homo isotactic or syndiotactic polymers, probably due to its double helical structure [15-17].

(2) Block copolymerizations of ethylene with polar monomers such as MMA and ε -caprolactone were performed using Sm(C₅Me₅)₂Me(THF) or [Sm(C₅Me₅)₂H]₂ as initiators (Fig. 6, Table 1). In these cases, upper limit of the molecular weight of polyethylene is approximately $M_n = 20,000$, and MMA, methyl acrylate or caprolactone was incorporated in 10–20 mol% in the copolymer. The resulting AB type block copolymer is insoluble in THF and chloroform, but is soluble in 1,2-dichlorobenzene or 1,2,4-trichlorobenzene at high temperature (100°C) [18]. The GPC traces of the block copolymers were in the high molecular weight region, showing a unimodal pattern. Higher molecular weight



Fig. 4. Proposed intermediate for syndiotactic and isotactic poly(MMA).



Fig. 5. Stereo complex between isotactic and syndiotactic poly(MMA).



Fig. 6. Block copolymerization of ethylene with polar monomers.

block copolymers ($M_n > 100,000$) were prepared when a bulky complex bearing a bridged Cp ligand was used, especially bis-bridged Cp complex (Me₂Si)₂(3-SiMe₃C₅H₂)₂SmH **10** [19]. Furthermore, a tri-block copolymerization of MMA, ε -caprolactone or trimethylene carbonate/ethylene/MMA, ε caprolactone or trimethylene carbonate was realized using Sm(II) complexes such as **9** (Fig. 7) by the polymerization of ethylene followed by the addition of MMA, ε -caprolactone or trimethylene carbonate (Table 1) [20]. The physical properties (break stress, elastic modulus, and break strain) of the ABA triblock copolymers were only slightly lower as compared with those for homo-polyethylene (Table 2). Thus, ABA type block copolymerizations of polar and nonpolar monomers were first realized using rare earth metal (II) complexes as initiators, yielding new functional polymers (Fig.

Table 1

Block copolymerizations of ethylene with MMA, ε -caprolactone and trimethylene carbonate (initiator, 1.18 mmol, polar monomer/initiator = 100 mol/mol, polymerization in toluene)

Comonomer	Poly. Time (min)	Polyethylene		ABA coplymer		Polar monomer
		$\overline{M_{\rm n}} 10^4$	$M_{ m w}/M_{ m n}$	$\overline{M_{ m n}} 10^4$	$M_{ m w}/M_{ m n}$	content/mol%
MMA	5	2.02	1.41	3.53	1.74	34.5
	11	2.72	1.39	3.02	1.57	10.1
	13	3.02	1.40	3.35	1.39	6.7
ε -Caprolactone	5	2.02	1.42	3.52	1.77	30.2
	10	2.67	1.41	2.77	1.99	3.3
Trimethylene carbonate	6	2.05	1.42	3.86	6.12	25.2



Fig. 7. Bis-bridged metallocene complexes.

Table 2 Physical properties of ABA type triblock copolymers (CL, ε -caprolactone; TMC, trimethylene carbonate; PE, polyethylene)

System	Comonomer content/%	Break stress (kg/cm ²)	Elastic modulas (kgf/cm ²)	Break strain (%)
PE	0	327	9222	48
MMA/PE/MMA	6.7	211	8610	14
CL/PE/CL	3.3	272	5560	28
TMC/PE/TMC	2.5	322	8729	15

8). The introduction of large quantities of polar monomer units into the copolymer can result in a marked decrease in physical properties. Therefore, the incorporation of polar monomers should be restricted to small amounts if possible. Dyeing of the resulting block copolymers (MMA/ethylene = 0.3 mol%) with dispersive dyes resulted in successful deep coloration of their films into three primary colors, while polyethylene itself was inert to these dyes. Thus, the new copolymers display desirable chemical properties. More convenient systems consisted of (C_5Me_5)₂SmCl₂Li(OEt)2 and BuMgEt are reported more recently for the polymerization of ethylene with polar monomers [21,22].

(3) ABA type triblock copolymers of MMA/butyl acrylate(BuA)/MMA (Fig. 9) with low polydispersities should provide thermoplastic elastomers, since MMA is a hard segment while BuA is a soft segment, where the hard segment will act as a node and the soft segment as elastomers in the resulting network system (Table 3) [9,10]. Since both MMA and butyl acrylate undergo the living polymerization using SmMe(C_5Me_5)₂(THF), the block copolymerization of MMA/BuA/MMA readily gives desired unimodal copolymers having ratios of 20:47:33, 8:72:20, and 6:91:3. Their physical properties are shown in Table 3. The elongation of the 8:72:20 copolymer is 163% and its compression set at 70°C for 22 h is 58 which indicates tht the resulting copolymer serves as a rubber-like elastomer, while the 20:47:33 copolymer showed an elongation of 83% and a compression set of 101. However, the tensile modulus and tensile strength of the 8:72:20 copolymer was poor. Therefore, MMA/ethyl acrylate/ethyl methacrylate was copolymerized in a 26:48:26 ratio, giving desirable properties, i.e. tensile modulas 119 MPa, tensile strength 22 MPa, elongation 276%, and compression set 62. Thus, a



Fig. 8. ABA type triblock copolymerization of MMA/ethylene/MMA.



Fig. 9. ABA triblock copolymerization of MMA/BuA/MMA.

rubber-like thermoplastic elastomer was obtained using the living polymerization character of organolanthanide complexes.

(4) The block copolymerization of trimethylsilyl methacrylate with BuA gave thermostable adhesive materials, poly(methacrylic acid)-*block*-poly(BuA) (Fig. 10), after hydrolysis of the resulting polymer, which showed a large storage modulus, G', especially at high temperatures such as 100–200°C presumably due to the effective formation of the poly(MAc) domain [23]. The holding power did not decrease significantly when the temperature was raised to 200°C, while the holding power of the random copolymer obtained by a radical initiator, poly(MMA-*ran*-BuA), decreased rapidly when the temperature was raised to 100°C.

(5) Copolymerizations of alkyl methacrylates containing a fluoro group with MMA or ε -caprolactone were carried out using SmMe(C₅Me₅)₂(THF) (Fig. 11) as an initiator catalyst in order to obtain weather-proof painting materials. If the random copolymerization proceeds, high contact angles are expected for these polymers because of the presence of fluoro groups in these. In fact, the copolymerization of 2,2,2-trifluoroethyl methacrylate (TFM), 2,2,3,3-terafluoropropyl methacrylate (TPM), or 2,2,3,3,3-pentafluoropropyl methacrylate (PFM) with MMA gave the copolymers of desired ratios with very narrow molecular weight distributions in quantitative yield [24]. The contact angle of homo-poly(MMA) is 71.6°, while the methacrylates bearing fluoro groups show 90–100° as summarized in Table 4. The improvement of contact angles has been realized by the triblock copolymerization of PFM/MMA/BuA in a ratio of 19:37:44. The contact angle increased from 93.5 to 98.4° of the PFM/MMA(24:76) copolymer. Furthermore, this tri-block copolymer maintains its clear film when

		•			
Copolymer (composition)	Tensile modulas (MPa)	Tensile strength (MPa)	Elongation	Izot impact strength	Compression set at 70°C
Poly(MMA/BuA/MMA) (25:51:24)	46	22	81	390	103
Poly(MMA/BuA/MMA) (8:72:20)	0.8	0.7	163	400	58
Poly(MMA/BuA/MMA) (6:91:3)	0.2	0.7	146	410	97
Poly(MMA/EtA/EtMA) (26:48:26)	119	22	276	34	62

Mechanical properties of triblock copolymers (polymerization in toluene, initiator $SmMe(C_5Me_5)_2(THF)$)

Table 3



Fig. 10. Copolymerization of trimethylsilyl methacrylate with BuA.



Fig. 11. Monomers containing fluoroalkyl groups.

the film was immersed in water for 4 days, while the di-block copolymer gradually changed to opaque. The use of ε -caprolactone in place of MMA is also effective to obtain the desired weather-proof material, contact angle being 102.5°.

2.2. Living polymerizations of trimethylene carbonates

The living polymerizations of trimethylene carbonate (TMC) and 2,2-dimethyl-trimethylene carbonate (Fig. 12) readily occurred in toluene at ambient temperature using SmMe(C₅Me₅)₂(THF) or YMe(C₅Me₅)₂(THF) as an initiator, and yielded polymers having M_n of $3-5 \times 10^4$ and very low polydispersity, $M_w/M_n = 1.0-1.1$ [25]. However, no detailed studies on its initiation and propagation mechanisms have as yet been made. The block copolymerization of trimethylenecarbonate with ε caprolactone (CL) was realized using Ln(ethyl acetoacetate)₂(O-iPr) (Ln = Y, Nd) as an initiator [26]. It took place by the addition of CL to the poly(TMC) end or the addition of TMC to the living poly(CL) end, with the formation of polymers having M_n of $4-5 \times 10^4$ and M_w/M_n of 1.2–1.4. More recently, the random copolymerizations of (R), (S) or racemic 1-methyl- and 1,3-dimethyltrimethylene carbonate with ε -caprolactone have been carried out using SmMe(C₅Me₅)₂(THF) as an initiator to

Table 4

Ratio $M_{\rm n}/10^4$ $M_{\rm w}/M_{\rm n}$ Yield (%) Contact angle (°) Copolymer TFM/MMA 0:100 5.01 1.03 99 71.6 78:22 1.10 98 90.1 3.09 49:51 1.78 1.12 99 89.7 20:80 2.35 1.09 100 89.0 TPM/MMA 73:27 4.55 1.05 99 88.8 47:53 4.26 1.04 99 86.3 22:78 3.38 1.05 98 78.1 PFM/MMA 100 72:28 3.89 1.16 100.4 47:53 3.18 1.11 99 97.2 PFM/CL 79:21 2.10 1.07 88 102.5

Contact angles of methacrylate copolymers containing fluoro group (polymerization conditions, initiator $SmMe(C_5Me_5)_2(THF)$, toluene for 3 h. CL, caprolactone)



Fig. 12. Copolymerization of trimethylene carbonate with caprolactone.



Fig. 13. Catalysts for polymerizations of alkylisocyanates.



Fig. 14. Polymerization mode for alkylisocyanates.

obtain the novel biodegradable polymers. The resulting copolymers exhibit $M_n = 4-15 \times 10^4$ and $M_w/M_n = 1.11-1.50$, and show the highest biodegradability with activated sludge or cholesterol esterase when these carbonates are incorporated into the copolymer in 10–20 mol% ratios [27].

2.3. Polymerizations of alkylisocyanates

Table 5

Polyisocyanates have attracted much attention owing to their liquid crystalline properties, stiff-chain

Initiator	$M_{ m n}/10^4$	$M_{ m w}/M_{ m n}$	Activity ^a
$(C_5Me_5)_2SmCH(SiMe_3)_2$ SiMe ₂ [2,4–(SiMe ₃) ₂ C ₅ H ₂] ₂ SmCH(SiMe ₃) ₂ (<i>racemic</i>) SiMe ₂ (Me ₂ SiOSiMe ₂)(3-SiMe ₂ –C ₅ H ₂) ₂ YCH(SiMe ₂) ₂ (<i>meso</i>)	No polymerization No polymerization No polymerization		
$SiMe_{2}[2(3),4-(SiMe_{3})_{2}C_{5}H_{2}]_{2}SmCH(SiMe_{3})_{2} (C_{1})$ SiMe_{2}[2(3),4-(SiMe_{3})_{2}C_{5}H_{2}]_{2}YCH(SiMe_{3})_{2} (C_{1})	41.3 33.1	2.19 1.65	3.3×10^4 18.8×10^4

Ethylene polymerization by organolanthanide(III) complexes

^a The g polymer/Ln mol h atm.; initiator concentration 0.2 mol% of monomer in toluene.

Table 6

Monomer	Initiator	$M_{\rm n}/10^{3}$	$M_{\rm w}/M_{\rm n}$
1-Pentene	Me ₂ Si(2-SiMe ₃ -4- <i>t</i> Bu-C ₅ H ₂) ₂ Sm(THF) ₂	13	1.63
	Me ₂ Si[2(3),4-(SiMe ₃) ₂ C ₅ H ₂] ₂ YCH(SiMe ₃) ₂	16	1.42
	$Me_2Si[(2-SiMe_3-4-tBu-C_5H_2)YH]_2$	20	1.99
1-Pentene	$Me_2Si(2-SiMe_3-4-tBu-C_5H_2)_2Sm(THF)_2$	19	1.58
	Me ₂ Si[2(3),4-(SiMe ₃) ₂ C ₅ H ₂] ₂ YCH(SiMe ₃) ₂	64	1.20
	$Me_2Si[(2-SiMe_3-4-tBu-C_5H_2)YH]_2$	24	1.75

Polymerization of 1-pentene and 1-hexene (initiator 0.2 mol% of monomer, solvent toluene, toluene/monomer = 5 (wt/wt))

solution characteristics, and induced optical activities associated with the helical chain conformation (Figs. 13 and 14). Pattern and Novak discovered that such titanium complexes as TiCl₃(OCH₂CF₃) and (C₅H₅)TiCl₂(OCH₂CF₃) **11** initiate the living polymerizations of alkyl isocyanates, giving polymers with narrow molecular weight distributions [28–31]. When hexyl isocyanate was added to TiCl₃(OCH₂CF₃), the polymerization took place at room temperature, with M_n increasing linearly with the initial monomer-to-initiator molar ratio or the monomer conversion over a wide range ($M_w/M_n = 1.1 - 1.3$). Shen reported the good catalysis of (MeC₅H₄)₂LnNiPr₂ for the polymerization of phenyl isocyanate. In this

 Table 7

 Ethylene polymerization by divalent samarocene complexes

Initiator	Time (min)	$M_{\rm n}/10^4$	$M_{ m w}/M_{ m n}$	Activity ^a
(C ₅ Me ₅)Sm(THF) ₂	1	2.28	1.25	43
	3	2.46	2.28	41
Racemic	1	11.59	1.43	6
	3	35.63	1.60	14
Meso	5	1.94	3.29	14
	10	4.73	3.49	47
C_1 symmetry	15	100.8	1.60	1.6
	30	110.0	1.64	1.1

^a The g polymer/Ln mol h/atm.



