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Accounts

Living Polymerizations of Polar and Nonpolar Monomers by the Catalysis of Organo Rare Earth Metal Complexes

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This review article deals with the rare earth metal initiated polymerization of polar and nonpolar monomers in living fashion ("living" means very active without termination and chain transfer reaction) to give monodisperse high molecular weight polymers at high conversion. A typical example is seen in the polymerization of methyl methacrylate with $[SmH(C_5Me_5)_2]_2$ or $[LnMe(C_5Me_5)_2(THF)]$ (Ln = Sm, Y, and Lu), giving high molecular weight syndiotactic polymers ($M_n > 500000$, syndiotacticity $> 95\%$) quantitatively at low temperature (−95 °C). The initiation mechanism was discussed on the basis of X-ray analysis of the 1 : 2 adduct (molar ratio) of $[SmH(C_5Me_5)_2]_2$ with MMA. Living polymerizations of alkyl acrylates (methyl acrylate, ethyl acrylate, and butyl acrylate) were also possible by the catalysis of $[LnMe(C_5Me_5)_2(THF)]$ (Ln = Sm, Y); i.e. poly(methyl acrylate) $M_n = 48\times10^3$, $M_w/M_n = 1.04$, poly(ethyl acrylate) $M_n = 55\times10^3$, $M_w/M_n = 1.04$, and poly(butyl acrylate) $M_n = 70\times10^3$, $M_w/M_n = 1.05$. By taking advantages of the living polymerization ability, we attempted ABA triblock copolymerization of MMA/butyl acrylate/MMA to obtain rubber-like elastic polymers. Lanthanum alkoxide(III) has good catalytic activity for the polymerization of alkyl isocyanates ($M_n > 10^6$, $M_w/M_n = 2.08$). Monodisperse polymerizations of lactones, lactide, and various oxiranes were also achieved by polymerization with rare earth metal complexes. C_1 symmetric bulky organolanthanide(III) complexes such as $\{SiMe_2[2(3),4\text{-}(SiMe)_2C_5H_2]_2LnCH(SiMe_3)_2\}$ (Ln = La, Sm, and Y) show high activity for linear polymerization of ethylene. Organolanthanide(II) complexes such as racemic $\{SiMe_2[2\text{-}SiMe_3\text{-}4\text{-}t\text{Bu-}C_5H_2]_2Sm(THF)\}$ as well as C_1 symmetric $\{SiMe_2[2(3),4\text{-}(SiMe_3)_2C_5H_2]_2Sm(THF)\}$ were also found to have high activity for the polymerization of ethylene. Thus, polyethylene of $M_n > 10^6$ ($M_w/M_n = 1.6$) was first obtained by using $\{SiMe_2[2(3),4\text{-}(SiMe_3)_2C_5H_2]_2Sm(THF)\}$. 1,4-Cis conjugated diene polymerization of 1,3-butadiene and isoprene became available by the efficient catalytic activity of $NdCl(C_5H_5)_2/AlR_3$ or $Nd(octanoate)_3/AlR_3$. The $Ln(naphthenate)_3/Al\textit{i}Bu_3$ system allows selective polymerization of acetylene in cis-fashion. Utilyzing the fact that rare earth metal initiated living polymerization proceeds for both polar and nonpolar monomers, researchers have attempted to block copolymerization of ethylene with MMA or lactones yielding polyethylene derivatives having high chemical reactivity.

In recent years it has been made clear that the rare earth metal initiated living polymerization of polar and nonpolar monomers allows synthesis of high molecular weight polymers with very narrow molecular weight distribution. The conditions required for ideal living polymerization may be the (1) number-average molecular weight $M_n > 100000$, (2) polydispersity index $M_w/M_n < 1.05$, (3) stereoregularity $> 95\%$, and (4) high conversion in a short period of time $> 95\%$. Even the famous living polystyrene system[1)] and the Group Transfer system[2)] do not simultaneously satisfy the conditions (1) and (2). Recently, to satisfy a long desire of many polymer chemists, all these four conditions were found to be met in the rare earth metal-initiated polymerization of methyl methacrylate (MMA). The success is mainly ascribed to the use of single crystalline rare earth metal complexes as initiator and that of a thoroughly dried monomer.