Fig. 15. Co-ordination of ε-caprolactone for organolanthanide complexes.



Fig. 16. Block copolymerization of MMA with ε-caprolactone.

case, the 1:1 adduct of phenyl isocyanate was isolated [16]. The resulting complex produces the yellow solid of poly(phenyl isocyanate), similar to that obtained by CpTiCl₂NMe₂ initiator [31]. Recently, Fukuwatari et al. found the lanthanum isopropoxide to serve as a novel anionic initiator for the polymerization of hexyl isocyanate at low temperature $(-78^{\circ}C)$, which led to very high molecular weight $(M_n > 10^6)$ and rather narrow molecular weight distributions $(M_w/M_n = 2.08 - 3.16)$ [32]. Other lanthanide alkoxides such as Sm(OiPr)₃, Yb(OiPr)₃, and Y(OiPr)₃ also induced the polymerization of hexyl isocyanate. Furthermore, it was shown that butyl, isobutyl, octyl and *m*-tolyl isocyanates were polymerized using lanthanum isopropoxide as an initiator. However, *t*-butyl and cyclohexyl isocyanates failed to polymerize with this initiator under the same conditions. When the reaction temperature was raised to ambient temperature, only cyclic trimers were produced in high yields. In an unpublished work, Tanaka et al. showed that La(C₅Me₅)[CH(SiMe₃)₂]₂ **12** also initiates the polymerization of butyl isocyanate and hexyl isocyanate in 50–60% yields [33,34]. The use of triphenylsamarium **13** was also found to give high molecular weight polymers of hexyl isocyanate and butyl isocyanate $(M_n = 410,000 - 730,000)$ with low polydispersity even at 25°C [34].

2.4. Living polymerizations of lactones

The AlEt₃–H₂O or AlEt₃ catalyzed polymerizations of β -methylpropiolactone (MePL) and ε -caprolactone (CL) have been reported [35–37], but these polymerizations generally give rise to broad molecular weight distributions. Yamashita et al. explored the polymerization of various lactones including β -propiolactone (PL), β -methylpropiolactone, δ -valerolactone (VL) and ε -caprolactone initiated by single organolanthanides to give polymers with narrow molecular weight distributions, and found that VL and CL led to the living polymerization yielding polymers with $M_w/M_n = 1.05-1.10$ in quantitative yields (Table 7) [11]. For CL, M_n obtained with the SmMe(C₅Me₅)₂(THF) or [SmH(C₅Me₅)₂]₂ system increased with an increase of conversion, but M_w/M_n remained constant, irrespective of the conversion. For PL, the use of YOR(C₅Me₅)₂ was more effective. On the other hand, though the divalent



Fig. 17. Lactide polymerization using Yb(OC₆H₃-2,6-iPr₂)₃/iPrOH.



Fig. 18. Catalysts for polymerization of styrene.

organolanthanide complexes initiated the polymerization of lactones, the resulting polymers had rather broad molecular weight distributions [38]. The Nd(acac)₃·3H₂O/AlR₃ and Nd(naphthenate)₃/AlR₃ initiators were effective to the ring opening polymerization of CL but no data for the molecular weight distribution are reported [39]. $Ln(OiPr)_3 Ln = La$, Pr, Nd, Gd, Y) also catalyzes the polymerization of CL, but the polydispersity index was larger $(M_w/M_n = 1.2 - 2.4)$ than that obtained with Ln(C₅H₅)₂Me(THF) [40]. Furthermore, (2,6-tBu₂-4-Me-C₆H₂O)₂Sm(THF)₄ initiates the polymerization of CL to form a polymer with M_n of $15-16 \times 10^4$ and M_w/M_n of 1.6 [41]. At the early stage of the reaction of CL with $LnOR(C_5Me_5)_2$, one mole of CL may coordinate to the metal, as is the case for the reaction of YCl₃ with CL giving the first six-coordinate mer complex, YCl₃ (ε -caprolactone)₃ 15 in which each CL molecule is coordinated as a monodentate ligand through its carbonyl oxygen [42]. Thus the polymerization starts with the coordination of CL to form the 1:1 complex $LnOR(C_5Me_5)_2$ (ε -caprolactone), and in its propagation step the alkoxide attacks the C=O group to produce $(C_5Me_5)_2LnO(CH_2)_5C(O)OR(\varepsilon$ caprolactone) 14 (Fig. 15). In the SmMe(C_5Me_5)₂ initiator system, the reaction is initiated by the attack of ε -caprolactone or δ -valerolactone without ring opening to form an acetal and then the ring opening polymerization follows. This process has been confirmed by ¹³C-NMR studies of the stoichiometric reaction products between a lactone and a rare earth metal complex.

The above noted organolanthanide complexes are less effective to obtain high molecular weight polymers of β -methylpropiolactone. However, the random copolymerization of MePL with THF occurred upon initiation with the Sm(OiPr)₃/AlEt₃-H₂O system (1:5-1:10), although the AlEt₃-H₂O system was completely inert to the polymerization of tetrahydrofuran (THF) [43]. The polymers produced were 43:57-24:76 in the lactone/THF ratio and had M_n of 10,000-200,000 and M_w/M_n of 1.08-1.26. In this system, some cationic initiator is supposed to be formed when the two components are mixed.

Anionic block copolymerizations of MMA with lactones (Fig. 16) proceeded smoothly to give the copolymers with $M_w/M_n = 1.11-1.23$ when the monomers were added in this order. However, when the order of addition was reversed, no copolymerization took place, i.e. no addition of MMA to the polylactone active end group occurred [7].

2.5. Living polymerization of lactide

Shen et al. succeeded ring opening polymerization of D,L-lactide (racemic species) using Nd



Fig. 19. Syntheses of *racemic* and C_1 symmetric metallocene complexes.

(naphthenate)₃/AliBu₃/H₂O (1:5:2.5), Nd(P₂₀₄)₃/AliBu₃/H₂O (P₂₀₄ = [CH₃(CH₂)₃(CH₂CH₃)CHCH₂]₂ P(O)OH), Nd(P₅₀₇)₃/AliBu₃/H₂O (P₅₀₇ = (iC₈H₁₇O)₂P(O)OH) and Nd(naphthenate)₃/AliBu₃/H₂O systems, obtaining the polymers whose molecular weights were $M_n = 3.1-3.6 \times 10^4$ and the conversions larger than 94% [44]. When the Ln(naphthenate)₃/AliBu₃/H₂O system was used, nearly the same results

were obtained irrespective of the metals used (La, Pr, Nd, Sm, Gd, Ho, Tm). Divalent $(2,6-tBu_2-4-Me-phenoxo)_2Sm(THF)_4$ was also found to be active for the polymerization of D,L-lactide at 80°C in toluene, giving M_n of $1.5-3.5 \times 10^4$ [45]. More recently, the Ln(O-2,6-tBu_2-C_6H_3)_3/iPrOH **16** (1:1–1:3) system (Fig. 17) was found to initiate a smooth homo-polymerization of L-lactide, CL and VL and gives relatively high molecular weights $(M_n > 24 \times 10^3)$ with low polydispersity indices $(M_w/M_n = 1.2-1.3)$ [46]. The ring-opening polymerization of D,L-lactide was also carried out by using Ln(OiPr_3)_3 as an initiator at 90°C in toluene. The catalytic activity increased in the order La > Nd > Dy > Y and the molecular weight reaches 4.27×10^4 (conversion 80%) [47]. However, the molecular weight distribution is not clear at present. A kinetic study showed that the rate of polymerization follows the first order regarding both monomer and initiator. The block copolymerization of CL with L-lactide also proceeded effectively and gave a polymer of very narrow molecular weight distribution $(M_w/M_n = 1.16)$ when the addition was carried out in this order. On the other hand, the reversed addition of CL to the living poly(L-lactide) end led to no success.

2.6. Polymerizations of styrene

The styrene polymerization was performed using binary initiator systems such as $Nd(acac)_3/AlR_3$ or $Nd(P_{507})_3/AlR_3$, and a syndio-rich polystyrene was obtained at a ratio of Al/Nd = 10-12 [48]. More recently, it was shown that the Gd(OCOR)₃/iBu₃Al/Et₂AlCl catalytic system initiates the copolymerization of styrene with butadiene, but gives only atactic polystyrene [49]. The Sm(OiPr)₃/AlR₃ or $Sm(OiPr)_3/AlR_2Cl$ (Sm/Al = 1–15) initiator system also initiates the polymerization of styrene to give a high molecular weight polymer ($M_n = 300,000$), low in polydispersity but atactic in stereoregularity [50]. The cationic polymerization of styrene using Ln(CH₃CN)₉(AlCl₄)₃(CH₃CN) was also examined [51], with the finding that the activity increased in the order La (conversion 73%) > Tb = Ho > Pr = Gd > Nd > Sm = Yb > Eu (conversion 54%), while M_n decreased with increasing the polymerization temperature from 0 (20×10^3) to 60°C (13×10^3). A more recent study showed that a single component initiator $[(tBuCp)_2LnCH_3]_2$ (Ln = Pr, Nd, Gd) initiated the polymerization of styrene at relatively high temperature, 70°C, with the conversion of 96% for $[(tBuCp)_2NdMe]_2$ and the M_n of 3.3×10^4 , though the stereoregularity was very poor [52]. The activity varied greatly with the lanthanide element, and the catalytic activity increased in the order $Nd > Pr > Gd \gg Sm$, Y (the Sm and Y complexes showed practically no activity). Therefore, the reaction is supposed to follow the radical initiation mechanism. The styrene polymerization was also performed successfully using the single component initiators, $[(Me_3Si)_2N]_2Sm(THF)_2$ 17, $[(Me_3Si)_2CH]_3Sm$ 18 (Fig. 18), and La(C₅Me₅)[CH $(SiMe_3)_2]_2$ (THF) at 50°C in toluene without addition of cocatalysts. The resulting polymers had $M_n =$ $1.5-1.8 \times 10^4$ and $M_w/M_n = 1.5-1.8$, and were only atactic [33,34]. Thus no success has yet been achieved in synthesizing a syndiotactic polystyrene using rare earth metal complexes, in sharp contrast to the synthesis of highly syndiotactic polystyrene with $(C_5Me_5)TiCl_3/(AlMe-O-)_n$ 19 (syndiotacticity >95%) [53,54]. More efficient catalytic activity was observed using complex 20, i.e. activity 3.8×10^7 g PS/Ti mol h, syndiotacticity 98.7%, $T_{\rm m} = 275.9^{\circ}$ C; **19** activity 2.1×10^7 g PS/Ti mol h, syndiotacticity 96.5%, $T_{\rm m} = 274.6^{\circ}$ C [55].

2.7. Polymerizations of 1-olefins

Bulky organolanthanide(III) complexes such as $LnH(C_5Me_5)_2$ (Ln = La, Nd) were found to initiate



Fig. 20. Structures of lanthanide hydrides.

with high efficiency the polymerization of ethylene [12]. These hydrides are, however, thermally unstable and cannot be isolated as crystals. Therefore, thermally more stable bulky organolanthanides were synthesized by introducing four trimethylsilyl groups into the Me₂Si bridged Cp ligand. The reaction of the dilithium salt of this ligand with anhydrous SmCl₃ produced a mixture of the two stereo-isomeric complexes **21** and **22** (Fig. 19). The respective isomers were isolated by utilyzing their different solubilities in hexane, and their structures were determined by X-ray crystallography. One of them has a C_2 symmetric (*racemic*) structure in which two trimethylsilyl groups are located at the 2,4-position of the Cp rings, while the other has a C_1 symmetric structure in which two trimethylsilyl groups are located at 2,4- and 3,4positions of each Cp ring. Both were converted to alkyl derivatives **23** by allowing to react with bis(trimethylsilyl)methyllithium [56,57]. The Cp'-Sm-Cp' angle of the *racemic*-type precursor is 107°, which is about 15° smaller than that of non-bridged SmMe(C₅Me₅)₂(THF).

Meso type ligands were synthesized by forcing two trimethylsilyl groups to be located at the 4-position of the ligand with introduction of two bridges. Actually, the complexation of this ligand with YCl_3 yielded a *meso* type complex, and the structure of the complex was determined by the X-ray analysis. Yasuda et al. were also able to synthesize the *meso* type alkyl complex **24** in a similar way, where the Cp'-Sm-Cp' angle is seen to be 108°, a very small dihedral angle.

Table 5 summarizes the results of ethylene polymerization with these organolanthanide(III) complexes. Interestingly, only the C_1 type complexes can initiate the polymerization, implying that the catalytic activity varies depending on the structure of the complex. The polymerization of ethylene using SmH(C₅Me₅)₂ in the presence of PhSiH₃ formed PhH₂Si capped polyethylene ($M_n = 9.8 \times 10^4$, $M_w/M_n = 1.8$), and the copolymerization of ethylene with 1-hexene or styrene gave the PhH₂Si capped copolymer (comonomer content 60 and 26 mol%, respectively; $M_n = 3.7 \times 10^3$, $M_w/M_n = 2.9$ for ethylene/1-hexene copolymer, $M_n = 3.3 \times 10^3$ for ethylene/styrene copolymer) [58].

Table 6 shows the results of polymerization of α -olefins catalyzed by trivalent complexes. When a more bulky *t*BuMe₂Si group instead of the simple Me₃Si group was introduced into the yttrium complex, the *racemic* complex was formed exclusively. However, this alkyl complex did not react with olefins, and hence the conversion to a hydride complex was examined by the reaction with H₂. The complex thus obtained was reactive to various olefins and produced the polymers in high yield. The resulting poly(α -olefin)s were highly isotactic with a *mmmm* content >95%, which shows the signal at 34.91 ppm in ¹³C-NMR. It also initiated the polymerization of 1,5-hexadiene, yielding poly(methylene-1,3-cyclopentylene) exclusively [59], whose M_n (13.5 × 10⁴) was much higher than that obtained with typical Kaminsky type catalysts ($M_n < 40,000$.) The conversions of poly(1-pentene) and poly(1-hexene) were much higher than those obtained by *rac*-Me₂Si(2-SiMe₃-4-*t*Bu–C₅H₂)₂YH **25** [60] or [(C₅Me₄)SiMe₂-N-*t*Bu)(PMe₃)ScH]₂ **26** (Fig. 20) [61].

Racemic 27, meso 28 and C_1 symmetric 29 divalent organolanthanide complexes (Fig. 21) can also be



Fig. 21. racemic, meso, and C₁ symmetric Sm(II) complexes.

synthesized by allowing the dipotassium salt of the corresponding ligand to react with SmI₂ [62]. Their structures were determined by ¹H-NMR and X-ray analyses. Table 7 shows the results of the olefin polymerization with the divalent samarium complexes. It is seen that the *meso* type complex has the highest activity for the polymerization of ethylene, but the molecular weights of the resulting polymers are the lowest. On the other hand, the *racemic* and C_1 symmetric complexes produce much higher molecular weight polyethylenes but the activity is rather low. Particularly, the very high molecular weight polyethylenes ($M_n > 100 \times 10^4$) obtained with the C_1 complex deserves attention. For the polymerizations of α -olefins, only the *racemic* divalent complexes showed good activity at 0°C in toluene: poly(1-hexene) $M_n = 24,600$, $M_w/M_n = 1.85$; poly(1-pentene) $M_n = 18,700$, $M_w/M_n = 1.58$. Thus, we see that the reactivity of divalent organolanthanide complexes depends on their structures. The poly(1-alkene) obtained revealed the highly isotactic structure (>95%) as analyzed by ¹³C-NMR. The dihedral angles of Cp'-Ln-Cp' of *racemic* and *meso* type divalent complexes were 117 and 116.7°, respectively, which are much smaller than those of Sm(C₅Me₅)₂(THF)₂ (136.7°) [63] and Sm(C₅Me₅)₂ (140.1°) [64]. Therefore, we can conclude that the complexes having smaller Cp'-Ln-Cp' angles are more active for the polymerization of ethylene and α -olefins. 1,5-Hexadiene



Fig. 22. Ethylene polymerization with organolanthanide complex.



Fig. 23. Early transition metal complexes for polymerization of ethylene.

was polymerized smoothly by the catalytic action of rac-Me₂Si(2-SiMe₃-4-tBu-C₅H₂)₂Sm(THF)₂ to give poly(methylene-1,3-cyclopentylene) at a ratio of cis/trans = 55 : 45.

More recently, ethylene polymerization was explored using a bulky non-metallocene type yttrium complex, tris(3,5-dimethyl-1-pyrazoyl)borohydride YPh₂ **30** (Fig. 22) [65]. The use of such bulky ligand displays many advantages over analogous cyclopentadienyl ligands due to the relative ease of tuning the blocking substituent groups on the 3-position of pyrazole rings. The polymerization of ethylene resulted in the high molecular weight polymer of $M_w = 1.0 \times 10^5 - 2.0 \times 10^6$ with molecular weight distribution $M_w/M_n = 2.5-4.1$. The turnover number is 1096–3000 (mol PE/mol of Y). The alkoxyyttrium complex **31** (Fig. 23) also conducts the polymerization of ethylene and 1-hexene to give the polymers of $M_w = 1.0 \times 10^5 - 2.0 \times 10^6$ with molecular weight polymers.

Table 8 Polymerization of ethylene catalyzed by metallocene/MAO or $B(C_6F_5)_3$ systems (activity, kg polyethylene/metal mol h atm.)

Complex	Temperature (°C)	Activity	$M_{\rm n}/10^3$	$M_{ m w}/M_{ m n}$	Reference
Cp ₂ TiCl ₂ /MAO	20	4300			[71]
Cp ₂ TiMe ₂ /MAO	20	9600	530		[72]
$S(2,2'-C_6H_2Bu-2-Me-4-O)TiCl_2/MAO$	20	39,300	188	2	[74]
Cp ₂ ZrCl ₂ /MAO	70	91,000			[71]
Cp ₂ ZrMe ₂ /MAO	50	9800	331	1.78	[73]
(Ind) ₂ ZrMe ₂ /MAO	50	66,000	395	2.20	[73]
Me ₂ Si(ind) ₂ ZrCl ₂ /MAO	65	3900	201	2.8	[75]
Cp ₂ HfMe ₂ /MAO	50	1700	361		[73]
$[Cp_2ZrMe][MeB(C_6F_5)_3]$	25	4500	612	2.0	[76]
$[(C_5H_3-1,2-Me_2)_2ZrMe][MeB(C_6F_5)_3]$	25	6800	367	1.4	[77]
$[(C_5H_4SiMe_3)_2ZrMe][B(C_6F_5)_4]$	21	2870	115	2.6	[78]
$[(C_2H_4)(ind)_2Zr(CH_2Ph)][B(C_6F_5)_4]$	60	17,000	36	4.0	[79]



Fig. 24. Catalysts for isotactic poly(propylene).

224, 300 ($M_w/M_n = 5.7$, activity 1350 polymer g/Y mol h atm.) and $M_w = 15,700$ ($M_w/M_n = 1.67$, isotacticity 87%), respectively. However, the polymerization of propylene has yet not been reported. The addition of excess Me₃SiC=CH results in no polymerization. Only the ethynyl compound was formed [66]. When the cationic species was used, cationic polymerization of isobutene proceeded successfully to result in the polymer of $M_w = 1180 \times 10^3$ ($M_w/M_n = 2.0$) [67]. Bis(benzamidinato) yttrium hydride complex **32** shows only a little catalytic activity toward the polymerization of ethylene and gave the polymer having high molecular weight, $M_n = 46,300$ (activity 4 g PE/Y mol h atm.), but the molecular weight distribution is rather wide, $M_w/M_n = 5.2$ [68].

3. Group 4 metal initiated polymerization

3.1. Ethylene polymerizations using metallocene/MAO or $B(C_6F_5)_4$ system

A catalyst system consisting of Cp₂TiCl₂ and alkylaluminum such as AlClEt₂ showed only a low activity for α -olefin polymerization [69]. The important breakthrough in this homogeneous catalyst system was reached serendipitously by Sinn and Kaminsky during the study of the effect of methylalumoxane (AlMe–O–)_n (MAO) on the polymerization [70]. Addition of an excess of MAO as a cocatalyst to a homogeneous solution of Cp_2TiCl_2 or Cp_2ZrCl_2 dramatically induced the rapid polymerization of ethylene to reach the activities of 10^4 and 10^5 kg of polyethylene (PE)/M mol h atm., respectively [71,72]. This unique catalyst system is known as the Kaminsky–Sinn catalyst. Since then metallocene complexes of Group 4 metals have attracted much interest in view of their suitability as catalysts for α olefin polymerizations and the zirconocene system has been found to have the most active metal center [71–73]. Typical examples are summarized in Table 8. The cationic metallocene species containing $B(C_6F_5)_4^-$ counter ion also exhibit good catalytic activities toward the polymerization of ethylene. The polymerization proceeds in a high catalytic activity to give sufficiently high molecular weights $M_{\rm n} >$ 360,000 with low polydispersities $(M_w/M_n < 2.0)$ even at low temperatures. In this case, the catalyst/ cocatalyst ratio is ca. 1/1, while in the Kaminsky catalyst systems the most suitable ratios were observed between 1:1000-1:10,000 ratios for the complex/cocatalyst. More recently, non-metallocene type complexes are frequently used as the catalyst. For example, the $(C_5Me_5)(2,6-iPr_2C_6H_3)ZrF_2/MAO$ 33 (Al/Zr = 1000–3000) system shows the high catalytic activity ($2-5 \times 10^5$ g PE/Zr mol h atm.) [80]. The borabenzene-zirconium complexes 34 ($R = NiPr_2$, 105 kg PE/Zr mol h atm.; R = Ph, 735 kg PE/ Zr mol h atm.; R = OEt, 240 kg PE/Zr mol h atm.) exhibit higher catalytic activity for the polymerization of ethylene than the Cp₂ZrCl₂/MAO system (91 kg PE/Zr mol h atm.) [81–85]. A linear polyethylene was formed when R is NiPr₂, while a 2-alkyl-1-alkene oligomer was obtained in the case of R = Ph.

Complex	Temp (°C)	Activity ^a	$M_{\rm n}/10^3$	$M_{\rm w}/M_{\rm n}$	Tacticity (%)	Reference
$rac-(C_2H_4)(IndH_4)_2ZrCl_2$	60	1100	73	2.6	<i>mm</i> 96	[87]
rac-Me ₂ Si(IndH ₄) ₂ ZrCl ₂	65	110	201	2.2	mm 96.2	[73]
Me ₂ Si(C ₅ HMe ₃ '2,3,5)(C ₅ HMe ₃ -2',4',5')ZrCl ₂	30	5300	67	2.0	<i>mmmmm</i> 97.7	[95]
$Me_2Si(C_5H_2Bu-3-Me-5)(C_5H_3Me-2'-Bu-4')ZrCl_2$	50	505	3.7	2.5	<i>mmmm</i> 94	[96]
$(C_2H_4)(C_5H_3Bu-3)_2$ ZrCl ₂ (rac 42%, meso 58%)	40	160	6.9	2.5	<i>mmmm</i> 97.6	[103]
<i>rac</i> -Me ₂ Si(Benz[e]Indenyl) ₂ ZrCl ₂	50	41,100	24	1.6	<i>mmmm</i> 90	[97]
<i>rac</i> -Me ₂ Si(2-Me-Benz[e]Indenyl) ₂ ZrCl ₂	40	29,000	114	1.7	mmmm 93	[97]
threo-Me ₂ Si(C ₅ H ₃ -3-tBu)(C ₉ H ₅ -3-tBu)TiCl ₂	1	1950	34.1	2.6	mm 99.6	[104]
<i>threo</i> -Me ₂ Si(C ₅ H ₃ -3- <i>t</i> Bu)(C ₉ H ₅ -3- <i>t</i> Bu)ZrCl ₂	60	42,000	9.0	2.7	mm 99.2	[104]
<i>threo</i> -Me ₂ Si(C ₅ H ₃ -3- <i>t</i> Bu)(C ₉ H ₅ -3- <i>t</i> Bu)HfCl ₂	40	1400	11.9	2.7	mm 99.3	[104]
erythro-Me ₂ Si(C ₅ H ₃ -3-tBu)(C ₉ H ₅ -3-tBu)ZrCl ₂	1	60	9.0	2.0	mm 51.8	[104]
$(C_2H_4)(Ind)_2HfCl_2$			329		mm 95-99	[91]
$(C_2H_4)(IndH_4)_2HfCl_2$			68		mm 95-99	[91]
$Me_2Si(C_5HMe_3-2,3,5)(C_5HMe_3-2',4',5')HfCl_2$			110		<i>mmmm</i> 98.7	[95]
$(C_2H_4)(Ind)_2TiCl_2$ (rac 56%, meso 44%)			97		<i>mm</i> 54	[81]
$rac-MeCH(Ind)(C_5Me_4)TiCl_2$			67		<i>mmmm</i> 40	[88]

 Table 9
 Isospecific polymerization of propylene initiated by metallcene/MAO systems

^a g PE/M mol h atm.

The Zr-salicylamidinate/MAO **35** system exhibits the highest catalytic activity for the polymerization of ethylene. When the R¹ group is a bulky alkyl group such as adamantyl or cumyl group (R² = H, Me), the resulting complexes show very high catalytic activities, 714–1131 kg PE/Zr mol h atm., and the molecular weight of polymers can be controlled ($M_n = 0.8-113 \times 10^4$) by introducing various kinds of alkyl groups into the R³ group [86]. Relatively high catalytic activity was also observed when we used the non-metallocene type derivative **36**. In the case of triisopropylphosphineimido ligand, the resulting complex show very high catalytic activity (1807 kg PE/Ti mol h atm.) giving the polymer with $M_w = 310,000$ using Ph₃C[B(C₆F₅)₄] as a cocatalyst [87].

3.2. Isospecific polymerizations of propylene catalyzed by metallocene compounds

In 1984, Ewen et al. reported that a mixture of *meso-* and *racemo-*isomers of $(C_2H_4)(Ind)_2TiCl_2$ **37** (Fig. 24) upon activation with MAO afforded iso- and atactic polypropylene [88]. Brinzinger et al. first used a chiral C_2 -symmetrical ethylene-bridged metallocene, *rac-*(C_2H_4)(Ind H_4)₂ZrCl₂ **38**, as a catalyst precursor for highly isotactic polymerizations of 1-alkenes [89]. This breakthrough was followed by the active and widespread research using Group 4 metallocene catalysts using a variety of bridging ligands. Some representative examples of isospecific polymerization are summarized in Table 9. The resulting



Fig. 25. Stereoerrors in isotactic poly(propylene).



Fig. 26. C₂-symmetric silylene bridged metallocenes for isotactic polymerization of propylene.

isotactic polypropylene was found to have stereoerrors of type 1 (the enatiomorphoric site control), which is sharp contrast to the unbridged metallocene catalysts that gave type 2 (Fig. 25) isotactic polymers through the chain end control.