The synthesis of monodisperse high molecular weight syndiotactic poly(MMA) mentioned above required as low a polymerization temperature as −95 °C.[3)] We still must find ways to produce it at relatively high temperature and also to synthesize its isotactic counterpart. When the latter is made available, synthesis of stereo-complexes of poly(MMA) will become a target of considerable interest.

Alkyl acrylates were for the first time polymerized in living fashion with the aid of the unique catalytic action of rare earth metal complexes.[4)] Since these monomers have an acidic α-H, termination and chain transfer reactions occur so frequently that their polymerization generally does not proceed in living manner. The lowest polydispersity index reported so far is 1.06 for poly(t-butyl acrylate, $M_n = 21000$) obtained using the RLi/LiCl system,[5)] 1.1 for poly(methyl acrylate, $M_n = 20000$) obtained by catalysis of

$[Sm(C_5Me_5)_2(CH_2\overset{...}{-}CH\overset{...}{-}CHCH_2-)_2]$,[6] and 1.03 for poly(ethyl acrylate, $M_n = 3300$) obtained by catalysis of a Group Transfer agent.[7]

By taking advantages of the living nature of both poly(MMA) and poly(alkyl acrylate)s, ABA type tri-block copolymerization of MMA/butyl acrylate(BuA)/MMA was performed to obtain thermoplastic elasticity. In fact, the poly(MMA/BuA/MMA) (8 : 72 : 20) system obtained exhibited good elastic properties,[4] while the 20 : 47 : 33 and 6 : 91 : 3 systems did not. We still must find how syndiotactic or isotactic poly(alkyl acrylate) with relatively large M_n and relatively small M_w/M_n can be made.

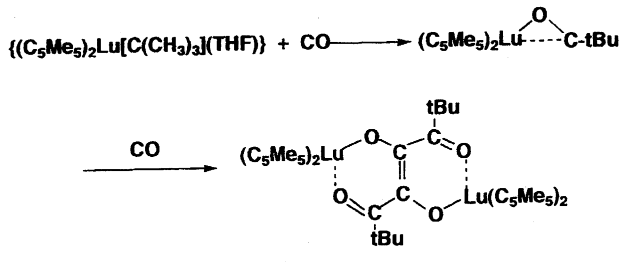
Living polymerization of lactones has been successfully performed by catalysis of rare earth metal complexes to get M_w/M_n values of 1.07—1.08.[8] Dielectric normal mode relaxation has been examined for this pure poly(lactone).[9] Cyclic carbonates such as trimethylene carbonate also undergo living polymerization.[10] However, it should be noted that their complete drying was necessary for the synthesis of high molecular weight polymers. More recently, polymerization of acrylonitrile and alkyl isocyanates has been made using $\{La[CH(SiMe_3)_2]_2(C_5Me_5)_2\}$, and also that of various oxiranes has been attempted using $Ln(acac)_3/AlR_3/H_2O$ system.[11] All these recent studies have made it clear that most polar monomers can be polymerized by using various organolanthanide catalysts. Rare earth metal initiators also show good activity towards non-polar monomers such as ethylene, 1-olefins, styrene, conjugated diene, and acetylene. In fact, poly(ethylene) of $M_n > 1000000$ with $M_w/M_n = 1.6$ was made available by the use of a C_1 symmetric complex, $\{Me_2Si[3,4\text{-}(SiMe_3)_2C_5H_2][2,4\text{-}(SiMe_3)_2C_5H_2]Sm(THF)_2\}$. This M_w/M_n value is the smallest ever obtained for poly(ethylene). The conventional $MgCl_2$-assisted Ziegler–Natta catalyst produced a polymer of $M_w/M_n = 4.0$, and the Kaminsky type catalyst a polymer of $M_w/M_n = 2.0$. However, the magnitudes of M_n for poly(olefin)s such as poly(1-pentene), poly(styrene), and poly(1,5-hexadiene) were not made high enough even with the help of the characteristic catalytic action of rare earth metal complexes. The maximum M_n of 60000 obtained was yet far below the desired minimum of 400000. Furthermore, synthesis of syndiotactic poly(1-olefin) is desirable because excellent physical properties are expected for it. Conjugated dienes and acetylene derivatives were polymerized by the use of rather complex rare earth metal catalysts, but the M_w/M_n obtained remained fairly large. This indicates that the polymerization is performed using multi-site catalytic species. The use of a mononuclear single-site catalyst is required for the polymerization of these derivatives.