A C_1 -symmetric ethylidene bridged titanium complex, rac-MeCH(Ind)(C_5Me_5)TiCl₂, showed rather low isospecificity [90]. The polymerization of propylene using this catalyst gives a stereoblock polymer comprising alternating sequences of stereoregular, crystallizable and stereoirregular, amorphous polypropylene units, which shows good thermoplastic properties [90–92]. The ethylene-bridged hafnium complexes, $(C_2H_4)(Ind)_2HfCl_2$ and $(C_2H_4)(IndH_4)_2HfCl_2$, upon activation by MAO also show good catalysis for the isospecific polymerization of propylene [93]. The stereospecificity is very sensitive not only to steric effects but also to the electronic effects. The isospecificity obtained by $(C_2H_4)(Ind)_2ZrCl_2/MAO$ decreases with increasing the polymerization temperature and decreasing the [Al]/[Zr] ratio. The polypropylene obtained by $(C_2H_4)(Ind)_2ZrCl_2/MAO$ at $T_p = 30^{\circ}C$ and [Al]/ [Zr] = 3200 has [mmmm] = 0.90 and $T_m = 132.3^{\circ}C$, while that obtained at $-15^{\circ}C$ and [AI]/[Zr] = 2700 shows [mmmm] = 0.98 and $T_m = 152.4$ °C [94]. The end group of isotactic polypropylene obtained by using $(C_2H_4)(Ind)_2TiCl_2/^{13}C$ enriched organoaluminum compound was confirmed to be controlled by the enantiomorphic site control of the chiral catalyst metal center [95]. Investigation on the regio-irregularity of the polypropylenes obtained by rac-(C₂H₄)(Ind)₂ZrCl₂ and (C₂H₄)(IndH₄)₂ZrCl₂ resulted in the same conclusion [96]. Among the C_1 complexes, three-Me₂C(3-tBu-C₅H₃)(3-tBu- C_9H_5 /ZrCl₂ **39** conducted the highly isotactic polymerization of propylene (isotacticity 99.2 %, activity 42,000 g PP/Zr mol h atm.) [96].



Fig. 27. Initiators for isotactic polymerization of propylene.



Fig. 28. Formation of isotactic-atactic stereoblock polypropylene.



Fig. 29. CGCT type catalysts for polymerizations of olefins.

Table 10 Syndiospecific polymerization of 1-alkene catalyzed by metallocene catalysts

Metal	Ligand	Alkene	Tacticity (%)	Reference
Zr	$Me_2C(Cp)(Flu)$	Propylene	86 (<i>rrr</i>)	[108]
	$Me_2C(Cp)(Cpphen)$	Propylene	72 (<i>rrr</i>)	[109]
	$Me_2Si(Cp)(Cpphen)$	Propylene	24 (<i>rrr</i>)	[110]
	$Me_2Si(Cp)(C_5Me_4)$	Propylene	14(<i>rrr</i>)	[110]
	$Me_2C(Cp)(Flu-2,7-tBu_2)$	Propylene	92 (rrr)	[111]
	MePhC(Cp)(Flu)	Propylene	97 (rrr)	[112]
	$(C_4H_8)C(Cp)(Flu)$	Propylene	92 (rrr)	[113]
	$Me_2C(Cp)(Flu)$	1-Butene	92 (rrr)	[114]
	(C_5Me_5)	1-Butene	68 (<i>rr</i>)	[114]
Hf	$Me_2C(Cp)(Flu)$	Propylene	74 (<i>rrr</i>)	[108]
	(C_5Me_5)	1-Butene	77 (<i>rr</i>)	[114]



Fig. 30. Non-metallocene type initiators for polymerizations of 1-alkenes.

The C_2 -symmetric silvene bridged metallocene such as rac-Me₂Si(Ind)₂ZrCl₂ 40 [73], $Me_2Si(C_5H-2,3,5-Me_3)(C_5H-2,4,5-Me_3)ZrCl_2$ 41 [97], $Me_2Si(C_5H_2-3-tBu-5-Me)(C_5H_3-2'-tBu-4'-$ Me)ZrCl₂ 42 [98], Me₂Si(Benz[e]indenyl)₂ZrCl₂ 43 [99], and Me₂Si(2-Me-Benz[e]indenyl)₂ZrCl₂ 44 [107] were used as the catalyst precursor for the isotactic polymerization of propylene (Fig. 26). The catalyst 42/MAO conducted the polymerization of propylene with high activity producing rather low molecular weight polymers (at 4 atm., $M_n = 2.8 \times 10^4$). On the other hand, 44/MAO yielded a polymer of higher molecular weight (at 4 atm., $M_n = 2.2 \times 10^5$). Thus, the 2-methyl substitution of the ansacyclopentadienyl derivatives effectively enhances the molecular weight of resulting polymers [100]. The use of dimethylbis[2-methyl-4-(1-aryl)indenyl]silane 45 and 46 (Fig. 27) as a ligand was found to give the polypropylene with high stereoregularities and high molecular weights [101]. The highest isospecificity among the metallocene catalysts was achieved by the system of 46. The C_2 -symmetric doubly bridged zirconocene complexes such as (Me₂Si)₂(1,2-C₅H-3,4-Me₂)₂ZrCl₂ **47** and (Me₂Si)₂(1,2-IndH₄)₂ZrCl₂ **48** were reported to have been converted into active catalysts for the polymerization of propylene, yielding polymers with relatively low isotacticities (mmm = 38 and 80%, respectively) [102].

By using conformationally variable non-bridged Cp ligands such as C_5H_4iPr , the change in the dominant mode of propylene polymerization from isotactic to syndiotactic was accomplished by varying the reaction temperature [103]. Waymouth and his coworkers reported a unique system where the unbridged bis(2-phenylindenyl)zirconium-based catalyst **49** and **50** (Fig. 28) gave elastomeric, isotactic–atactic stereoblock polypropylene, controlled by rotation of the 2-phenylindenyl [104].

3.3. Syndiospecific polymerizations of propylene catalyzed by metallocene complexes

Highly syndiotactic poly(alkene) (Fig. 29) has been obtained by Ewen and his coworkers using $Me_2C(Cp)(Flu)MCl_2$ **51** (M = Zr, Hf) [105]. The site control in their coordination of alkene to a metal center is accounted for the stereochemistry during the propagation. It has been proposed that the fluorenyl group causes direct prochiral face control of the coordination of alkene to active site by the direct steric interaction. Recently, however, indirect control by the fluorenyl group has been suggested

Monomer	Cocatalyst	Time (min)	Solvent	$M_{\rm n}/10^{3}$	$M_{ m w}/M_{ m n}$	Activity ^a
1-Hexene	$B(C_{6}F_{5})_{3}$	30	Toluene	19.1	1.05	3-40
1-Octene	$B(C_{6}F5)_{3}$	30	Toluene	15.5	1.09	
1-Decene	$B(C_6F5)_3$	30	Toluene	15.8	1.05	
1-Hexene	$B(C_6F_5)_3$	30	CH ₂ Cl2	164.2	1.07	
1-Octene	$B(C_6F_5)_3$	10	CH_2Cl_2	138.2	1.07	
1-Decene	$B(C_6F_5)_3$	10	CH ₂ Cl ₂	121.5	1.07	
1-Hexene	MAO	0.5	Toluene	47.0	1.73	290,000
1-Hexene	$B(C_6F_5)_3/MAO$	5	Toluene	16.1	1.81	2000
1-Hexene	MAO	0.5	Toluene	31.0	1.79	115,000

Living polymerization of 1-olefins by TiMe₂[RN(CH₂)₃NR]/B(C₆F₅)₃ or MAO

^a g poly(1-olefin)/ T_2 mol h atm.

Table 11

by the detailed conformational analysis using molecular mechanistics [106,107]. According to the study, the direct interactions of the $Me_2C(Cp)(Flu)$ ligand with the growing chain determine its chiral conformation, which, in turn, discriminates between the two prochiral faces of the propylene monomer. A great variety of modifications to the steric properties, based on the Ewen's work, has been carried out in order to control the stereoselectivity. Some representative examples are summarized in Table 10. Using modified $Me_2C(Cp)(Flu)MCl_2$ (M = Zr, Hf) species, high syndiospecificity has been achieved as reported by Fina, Hoechst and Mitsu Chemical Inc.

3.4. Non-metallocene type Group 4 metal complexes for polymerization of 1-alkenes

The Dow corporation has recently developed constrained geometry addition polymerization catalysts (CGCT), typically Me₂Si(C₅Me₄)(NtBu)MCl₂ **52** (M = Ti, Zr, Hf) activated with MAO. The homopolymerization of 1-alkenes by CGCT affords atactic or somewhat syndiotactic polymers (polypropylene, rr = 65-69%). The metal center of the catalyst opens the coordination sphere and enables the copolymerization of ethylene to take place, not only with sterically hindered 1-alkene such as styrene and 4-vinylcyclohexene [115]. As an extension of this research, other CGCT catalyst such as **53–56** was explored to obtain high activity. However, the original CGCT catalyst shows highest activity, but 2,1-insertion decreased significantly when we used the complex **56** [116]. More recently, McConville and co-workers have developed titanium diimido complexes such as TiMe₂[2,6-iPr₂-C₆H₃N(CH₂)₃N-2,6-iPr₂C₆H₃] **57** (Fig. 30) coupled with B(C₆F₅)₃ or MAO [117,118]. These initiators conduct the living

Table 12

Copolymerization of ethylene with 1-butene (MMAO (AlMeO)_m(AliBuO)_n, MAO (AlMeO)_n, B/Al $Ph_3CB(C_6F_5)_4/AliBu_3(1:500)$)

Initiator	Cocatalyst	Activity ^a	1-Butene content/%	$M_{\rm n}/10^4$	$M_{ m w}/M_{ m n}$
61	MMAO	1050	18.6	3.3	5.7
61	MAO	8560	6.7	32.2	4.0
61	B/Al	12,400	31.3	7.0	2.2

^a g poly(1-butene)/ T_2 mol h atm.



Fig. 31. Non-metallocene type initiators for polymerizations of 1-olefins.

polymerization of 1-hexene, 1-octene and 1-decene. The activities increased when CH₂Cl₂ was used as a solvent in place of toluene (Table 11). The catalytic activity increased to 290 kg poly(1-hexene)/ Ti mol h atm. when MAO was used. However, the use of TiCl₂[2,6-iPr₂-C₆H₃N(CH₂)₃N-2,6-iPr₂C₆H₃] coupled with $B(C_6F_5)_3/MAO$ as a cocatalyst resulted in lower catalytic activity. Mulhaupt et al. studied the copolymerization of ethylene with styrene using bis(phenoxy) ligands bridged by S, S=O, CH_2 or CH_2CH_2 group [119,120]. The amount of MAO was fixed to be Al/Ti = 1000 mol/mol. The complexes SBP 58 and SBC 59 show relatively high activity and the styrene content in the copolymer is ca. 5-6%when the feeding ratio of ethylene to styrene was 0.22:1.1. The styrene content in the copolymers increased to 17% by the addition of excess styrene (ethylene/styrene = 9.13:2.2) but the catalytic activity and the molecular weight decreased significantly (29 kg polymer/Ti mol h atm., $M_n = 6000$). The titanium complex 60 showed high catalytic activity towards the polymerization of propylene and 1-butene. When MAO was used as a cocatalyst (Al/Ti = 500 mol/mol), the activity reached to 59.5 kgpolymer/Ti g h and the use of iBuAl₃/B(C_6F_5)₃ resulted in the activity of 33 kg polymer/Ti g h [121]. Schrock and his coworkers have found the living polymerization ability of the complex 61 for 1-hexene [122–124]. The molecular weight increased straightforwardly by increasing the ratio of 1-hexene/Zr. The resulting polymer maintains the low polydispersity $(M_w/M_n = 1.04-1.08)$. The main disadvantage of the resulting complex is the lack of thermal stability. The complex is stable at 0°C while it decomposes gradually at 20°C. Analogous complex 62 enables the catalytic polymerization of 1-hexene in good yield (98–100% yield after 1 h). The upper limit of the molecular weight is 25,000 and this complex is also thermally very unstable [124]. Both complexes give rise to the formation of atactic poly(1-hexene).

The copolymerizations of ethylene with 1-butene proceeded successfully using the complex **63** (Fig. 31, Table 12) [125]. The product of the monomer reactivity ratios, $r_{\text{ethylene}} \times r_{\text{propylene}}$ ranges 0.27–0.36 to indicate that this complex catalyzes the desired random copolymerization, while CGCT type complex



Fig. 32. Group 5 carbene complexes for metathesis polymerizations.



Fig. 33. Ring-opening polymerization of 3,4-diisopropylidenecyclobutene.

showed $r_{\text{ethylene}} \times r_{\text{propylene}} = 2.45$ to indicate that the block copolymerization proceeds preferentially. Highly isotactic polypropylene could be obtained using the non-metallocene type zirconium catalyst **64**, i.e., 98.9% isotacticity (*mmmm*%), activity 200 g PP/Zr mol h, $M_n = 318,000$ at 0°C and 79.5% isotacticity (*mmmm*%), activity 9230 g PP/Zr mol h, $M_n = 7750$ at 70°C [126]. Analogous complex **65** also showed high isotacticity, 98.3% with moderate catalytic activity, 2.7×10^3 g PP/Zr mol h atm. The M_n is 35,000–88,000 and T_m is 145–153°C [127].

The ring opening of 3,4-diisopropylidenecyclobutane with titanium-carbene catalysts gave a colorless, soluble, cross-conjugated polymer after quenching with methanol (Fig. 33). The electric conductivities were observed in the range of 10^{-3} – 10^{-4} S cm⁻¹ after heavily doping this material with iodine. The doped material is black, brittle, and air-sensitive, similar to the traditional Shirakawa's polyacetylene [128,129].

4. Group 5 metal initiated polymerization

Tantalum alkylidene complexes have been useful for outlining the principles of olefin metathesis [130,131], but none has been long-lived enough to be practical for the metathesis of ordinary olefins. $(tBuO)_2Nb=CH(tBu)Cl$ **66** performs the olefin metathesis reaction. For example, 3-hexene and 2-butene were formed in ca. 15% yield from *cis*-2-pentene after the elapse of 100 min, in the presence of phosphine ligand. In this case, no polymerization was initiated. Therefore, Schrock and his-coworkers explored the controlled ring-opening polymerization of strained cyclic olefins, norbornene derivatives, using complexes **67** and **68** (Figs. 32 and 34) [132–134]. For example, the complex **67** conducted the polymerization of norbornene to give the polymer of $M_n = 18,000-26,000$ with low polydispersity, $M_w/M_n = 1.06-1.09$. The stereoregularity is 55–65% *trans* and 45–35% *cis* as analyzed by NMR. The reaction mechanism was proposed as follows on the basis of ¹H NMR data. A similar reaction mechanism was proposed by Grubbs for the titanacyclobutene derivatives **70** [134]. The titanacycle is in



Fig. 34. The mechanism for ROMP of norbornene with Ta-carbene.



Fig. 35. Ethylene dimerization by Ta-carbene.

equilibrium with a small amount of the alkylidene complex formed by opening the titanacycle ring. The alkylidene complex can be trapped by norbornene to give new titanacycle. Repetition of these steps leads to the formation of polymers in which the ratio of *trans* to *cis*bonds is ca. 1.5. The complex **68** reacts with 2-butyne to afford a tantalacyclobutene **69**, which is very reactive for the polymerization of 2-butyne to give $M_n = 17,900$ with $M_w/M_n = 1.03$. The color of the solution changed from dark purple to deep red during the reaction. The *cis/trans* ratio about the double bond is determined for this polymer. Block copolymerization of 2-butyne with norbornene was also successful. The 1:1 copolymer exhibits molecular weight of 400,000 ($M_w/M_n = 1.50$) [135]. Acetylene derivatives can be polymerized more effectively by the use of simple catalytic species, TaCl₅/Bu₄Sn. Thus, high molecular weight polymers of PhC=C(C₆H₄)SiMe₃ ($M_w = 2.2 \times 10^6$) and PhC=C(C₆H₄)tBu ($M_w = 3.6 \times 10^6$) were obtained in high yields, and these polymer can be used as oxygen permeability materials [136–139] The polymerization of 1-trimethylsilyl-1-propyne also affords high molecular weight polymers ($M_n = 173,000$) with relatively low polydispersity ($M_w/M_n = 1.36$) [140–142]. In the case of the polymerization of 3-trimethylsilyl-1-octyne, only cyclic trimer was obtained using TaCl₅ or NbCl₅ as a catalyst [143].



Fig. 36. Tantalum complexes for polymerizations of 1-olefins.



Fig. 37. Vanadium, molybdenum, and tungsten complexes useful for polymerization of olefins.

In general, the tantala-carbene complexes do not bring about the formation of high molecular weight polymers from linear olefins such as ethylene and propylene. Ta = $CHtBu(CH_2tBu)_2$ in the presence of PMe₃(2 molar ratio) and ethylene (40 psi) in pentane at 25°C produced a homogeneous catalyst which performs dimerization of ethylene selectively to 1-butene (Fig. 35). The formation of 1-butene was concluded to follow the reaction mechanism listed above [144]. When $Ta = CHtBu(H)(PMe_3)_3I_2$ 71 was used, the ethylene oligomerization took place. The field-desorption mass spectrum shows a distribution of molecular ions (C22–C40) separated by 14 mass unit [145]. More efficient catalytic activity for the polymerization of ethylene was observed using complexes 72–75 (Fig. 36). The complex 72 polymerizes ethylene in the presence of $Ph_3C^+[B(C_6F_5)_4]^-$ or $B(C_6F_5)_3$ (activity 38 kg PE/Ta mol h atm., $M_{\rm n} = 1.3 \times 10^6$, $M_{\rm w}/M_{\rm n} = 17.4$), while chloride **73** and alkyl derivatives are inactive in the presence of MAO or an alkyl abstraction reagent. Thus, the catalytic activity changes significantly by the subtle difference of coordinating ligands [146]. Polyethylene with narrow molecular weight distribution was obtained using the tantalum(V) aminopyridinato complex 74-75/MAO system. Both 74 and 75 produced high molecular weight polyethylene ($M_n = 60,000-200,000$) with low polydispersity $(M_w/M_n = \text{ca. 2})$, whose melting point ranges 136.3–137.7°C, when Al/Ta = 2000 [147]. More efficient catalytic activity was observed when the complex 73 was used together with MAO (Al/Ta = 500 mol/mol) at -20°C [148,149]. The activity is 4.5 kg PE/Ta mol h atm and the resulting molecular weight is $2.04 \times 10^4 (M_w/M_n = 2.06)$. A very narrow molecular weight distribution $(M_w/M_n = 1.10)$ was obtained when the polymerization was carried out at 0°C. The use of $(C_5H_5)Ta(C_4H_6)Me_2$ in place of $(C_5Me_5)Ta(C_4H_6)Cl_2$ 77 resulted in the formation of higher molecular weight of polymers. The catalytic activity increased to 35 kg PE/metal mol atm. h by the use of (C₅Me₅)NbCl₂(CH₂CMe-CMeCH₂) 76. Ring opening metathesis polymerization (ROMP) of norbornene was also realized using 76 as a catalyst. The resulting polymer exhibits 90% trans vinylidene structure and $M_n =$ 22,200 ($M_w/M_n = 1.14$). The complex 77 also showed the catalytic activity towards the polymerization of dicyclopentadiene [150]. The complex 78 conducts the polymerization of norbornene in extremely high selectivity. The cis-vinylidene structure exceeds 99% and the molecular weight reaches 32,300 ($M_w/M_n = 2.04$) when the polymerization was carried out in the bulk conditions [151].



Fig. 38. Polymerization of norbornene with tungsten complex.

Table 13 Monomers possible to ROMP



V(acac)₃(acac = acetylacetonate) in conjunction with Et₂AlCl shows high catalytic activity towards the polymerization of propylene [152]. Resulting polymer exhibits $M_n = 3.5 \times 10^4$ with $M_w/M_n = 1.1$. However, syndiotacticity is rather low, rr = 52%. This initiator can proceed the block copolymerization of non-polar monomers with polar monomers, e.g. propylene with methyl methacrylate. A living polypropylene ($M_n = 16,000, M_w/M_n = 1.2$) was prepared at -78° C in toluene solution, and then MMA was copolymerized by the addition of excess MMA [153]. The block copolymerization proceeds at 25°C for 5 h, resulting in the formation of an almost monodisperse block copolymer ($M_n = 18,000, M_w/M_n = 1.2$) [154]. However, the content of polar monomers in the copolymer is only 0.1–0.2 mol%.

Table 14 Polymerizable monomers by molybdenum catalysts





Fig. 39. Polymerization of 2,3-dicarbo-methoxynorbonadiene and regeneration of metalcarbene by heating.

V(acac)₃, Cp₂V, or Cp₂VCl₂ combined with MAO give rise to the formation of high molecular weight poly(MMA) in ca. 50% syndiotacticity. In these cases, M_w/M_n is very wide (14–27). When the polymerization of ethylene using the V(acac)₃/MAOsystem, the polymers with very large polydispersity ($M_w/M_n = 200$) were obtained [155]. The CGCT type vanadioum complex, Cp(CH₂)₂NiPrVCl₂ **79**, combined with MAO exhibits a moderate catalytic activity (209 kg PE/mol V h) and gives relatively low molecular weight polyethylene ($M_w = 14,900, M_w/M_n = 3.0$). The polymer end assume the CH₂-CH=CH₂ structure to indicate that the β-elimination occurs very frequently in this case [156].

5. Group 6 metal initiated polymerization

Molybdenum and tungsten complexes of the type $M = CHtBu(NAr)(OR)_2$ **80** (Fig. 37) all react rapidly with norbornene, but only those in which OR=OtBu yield relatively stable living polymers, i.e. ones in which the M=C bond does not react readily with olefinic bonds in the chain [101]. The conversion of initiating to propagating species is high enough (>90%) when n = 10, so the polydispersity is relatively unaffected for polymers in which n > 50 [157]. Initiation appears to be solely *trans*, and the polymer can be cleaved off rapidly by benzaldehyde. Polynorbornene [poly(NBE)] containing up to 1000 equiv. of NBE has been prepared in this manner with a polydispersity as low as 1.03 (Fig. 38). Metallacycles that contain NBE have never been observed. Benzaldehydes substituted in the *para* position with $X = CF_3$, OMe, NMe₂, CN, NO₂, CHO, COOMe, NH₂, and Cl have been employed successfully to cleave the poly(NBE) (100-mer) from molybdenum [158], although some slight increase in polydispersity was observed in the case of NO₂ and CHO. The Wittig-like reaction has been shown to proceed via oxametallacyclobutane intermediates in the case of C₆F₅CHO [159]. Square pyramidal



Fig. 40. 7-Oxanorbornadienes for reaction with Mo=CH-t-Bu(NAr)(O-t-Bu)2.





oxametallacycles (M = Mo, W) could be observed, and the crystal structure of the tungsten complex was determined. The monomers which permits the ROMP is summarized in Table 13.

An important feature of the molybdenum catalyst system is that it often appears to be more tolerant of functionalities than the tungsten system [160-162]. Some of the monomers that have been polymerized successfully in a living manner using molybdenum are summarized in Table 14.

Solvent is an important, and still poorly understood, variable. For example, it is not possible to polymerize 5-cyanonorbornene with W=CH-*t*-Bu(NAr)(O-*t*-Bu)₂ or Mo=CH-*t*-Bu(NAr)(O-*t*-Bu)₂ in a typical noncoordinating solvent such as toluene and benzene. In THF, however, Mo(=CH-*t*-Bu)(NAr)(O-*t*Bu)₂ will initiate the polymerization of 200 equiv. of 5-cyanonorbornene rapidly to give a homopolymer with a polydispersity of 1.05. In several cases, the stereoregularity of the ring-opening reaction is unusually highly *trans* [160]. Poly[2,3-bis(trifluoromethyl)norbonadiene] contains >98% *trans* double bonds as determined by ¹³C NMR. A melting point was observed at 200°C and a T_g at ~100°C by differential calorimetry. On following the polymerization by ¹H NMR at low monomer levels, alkylidene proton resonances for each living oligomer Mo[(monomer)_xCH-*t*Bu](NAr)(O-*t*-Bu)₂ where x = 1, 2, 3 and 4 or greater could be observed. Two nearly coincident alkylidene proton resonances were observed in a ratio of ~6:1 for the living oligomers in which x > 10. The polymer is believed to be tactic, although that has not yet been proven. 2,3-Dicarbomethoxynorbornadiene is also polymerized to a highly *trans* polymer (90–95%). Both derivatives are polymerized much more slowly than norbornene, partially for steric reasons, but also for electronic reasons; electron-withdrawing substituents reduce the nucleophilicity of the olefin on the other side of the ring sufficiently to

significantly retard at which the monomer attacks the metal. 2,3-Bis(trifluromethyl)norbornadiene is polymerized by $W=CH-tBu(NAr)(O-tBu)_2$ to give only a low polydispersity polymer, but addition of one equivalent of this monomer at 0°C gives an unstable, but isolable, square pyramidal metallacycles. In general, tungstacycles are more stable than molybdacycles [160–163]. A low temperature X-ray study of the tungstacycle showed it to be a square pyramidal metallacycle obtained by adding the *exo* face of the monomer to the *syn* rotamer of the neopentylidene complex, the only rotamer observable in that case. The imido ligand is oriented so that one isopropyl group partially blocks one face of the W=C bond, a fact that would help explain the high *trans* stereoselectivity, where this particular metallacycle structurally similar to the transition state. This tungstacycle rearranges in the first-order manner to give a mixture of *anti* and *syn* forms of the first insertion product, but alkylidene species is unstable, a fact that may explain the failure to form the polymer using the tungsten catalyst.

The rate of formation of the metallacycle is greatly influenced by the electron withdrawing ability of substituents in the norbornene or norbonadiene system. For example, the reaction between $Mo=CH-t-Bu(NAr)(O-t-Bu)_2$ and 7-isopropylidene-2,3-dicarbomethoxy-norbonadiene is extremely slow at room temperature, approximately 350 times slower than the rate of polymerization of 2,3-dicarbomethoxy-norbonadiene. The structure of this first insertion product was found to be *syn* with a *trans* terminal bond and carbomethoxy group that does not interact with metal **81** (Fig. 39). Note how the isopropylidene group protects one side of the Mo=C bond while a carbomethoxy group protects the other side, making it especially difficult for the next equivalent of monomer to react with the alkylidene.

2,3-Dichloro-2,3-carbonatonorbornene reacts slowly with Mo=CH-t-Bu(NAr)(O-t-Bu)₂ to give an observable square pyramidal metallacycle [161]. When this metallacycle **82** is heated the monomer is regenerated to give 50% of the starting neopentylidene complex. The liberated monomer adds to the alkylidene that is formed when metallacycle rearranges to give a living oligomer. This is the first observed circumstance where metallacycle formation is reversible for norbornene.

7-Oxanorbornadienes react unexpectedly rapidly with $Mo=CH-t-Bu(NAr)(O-t-Bu)_2$ to give isolable and extraordinarily stable square pyramidal t-butyl-substituted metallacyclobutene complexes [163,164]. The high reactivity of the 7-oxa derivatives can be attributed to a coordination of an electron pair on an oxygen above the double bond to be attacked. The molybdacycle prepared from 83 is the most stable toward rearrangement to an alkylidene complex and that prepared from 84 is the least stable (Fig. 40). Those prepared from 84 will rearrange slowly at 25° C to give the expected first insertion product. Therefore, 84 can be polymerized (100 equiv.) to a polymer with a polydispersity of 1.05, but only if the initial metallacycle prepared from 2-3 equiv. of 84 is allowed to rearrange completely to the first insertion product before the remaining 84 is added. Therefore, metallacycles that contain the growing polymer chain rearrange significantly more quickly than the initial one. A significantly higher polydispersity (~1.2) results if all 84 is added at once to Mo=CH-t-Bu(NAr)(O-t-Bu)₂. The compound 83 cannot be polymerized by $Mo=CH-t-Bu(NAr)(O-t-Bu)_2$ because the intermediates are not stable at the temperatures that are necessary to open the metallacyclic ring. However, it can be polymerized in a living manner starting with Mo=CH-t-Bu(NAr)[OCMe₂(CF₃)]₂. In this case, both the living alkylidene α -carbon atom and the double bonds in the chain can be said to be less nucleophilic, so in spite of the increased electrophilic character of the metal, secondary metathesis is slow. These are typical of the subtleties that are becoming apparent and that can be used to advantage in these well-defined catalyst systems.

The tolerance of the $M=CH-t-Bu(NAr)(O-t-Bu)_2$ catalyst for functionalities allows them to be used to ring-open norbornene that contain metals (Table 15). The first monomer of this type, Pb(NBECp)₂,



Fig. 41. Preparation of di-tBu-capped polyenes.

contained lead **86** [165]. The fact that two norbornene double bonds are present per metal created the possibility that the metal complex would behave as a cross-linking agent. Lead-containing block copolymers could be prepared. Treating static cast films of such polymers with hydrogen sulfide yielded nano-clusters of the semiconductor PbS within the polynorbornene matrix. Block copolymer synthesis could be controlled to a much greater degree by using Pb(NBECp)Cp* **87** [166], since although scrambling to give Pb(NBECp)₂ and PbCp^{*}₂ occurs, the equilibrium lies far toward Pb(NBECp)Cp* under the conditions employed. Microphase separation in static cast films of NBE/Pb(NBECp)Cp* block copolymers was observed. The idea of carrying a metal into a well-defined microphase region by attaching it to a polynorbornene-like backbone in a low polydispersity block copolymers may create opportunities for controlling the size of metal-containing materials formed after further chemistry is carried out on microphase-separated materials.

A type of the monomer that potentially can be used to carry a variety of metals into microphaseseparated materials is a chelating bisamido ligand, 2,3-*trans*-bis(t-butyl-amidomethyl)norbor-5-ene (bTan). A Sn(IV) complex, Sn(bTAN)Cl₂ **89**, can be polymerized smoothly by Mo=CH-*t*-Bu(NAr)(O-*t*-Bu)₂ in THF, and the block copolymers containing norbornene have been prepared in which the ratio of norbornene to Sn(bTAN)Cl₂ has been varied to give lamellae(NBE/ Sn(bTAN)Cl₂ = 1:1), cylinders, and spheres(NBE/Sn(bTAN)Cl₂ = 7:1) of Sn-containing derivative in polynorbornene [168]. The M_n are 11,000–19,000 ($M_w/M_n = 1.05-1.33$). This work demonstrates that classical morphologies of metal-containing microphase-separated block copolymer materials are accessible relatively routinely by the ROMP method. Monomers that contain Sn(II) and Pb(II) and the bTAN ligand were found to be unstable toward decomposition to give metal, but analogous monomers in which trimethylsilyl groups replace the *t*-butyl groups, Sn(bSAN) and Pb(bSAN) **90**, are stable in solution at room temperature for days.



Fig. 42. ROMP of cyclododecatetraene by the W-carbene complex.



Fig. 43. α , ω -Acyclic diene methathesis reaction.

A zinc-containing monomer, $Zn_2R_2(bTAN)$ **91**, also has been prepared [167]. The block copolymers containing this monomer and methyltetracyclododecene (MTD) have been prepared and treated with hydrogen sulfide to yield materials that have a lamellar morphology. The nature of the zinc-containing phase after treatment with hydrogen sulfide has yet to be elucidated. It should be kept in mind that the chemistry required to generate materials such as ZnS clusters in one microphase of a polymer would not necessarily be rapid. Intermediates must decompose readily and zinc compounds must aggregate, perhaps even before the molecular ZnS actually is formed. Similar techniques can be used to generate the zero valent metals in microphase-separated block copolymer films [169–171]. The organometallic palladium derivative, Pd(NBECp)(allyl) **88** which is relatively stable thermally, but which react with hydrogen gas to give Pd(0), can be polymerized smoothly to give the block copolymers containing MTD. The cast films show the expected morphologies and can be treated with hydrogen gas at 100°C to generate palladium clusters $\sim 25-50$ Å in diameter within poly(MTD). As an extension of this study, silver (particle size 20 Å) dispersed polymer could be obtained by mixing Ag(COD)[CF₃C(O)CH-C(O)CF₃] with the copolymer of **85** with NORPHOS followed by heating to 90°C in water [171].

Monomers that contain redox-active ferrocene, e.g. FeNBE **92**, have been polymerized along with monomers that contain other redox-active groups such as phenothiazine to give small block copolymers. Polydispersities for the longer block copolymers containing up to \sim 80 monomer units were found to be as low as 1.05. The solution electrochemistry of these materials shows them to be well defined and well behaved. Analogous more elaborate oligomers that contain several redox-active groups along with several equivalents of trialkoxysilylmethylnorbornene have been prepared and shown to derivatize Pt electrodes with well-defined monolayers [172–174]. In one case M(CHFc)(NAr)(OtBu)₂ (Fc = ferrocenyl) was employed as the initiator and octamethyl-ferrocenealdehyde was employed as the capping agent. Well-defined redox chemistry was observed for all redox-active groups in the oligomer, both in solution and bound to an electrode surface.

Several other strained monomers have been polymerized in a living fashion by $M=CH-t-Bu(NAr)(O-t-Bu)_2$ catalysts. This type of catalysts ($M = M_0$ [175], W [176]) will ring open polymerize 7,8-bis(trifluormethyl)tricyclo[4.2.2.0^{2.5}]deca-3,7,9-triene(TCDT-F₆) **93** in a controlled fashion (Fig. 41) [177–179]. The cleavage of the polymer with pivaldehyde gives a precursor to di-*t*Bu-capped polyenes [180,181]. Analogous techniques have been used to prepare low polydispersity diblocks and triblocks



Fig. 44. Chromium complexes for polymerizations of olefins.

containing up to 100 equiv. of norbornene and up to a "40 ene" on the average [182], although the short polyenes found in such materials now appear to be random copolymer sequences arising from incomplete reaction of the Feast monomer before addition of norbornene.

Rhenium catalysts of the type $\text{Re}(\equiv \text{CCMe}_2\text{Ph})(=\text{CHMe}_2\text{Ph})[\text{OCMe}_2(\text{CF}_3)]_2$ **94** and $\text{Re}(\equiv C + t\text{Bu})(=\text{CH}t\text{Bu})[\text{OCMe}_2(\text{CF}_3)]_2$ have been found to ring open polymerize norbornenes and norbornadienes in a living manner [183,184]. Although $\text{Re}(\equiv C - t\text{Bu})(=\text{CH}t\text{Bu})(\text{O}t\text{Bu})_2$ has been known for several years [185], it does not react with norbornene under the mild conditions (25°C, 1 h) in noncoordinating solvents. The OCMe(CF_3)_2 derivatives [186], on the other hand, are active for metathesis of ordinary double bonds. Although low polydispersity polymers can be prepared with the OCMe_2(CF_3) catalysts, there appear to be several problems. First, the neopentylidene or neophylidene initiators cannot be isolated in the crystalline form. Therefore, there is always some uncertainty as to whether some impurity is present that would adversely affect polymerization. Second, propagating species are unstable toward bimolecular decomposition reaction. For this reason, the concentration of the catalyst must be kept below 0.01 M. Third, these rhenium catalysts are extraordinarily sensitive to oxygen, a fact that is believed to result in formation of a doubled molecular weight material.

One potentially useful method of preparing polyacetylene without loss of mass is via the ring-opening polymerization of benzvalene (Fig. 42) [187]. The successful catalysts were W=CH*t*Bu(OCH₂*t*Bu)₂Br₂, W=CH*t*Bu(NAr)[OCMe(CF₃)₂]₂, and W=CH*t*Bu(NAr)–(O*t*Bu)₂. The resulting polymer could be rearranged by heat, light, or metals such as HgCl₂. However, this strained precursor polymer cross-links readily, or actually explodes under high mechanical stress or on heating too rapidly. After rearrangement it also was difficult to get rid the polymer entirely of residual metal. Nevertheless, polyacetylene-like materials were obtained which had conductivities (S cm⁻¹) of 10^{-8} – 10^{-7} before doping, and 0.1–1 after heavy doping with iodine. Another potentially useful method of preparing polyacetylene is by ring-opening polymerization of cyclooctatetraene by W=CH*t*Bu(NAr)–[OCMe(CF₃)₂]₂ [188]. Cyclooctatetraene can be polymerized neatly to give free-standing films that appear to be very similar to classical polyacetylene. It may involve ring opening of bicyclo[4.2.0]octa-2,4,7-triene, a molecule with which cyclooctatetraene is in equilibrium. An extension of this ring-opening reaction is the polymerization of trimethylsilyl (TMS)-substituted cyclooctatetraene to give a soluble polyacetylene substituted with one TMS group to every eight carbon atoms on an average.

 α,ω -Acyclic diene metathesis is a method of indirect ROMP [189–191]. Usually, a relatively active catalyst such as W=CH*t*Bu(NAr)[OCMe(CF₃)₂]₂ is employed. Ethylene is evolved quickly and polymer



Fig. 45. Initiators for living radical polymerizations.

is formed in a step-growth manner. Polymerizations of this type have not been successful with classical catalysts, perhaps in part because Lewis acids are usually present, and these produce deleterious side reaction. Only the Lewis acid-free, well-defined catalysts have been successful for acyclic diene metathesis.

Acyclic diacetylene derivatives are polymerized successfully by Mo=CH*t*B(NAr)[OC*t*Bu(CF₃)₂]₂ **95** (Fig. 43) to give a mixture of soluble polymers containing 5-membered cyclic ring and 6 membered cyclic ring skeletons in the ratios of 44:56–68:32 [192]. The electric conductivities of the doped 1,6-heptadiyne cyclopolymer is lower than that of polyacetylene. The highly conjugated soluble polymer containing only 6-membered cyclic ring is obtained by the use of the complex **96** [193,194]. The resulting molecular weight ranges from 60,000 to 90,000 and the molecular weight distribution is 1.5-1.7. The doped polymer shows rather low conductivities.

The heterogeneous Phillips catalysts composed of chromium oxide, CrO₃, and some supports such as SiO₂ or Al₂O₃ have been widely used for the industrial production of polyethylene, since this system produces highly flexible polymers due to its branched structure. Recently, homogeneous Cr catalyst systems such as 97, 98/MAO (1:100 ratio) have been developed for the copolymerization of ethylene with norbornene (Fig. 44). The complex 98 shows highest activity, but the crystallinity of the polymer was poor. By using the complex 97, a high molecular weight ($M_n = 420,000, M_w/M_n = 1.38$) copolymer of ethylene/norbornene (80:20 ratio) could be obtained in high yield [195]. The homogeneous catalyst system composed of 100 and MAO shows very high catalytic activity, 16.6 kg PE/Cr mmol h, nearly the same value for the CrO_3/SiO_2 system in the polymerization of ethylene [196,197]. On the other hand, conventional Cr(acac)₃/MAO system gives rise to the formation of polyethylene with very large polydispersity, $M_w/M_n = 150$. The complex **99**/MAO system (M = Cr) also gives rise to the formation of polyethylene with wide molecular weight distribution $(M_w/M_n = 53.9 \text{ when } M_n \text{ is})$ 2050), while the corresponding vanadium complex produces polyethylene with rather narrow molecular weight distribution [197]. The catalytic activities of substituted cromocenes coupled with silica were explored at 70°C and the highest catalytic activity was observed using non-substituted cromocene system 101 (33.4 kg PE/Cr g h). Molecular weights of polymers can be controlled by the addition of hydrogen but no copolymerization occurred between ethylene and 1-olefins [198].



Fig. 46. Additions of living poly(MMA) end to the poly(isobutene) or poly(THF) units.

6. Group 8–10 metal initiated polymerization

The noteworthy topic in this area is the living radical polymerizations of styrene or methyl methacrylate catalyzed by iron, ruthenium, copper or nickel/haloalkanes, haloketones, or haloesters systems to generate the polymers with very low polydispersities. For example, Matyjaszewski et al. reported that the CuCl(I)/CH₃CHPhCl/2,2'-bipyridyl **105** system (Fig. 45) conducts the living polymerization of styrene in the bulk conditions at 130°C to give the polymers with low polydispersity ($M_w/M_n = 1.3$) [199,200]. The catalytic system changes from the heterogeneous to the homogenous system by using 4,4'-diheptyl-2,2'-bipyridine/CuCBr(I)/CH₃CHPhCBr in place of chloro derivatives and resulted in the polymer with more low polydispersity ($M_w/M_n = 1.1$). [201]. The styrene/MMA random copolymer is available using CuCl/4,4'-di(5-nonyl)-2,2'-bipyridyl/C₆H₅Cl as catalyst and the copolymer of $M_n =$ 6000 ($M_w/M_n = 1.10$) was obtained in high yield [202]. Addition of a little amount of Cu(0) species demonstrated in the increase of the rate of polymerization more than 10 times higher [203]. Since the present system involves the halogen atom transfer from and to the polymer end, the generic name of this system is called as the atom transfer radical polymerization (ATRP). The use of CuCl₂ of high oxidation state is also effective when this type of species matches with the conventional radical initiator, AIBN(azobisisobutyronitrile), i.e. the AIBN/CuCl₂/2,2'-bipyridyl system gave polystyrene with narrow molecular weight distributions ($M_n = 23, 300, M_w/M_n = 1.30$) [204]. The FeBr₂/1-phenylethylbromide/PBu₃ (1:1:3) system generates polystyrene of $M_n = 9600$ ($M_w/M_n = 1.13$). RuCl₂(PPh₃)₃**102**/CCl₄ or CHCl₂COPh/AlOiPr₃ system also gave poly(methyl methacrylate) of $M_n = 120,000 \ (M_w/M_n = 1.29)$ [205]. The addition of water or methanol did not affect the rate of polymerization, while the addition of radical scavenger, TEMPO, stops the polymerization. The ABA triblock copolymerization of MMA/ butyl methacrylate/MMA was also possible using the RuCl2(PPh3)3/CCl4/Al(OiPr)3 system leading to polymers of $M_w/M_n = 1.29$ ($M_n = 7000$) [206]. The use of ruthenium hydride **103** in place of ruthenium



Fig. 47. Synthesis of ruthenium alkylidene 115.



Fig. 48. Preparations of hydrophobic and hydrophilic polymers using Ru-carbene complexes.

chloride resulted in the polystyrene with much lower polydispersity $(M_w/M_n = 1.1)$ even at 30°C [207]. The complex **104** is also useful [208].

Nickel complexes such as **106**–**109** coupled with bromoalkanes also exhibit good activities toward the polymerization of alkyl methacrylates and alkyl acrylates. The living radical polymerizations of alkyl methacrylates and alkyl acrylates were realized using the NiBr₂(PBu₃)₂/CCl₃Br **107** system in the presence or absence of Al(OiPr)₃. For example, this system gave poly(methyl methacrylate)(MMA) in quantitative yield to give the polymer with $M_n = 13,400 \ (M_w/M_n = 1.20)$ in the presence of Al(OiPr)₃, while the polymer obtained by NiBr₂(PPh₃)₂ **106**/CCl₃Br/Al(OiPr)₃ exhibits $M_w/M_n = 1.36$ when M_n is 10,800 (90% conversion). Although the use of Al(OiPr)₃ is a requisite in the case of NiBr₂(PPh₃)₂/CCl₃Br/Al(OiPr)₃ system for the production of narrow molecular weight distribution of poly(MMA), the NiBr₂(PBu₃)₂/CCl₃Br system does not require the presence of Al(OiPr)₃. [209–212]. A diamine complex **109** coupled with CCl₄ induced the living polymerization of MMA [213]. The activity of the iron complex **110** is higher than that of the corresponding ruthenium complex in the absence of aluminum compounds [214]. 4,4'-Bis(5-nonyl)-2,2'-bipyridine/FeBr₂/2-bromopropionitrile system



Fig. 49. Ru catalysts useful for polymerizations of olefins.



Fig. 50. Metal complexes with nitrogen containing ligands.

(1:1:1) is useful for the living radical polymerization of methyl methacrylate to give $M_w/M_n = 1.25$ ($M_n = 12,800$). However, stereoregularity is very poor since these systems proceed via a radical polymerization mechanism [215,216]. The rhodium complex **111** and the palladium complex **112** are also active for the polymerizations of MMA and styrene, but gave rather wide molecular weight distributions ($M_w/M_n > 1.5$) [217–219]. Rhenium complex **113** (Fig. 46) produced the living polystyrene in the presence of iodide [220]. These catalyst systems are effective also for the polymerizations of acrylonitrile, acrylamide, and norbornene derivatives, but ineffective for the polymerization of butadiene, vinyl chloride and vinyl acetate. As an extension of this research, the AB or ABA type block copolymerizations became possible. For example, the living radical polymerizations of MMA to the cationic polymer end of poly(THF) or poly(isobutene) using CuX(I) initiator was obtained [221–223] (Fig. 46).

A wide variety of Group 8 complexes such as RuCl₃ and Ru(II)(H₂O)₆(tos)₂ (tos = *p*-toluenesulfonate) demonstrate high catalytic activity for the polymerizations of norbornene and oxanorbornene in protic media such as water and methanol [224–226]. Ruthenium vinylalkylidene complex **114** of the type RuCl₂(=CHCH=CPh₂)(PR₃)₂ was synthesized by the reaction of cyclopropene with RuCl₂(PPh₃)₃ (Fig. 47). This complex catalyzes the polymerization of norbornene leading to the polymer of *trans* structure (>90%) even in the presence of water and methanol [227,228]. The use of cationic emulsifier is especially effective in order to obtain the polymer in high yield. When the reaction of *cis*-2-pentene was performed, catalytic metathesis reaction occurred in high activity. The turnover number is 103 equiv./h [229]. More reactive novel penta-coordinate ruthenium alkylidene complex **115** could be synthesized by the reaction of RuCl₂(PPh₃)₃ with diazoalkanes at low temperature. This complex is soluble and stable in water. *exo*, *exo*-5,6-Bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene and 7-oxanorbornene derivative could be polymerized in water using the complex **116** or **117** (Figs. 48 and 49). Thus, we could synthesize both hydrophilic and hydrophobic polymers, whose molecular weight distributions are very narrow, 1.1–1.3 [230–232]. Norbornene can also be polymerized in a moderate activity using the complex **118** leading to poly(norbornene) with high *trans* structure, 80–85% [233]. Analogous

Fig. 51. Metal-diimine complexes for polymerizations of olefins.



Fig. 52. Brookhart type polymerization.

complex RuCl₂(*p*-cymene)(PPh₃) **119** (Fig. 49) can initiate the ring-opening polymerization of cyclooctene in high yield, 90–100%. Resulting polymer exhibits $M_n = 113,400 M_w/M_n = 1.73$ with high *trans* structure [234]. Sandwich complex [(C₆H₆)₂Ru](tos)₂ is also active for the polymerization of norbornene. However, the resulting polydispersity is rather wide (3.2–3.5) although the molecular weight of polymer is sufficiently high $M_n = 638,000$ and the polymer assumes 90% *trans* structure [235]. The complexes **120** and **121** showed high catalytic activity for ROMP of norbornene $M_n = 1.5 \times 10^6$), but the resulting polymers again assume rather high polydispersity, 2.2–2.5 [236].

Brookhart et al. reported the synthesis of polyethylene ($M_w = 26,000-31,000$) using the complex **122**/MMAO (Fig. 50) in a 1:300 molar ratio [MMAO = modified MAO, (AlMe-O-)_m/ (AliBu-O-)_n = 3:1] in high activity (turnover frequency 4–11 × 10⁶/h, 3.3×10^5 kg PE/Fe mol h) when the pressure of ethylene is 400 Psi g and the R¹ and R² substitution are ispropyl group, while the corresponding Co complex **123**/MMAO shows much smaller catalytic activity (turnover frequency 0.36–0.40 × 10⁶/h)) and produces smaller molecular weights ($M_w = 8900-11, 300$). When the **122**/ MMAO system was used, M_n decreased significantly by the addition of MMAO in a ratio of 1:1500 or 1:4500. In these cases, the molecular weights of resulting polymers become 709 and 390, respectively. The exchange of substitutions of R¹ and R² with *t*Bu or Me group did not effect so much on the molecular weight of polymers, molecular weight distributions, and the activity [237–239]. The polymerization of propylene has been tested using **123**/MAO (1:100) and was found to produce the isotactic rich oligo-propylene *mm* = 66–69%) involving 2,1 insertion [240]. Radical polymerizations of methyl acrylate to give very low polydispersity were realized using tetramesityl(porphynato)cobalt neopentyl complex **124** in benzene at 60°C. The resulting M_w/M_n is 1.21 when M_n reached 170,000, but the stereoregularity was very poor [241].



Fig. 53. Reaction mechanism for formation of ethylene/acrylic ester copolymer.



Fig. 54. Plots of M_n and M_w/M_n as a function of reaction time for polymerization of propylene at -10° C using **125b**/MAO system.

Brookhart et al. also found the random copolymerization ability between ethylene and an acrylate using diimide complexes **125** and **126** coupled with MAO or B(C₆F₅)₃ (Fig. 51) [242]. Random copolymerizations proceed successfully reflecting the small oxophilicity of these metals. In this type of polymerizations, acrylic esters such as methyl acrylate, *t*-butyl acrylate and CH₂=CHC-(O)OCH₂(CF₂)₆CF₃ always locate at the terminal end of the resulting side chain. The complex ¹³C NMR spectrum indicates extensive branching along the main chain, with branches randomly distributed and of variable length. For example, the initiator **125** yields polyethylene with 103 branches/1000 carbon atoms (Fig. 52). The resulting M_n reaches 88×10^3 with $M_w/M_n = 1.6-1.8$. The catalytic activity (turnover frequency) is 7000–8000/h. Low temperature NMR studies provide insight into the copolymerization mechanism. The reaction of ether adduct **125** with MA at -80° C produces *p*-acrylate complex, which undergoes the 2,1-migratory insertion with 95% regioselectivity to yield the four membered chelate. At -80 to -60° C, the four membered chelate isomerizes to the five-membered chelate, which arranges to the six-membered chelate at -20° C (Figs. 53 and 54). Further chain growth requires



Fig. 55. Transition metal complexes for polymerizations of olefins.



Fig. 56. Ni complexes for oligomerization of ethylene.

the coordination followed by the insertion of ethylene. Thus, the acrylate unit locates at the end of the side chain. When a nickel complex **126b** was used with MAO (Al/Ni = 10:1) in toluene at 25°C for polymerization of ethylene, we could obtain the polyethylene with $M_n = 65 \times 10^4$ and $M_w/M_n = 2.4$, whose T_m is 112°C [243]. 1-Olefins such as propylene, 1-hexene, and 1-octene undergo controlled polymerizations at -10° C to afford $M_{\rm p}$ of 90,000–190,000 with low polydispersities ($M_{\rm w}/M_{\rm p}$ = 1.13-1.20) in high activities (turnover number 2500-2800). The block copolymerization of 1-octene/ propylene/1-octene is also possible using the 126b/MAO system to lead to the copolymer of $M_n =$ $163-253 \times 10^3$ with $M_w/M_p = 1.09-1.13$ [244]. When the substitution took place at p-position instead of o-position of aromatic group, only the production of oligo-ethylene occurs to give $(CH_2CH_2)_n$, where n = 7-23. The use of the complex 128 resulted in rapid chain transfer preferentially, relative to the chain propagation [245]. Souza et al. reported the moderate activity (3×10^5 PE/Ni mol h) for polymerization of ethylene using 129/AlEt₂Cl (Al/Ni = 100 mol/mol). The maximum activity was observed at 20°C and the ¹³C NMR spectrum revealed the extensive branching along the main chain. The $T_{\rm m}$ of the polymer reaches to 125° C when the polymerization temperature was as low as -20° C. However, the T_m significantly decreased when the reaction temperature was raised to 30°C [246]. Hyperbranched oligoethylene could be obtained using the nickel complex 130 or the palladium complex **131** combined with AlCl₃ and 1,3-bis(diphenylphosphino)propane in CHCl₃ or C_6H_5Cl . The resulting



Fig. 57. 2, ω-coupling polymerization of 1-olefins.



Fig. 58. Ni or Pd catalysts for polymerizations of olefins.

 $M_{\rm w}$ is 800-1100 with $M_{\rm w}/M_{\rm n} = 1.1-1.2$ and the turnover frequency reached 10,000/h. The ratio of methyl hydrogens/total aliphatic hydrogens of the resulting polymer increased from 0.43 to 0.58. Thus the polymers are highly branched with no discernible backbone. The branching is thought to arise from β-hydrogen abstraction followed by re-addition of the resulting coordinated vinyl-ended polymer to the metal-hydride [247]. The complex 132/MAO system is active for the polymerization of ethylene, styrene and butadiene. The use of excess amount of MAO resulted in the formation of high molecular weight polyethylene (Al/Ni = 8000 mol/mol) in rather high activity (200–300 g PE/Ni mol h). The M_n is 143– 550×10^3 and the M_w/M_n is 2.2. The Cp₂Ni/MAO system is also active for polymerization of butadiene affording the *cis*-1,4-structure, and is active for the polymerization of styrene leading to isotactic rich polymer [248]. The cobalt complexes 133 and 134 (Fig. 55) exhibit the living polymerization ability towards norbornene when these initiators were used with MAO simultaneously. The catalytic activity is 2500-3100 g Polynorbornene/Co mol h and the resulting molecular weight is very high $(131-147 \times 10^{-3})$ 10⁴) with narrow molecular weight distributions ($M_w/M_n = 1.8-1.9$). The polymer contains no olefinic unsaturation. The turnover number gradually decreased with the elapse of reaction time [249]. Various α -keto ylides reacted with (COD)₂Ni to show high polymerization activity towards the oligomerization of ethylene. The product formed by the reaction of Ph₃P=CH-COPh with (COD)₂Ni in the presence of PPh₃ may assume the structure **135** (5-membered ring). The complexes **135** and **136** (Fig. 56) are the precursor complex leading to an active nickel hydride species liberating Ph–CH=CH₂ or COD. The resulting molecular weight of the oligoethylene is 400–600 ($M_w/M_n = 2-3$) [250–252]. The ring size is very important and the use of $Ph_2P(CH_{2)2}COOH$ as a ligand resulted in the formation of 1-butene exclusively and the use of Ph₂P(CH₂)₃COOH shows no activities. Fink et al. discovered the novel type of $2,\omega$ -coupling polymerization of 1-olefins using Ni(COD)₂/bis(trimethylsilyl)aminobis(trimethylsilylamino)phosphorane **137** (Fig. 57), in place of the conventional 1,2-addition polymerizations. They propose the migration of the nickel catalyst via β -hydride-elimination/addition reaction as shown above [253,254]. Ziegler–Natta catalyst systems such as TiCl₄/I₂/AliBu₃, Co(O2CR)₂/H₂O/AlEt₂Cl, $Ni(O_2CR)_2/BF_3 \cdot Et_2O/AlEt_3$ exhibit high catalytic activity towards the *cis*-1,4-polymerizations of butadiene. More recently, allylnickel (II) complexes such as [C3H5NiCl]2 and cationic complexes such as [C₃H₅NiCl]PF₆ were found to show high catalytic activity towards the cis-1,4-polymerization of butadiene. By the use of $[C_3H_5NiCl]_2$ we could obtain *cis*-1,4-polybutadiene in 92% selectivity, while the use



Fig. 59. Polymerization of 3,3-dialkylcyclopentene.

of $[C_3H_5NiI]_2$ resulted in the formation of *trans* 1,4-polybutadiene in 95% selectivity [255]. The complex $\{C_3H_5Ni[P(OPh)_3]_2\}PF_6$ again produces *trans* 1,4-polybutadiene in 96% selectivity but $[C_3H_5Ni(COD)]PF_6$ generates the *cis*-1,4-butadiene exclusively. More recently, Taube et al. reported the formation of *trans* or *cis*-1,4-polybutadiene by using organo-lanthanide complexes. For example, $Li[C_5H_5Ln(C_3H_5)_3]$ produces *trans* polybutadiene. On the other hand, $Li[Nd(C_3H_5)_4]$ in the presence of Et_2AICI or MAO produced the *cis* polybutadiene in 89–93% selectivities. *cis*-1,4-Polybutadiene was obtained by using $La(C_3H_5)_2I$ or $La(C_3H_5)_2Pr$ [256,257].

The palladium complex 138/MAO (Fig. 58) accomplished the similar reaction of norbornene generating high molecular weight polymers without ring opening in high conversion. The copolymerization of norbornene with 5-norbornene-2-carboxylic acid methyl ester using complex 139 gives rise to the formation of high molecular weight polymers ($M_n = 12 \times 10^4$, $M_w/M_n = 2.2-2.4$) in the ratios of 86:14-79:21. From an industrial point of view, this system can produce 140t of poly(norbornene) per mol palladium per hour and the residual palladium content in the polymer is less than 10 ppm [258]. The copolymerization of styrene with norbornene takes place in a short time (15 min/h) using 140/MAO (Al/ Ni = 150-200 mol/mol to give vinylic polymers without ring opening. Even when feeding ratio of styrene is 23%, the ratio of incorporated styrene is only 1.5%. The monomer reactivity ratio of styrene (r_{styrene}) is 0.02, and that of norbornene $(r_{\text{norbornene}})$ is 20.8. Thus, norbornene exhibits much higher reactivity [259]. Grubbs et al. reported the polymerization of ethylene using nickel complex 141 together with Ni(COD)₂ as cocatalyst. The resulting molecular weight is 242,000 ($M_w/M_n = 2.1$) and the degree of branching is $5-22/1000^{\circ}$ C. The branching and the molecular weight can be controlled by the substitution of bulky ligands at position 3 of salicylaldiminao ring. The catalytic activity increases when the 5position was substituted with an electron withdrawing group [260]. Palladium and nickel complexes like Pd(Cp)(p-allyl) or NiEt₂(2,2'-bipyridyl) show high activity toward the polymerization of MMA. Pd(Cp)(p-allyl) produces the polymer in 92% conversion to afford $M_n = 170 \times 10^4$ with $M_w/M_n =$ 1.2 (70% syndiotacticity). The resulting polymer exhibits 70% syndiotacticity when the polymerization



Fig. 60. Ethylene/CO alternative copolymerization and its mechanism.



Fig. 61. Pd initiators useful for copolymerizations of CO with olefins.

was carried out at 25°C [261]. Similarly NiEt₂(2,2'-bipyridyl) conducted the polymerization of MMA at 25°C. In this case, M_n is $32 \times 10^4 (M_w/M_n = 1.74)$, syndiotacticity 68%, conversion 65%) [262]. In order to elucidate the polymerization mechanism, we have performed the copolymerization of styrene with MMA in a 1:1 ratio using these complexes. If these polymerizations proceed via a radical polymerization mechanism, the composition of resulting polymer should be ca. 50% of MMA and ca. 50% of styrene. As a consequence, the resulting polymer is composed of only poly(MMA). Therefore, we can conclude that this type of polymerization proceeds in an anionic polymerization mechanism.

Palladium cationic complexes **142** and **143** (Fig. 59) proceed the vinylic polymerization of 3,3dialkylcyclopentene into high yields. The reaction takes place without ring opening. The structure of the resulting polymer is 1,2-*cis* with *meso* configuration. Thus, the palladium complexes generally proceed the polymerization of cyclic olefins without ring opening [263].

Palladium initiated polymerization of ethylene with CO provides the alternate copolymer of these monomers (polyketone). The maximum activity (6000 g polymer/Pd mol h) and the maximum molecular weight ($M_w = 6000$) were observed when bis(phenyl)phophinopropane was used as a ligand 144.



Fig. 62. Styrene/CO alternative copolymerization.



Fig. 63. Alternate polymers between CO and allene or 1,5-hexadiene.



Fig. 64. Coupling reaction to induce the polymers.

The use of phosphinoethane and phosphinobutane resulted in the significant decrease of both activity and molecular weight. We can select various type of anions as X, i.e. $PhSO_3-$, CF_3SO_3- , CF_3COO- , BF_4- , and BAr_4- [264,265]. These types of polymers serve as engineering thermoplastics with high crystallinity, high mechanical properties and high chemical resistivity. The insertion between alkyl-M bond is favored by CO than olefins, and insertion between the M-acyl group is favored by olefins (Fig. 60). The double carbonylation or the double insertion of ethylene was strictly inhibited. Alternative copolymerization of propylene with CO was first realized by Consiglio using a chiral Pd complex **145** (Fig. 61) with dialkylaryl ligand [266]. The resulting polymer exhibits molecular weight of 3400 and activity of 5.6 g polymer/Pd mol h. In 1995, Sen et al. reported the synthesis of alternate copolymer between propylene and CO using **146**. In this case, the isotacticity increased to > 90% and the molecular

> a) Dehydrohalogenation $MCl_{2} + HC \equiv C-C \equiv C-M-C \equiv C-C \equiv CH \xrightarrow{CuX}_{R_{3}N} + -M-C \equiv C-C \equiv G-_{n}$ $M = trans-Pt(PR_{3})_{2}, trans-Pd(PR_{3})_{2}, Ni(PR_{3})_{2}$ b)Oxidative coupling $HC \equiv C-Y-C \equiv C-M-C \equiv C-Y-C \equiv CH \xrightarrow{CuCI/O_{2}}_{TMEDA} + -M-C \equiv C-Y-C \equiv C-Y-C \equiv G-_{n}$ $Y = -\bigcirc -, -\bigcirc -\bigcirc -\bigcirc$ c) Tin acetylides $MCl_{2} + Me_{3}SnC \equiv C-Y-C \equiv CSnMe_{3} \xrightarrow{CuX} + -M-C \equiv C-Y-C \equiv C-_{n}$

Fig. 65. Reaction routes for formation of metal-poly-yne polymers.



Fig. 66. Ethylene polymerization with organoaluminum compounds.

weight reached to 360,000 ($M_w/M_n = 2.4$) [267]. Furthermore, the polymer is composed by only tail-tohead structure (Fig. 62). Takaya et al. reported highly efficient catalysis of **147** composed of phosphine and phosphate ligands. This initiator gives rise to the formation of highly isotactic (99%) polymer with $M_w = 10,400$ and $M_w/M_n = 1.6$ [268]. Asymmetric copolymerization of styrene with CO was also realized using 2,2'-bipyridyl complex of Pd **148** to give syndiotactic alternate copolymers [269], while the use of the chiral bis(oxazoline) complex **149** allows us to obtain the isotactic copolymer [270]. Alternative copolymerization of an allene, 1,1-dimethyl-1,2-propadiene, with CO has also been realized using [Pd(PPh_3)_2(MeCN)_2](BF_4)_2 [271] (Fig. 63). On the other hand, arylallene has been copolymerized with CO using Rh(L)(PPh_3)_2 [272]. High activity of Rh complex is particularly interesting from the view point of industrial production. 1,4-Pentadiene also copolymerizes with CO to give the polymer containing cyclopentanone ring. However, the resulting molecular weight is rather small ($M_w =$ 2400, $M_w/M_n = 1.23$) [273]. The *cis/trans* ratio of the copolymer is ca. 1:1. Similar reaction was also observed in the copolymerization of 1,5-hexadiene with CO [274].

Nickel-phosphine complexes are known to be useful as reagents for cross-coupling reactions of alkylhalide (Figs. 64–66) [275]. By taking advantage of this utility, Yamamoto et al. synthesized poly(phenylene) and poly(thiophenediyl) using NiCl₂(PR₃)₂. The resulting polymers are useful as electro-conducting polymers after doping with iodine or Na [276–278]. Similar coupling reaction between 2,5-dibromothiophene and 1,2-distanylethylene produces poly(thienylenevinylene) in high yield (Fig. 64). This polymer is useful as a new material which shows strong electrochromism after doping [279]. Poly(arylenevinylene) could be prepared by the elimination of hydrogen chloride with Pt(acac)₂/PPh₃ (Heck reaction) [280]. Poly(pyridinediyl) and poly(arylene) could be prepared by using similar reaction [281].



Fig. 67. Isobutene polymerization using aluminum compound.

Organometallic polymers containing M–C(sp) σ -bonds (Fig. 65) in the main chain could be prepared according to the procedures listed above. The first synthesis of metal-poly-yne polymers was reported by Hagihara et al. in 1977 [282]. The polymers consist of platinum atoms and butadiynediyl units, and were made by a novel method that uses a copper(I) catalyst and an amine for the condensation polymerization between platinum halides and terminal acetylenes (Method a) [283]. This method affords platinum-poly-yne polymers having a variety of polymer sequences with butadiene and diethynylbenzene bridging ligands [284]. Palladium and nickel-poly-yne polymers were also synthesized by the same method [285,286]. Although the conventional method for the preparation of σ -alkyl transition metal derivatives from the reaction of metal halides with alkynylating reagent such as alkali metal and magnesium acetylides did not give the polymeric product, but tin acetylides may be useful for the polymer synthesis (Method c) as developed by Khan et al. [287]. This method is especially useful for the preparation of nickel- and iron-poly-yne polymers because the tin acetylide method does not need an amine reagent, which reacts readily to decompose the phosphine complexes of nickel and iron halides prior to start the polymerization. A cobalt-poly-yne polymer was also made by the Method c. Platinum- and palladium-poly-yne polymers are isolated as air stable yellow solids that are fairly soluble in common organic solvents such as benzene, dichloromethane and tetrahydrofuran. The high solubility of the polymer is due to the presence of tri-butylphosphine ligands around the metal moieties, which cover the polymer main chain and prevent intermolecular interaction. Polymers of the type $[Pt(PBu_3)_2 - C \equiv C - C \equiv C]_n$ prepared by Method a have a molecular weight (M_w) of 105. The rod-like structure of the polymer reflecting straight acetylenic bonding have been confirmed by ³¹P-NMR(trans-configuration of square-planner Pt(II) atom) and by the solution properties (viscosity vs. solubility parameter or molecular weight) [194]. The physical properties of metal-poly-yne polymers are especially interesting because of their rod-like molecular structure and conjugated π -electron system along the main chain. Because of the rod-like molecular structure and high solubility of the group 10 metal-poly-yne polymers, nematic liquid crystals form in concentrated solution [288]. Interestingly, the liquid crystal shows strong response toward an applied magnetic field and aligns their main chain in a direction parallel or perpendicular to the field, depending on the molecular structure of poly-yne polymers [289].

7. Main group metal initiated polymerizations of ethylene

Recently, the ethylene polymerization can be realized using cationic aluminum species **150**, **151**, **152** and **153** (Fig. 66) by Jordan et al. The combination of an electrophilic cationic Al center and a potentially reactive Al–X bond should promote coordination and activation of a range of substrates. In fact, the complex **150** is active for the polymerization of ethylene in toluene at 60°C and the polyethylene bearing molecular weight $M_w = 176$, 100 ($M_w/M_n = 2.84$) was obtained. The activity of the initiator is rather low, 700 g PE/Al mol h atm. More active initiator **151** could be obtained by the addition of Ph₃C[B(C₆F₅)₄] to a neutral Al derivative. The activity increased to 3050 g PE/Al mol h atm ($M_w = 184,700, M_w/M_n = 2.23$) [290]. The use of aminotroponiminate ligand **152** did not improve the catalytic activity (2600 g PE/Al mol h atm.) and molecular weight ($M_n = 10,655, M_w/M_n = 2.4$), while dinuclear compound **153** showed only a little activity for polymerization of ethylene. In contrast to these, **152** or the neutral aluminum compounds show no catalytic activity for polymerization of MMA. Nevertheless, dinuclear compound exhibits rather high activity towards the polymerization of MMA. The yield is quantitative

and M_n is 22,800 ($M_w/M_n = 1.8$, syndiotacticity 88% at 23°C) [291]. Aluminocenium cation, [AlCp₂]⁺ (Fig. 67), which has been prepared from the reaction of AlCp₂Me with B(C₆F₅)₃ shows the high catalytic activity towards the polymerization of isobutene. Strong cationic property of the resulted complex is reflected in the polymerization [292]. The molecular weight is $M_w = 1800 \times 10^3$ and M_w/M_n is 2.0–3.0. As a consequence, the polymerization is believed to occur following the equation listed above.

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