General Remarks on Organolanthanides

Rare earth elements are the general term for 15 kinds of lanthanide elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Py, Ho, Er, Tm, Yb, and Lu) together with Sc and Y elements. They prefer tri-valent states in the complex formation, though four elements (Sm, Eu, Tm, and Yb) can assume tri- and divalent states, and three elements (Ce, Pr, and Tb) tri- and tetra-valent states. Their ionic radii are fairly large (1.0—1.17 Å) and their electronegativities are low (1.1—1.2). In fact, the former are much larger than those of main group metals (Li 0.73; Mg 0.71; Al 0.68 Å) and transition metals (Ti 0.75; Mo 0.75; Fe 0.75 Å), and the latter are similar to those of Li (1.0) and Mg (1.2) (Table 1). For these properties, the organometallic complexes of rare earth metals have strong basicity and therefore allow anionic polymerization to take place.

Rare earth metal complexes often form ate-complexes such as $R_2LnClNaCl(THF)_2$, but it was possible to obtain neutral complexes by using a bulky C_5Me_5 or a C_8H_8 ligand. Characteristic reactions were observed in their reaction with CO. For example, when it react with CO, $[Lu\textit{t}Bu(C_5H_5)_2(THF)_2]$ gives acyl complexes, which lead to a double insertion complex of CO by reaction with two equivalents of CO (Scheme 1).[12] The double insertion of the CO molecules into the C=C[13] or N=N double bond[14] was also observed for rare earth metal complexes.

Characteristic initiation behavior of rare earth metals was also found in the polymerization of polar and non-polar monomers. In spite of the accelerated development of living isotactic[15] and syndiotactic[16] polymerizations of MMA, the



Scheme 1.

Table 1. Ionic Radii and Electronegativities of Rare Earth Elements

Elements	Ionic radius (Å)	Electronegativities	Elements	Ionic radius (Å)	Electronegativities
Sc	0.89	1.1—1.2	Li	0.73	1.0
Y	1.04		Mg	0.71	1.2
La	1.17		Al	0.68	1.5
Sm	1.11		Ti	0.75	1.5
Eu	1.09		Mo	0.75	1.8
Yb	1.01		Fe	0.75	1.8
Lu	1.00		Pt	0.94	2.2

lowest polydispersity indices so far obtained remain in the region of $M_w/M_n = 1.08$ for M_n of only 21200. Thus, the synthesis of high molecular polymers ($M_n > 100 \times 10^3$) with $M_w/M_n < 1.05$ is still an important target in both polar and non-polar polymer chemistry. The availability of compositionally pure materials is a must for the accurate physical and chemical characterization of polymeric materials.

Highly Stereospecific Living Polymerization of Alkyl Methacrylates

As is evident from what has been mentioned above, it is very significant to find ways which synthesize highly syndiotactic or isotactic polymers with $M_n > 500000$ and $M_w/M_n < 1.05$. Although various living polymerization systems have been proposed for this purpose, anionic,[17] cationic,[18] Group Transfer,[2] and metal carbene initiated polymerizations[19] achieved no success. Therefore, it is remarkable that in recent years, high molecular weight poly(MMA) having an unusually low polydispersity has been synthesized by utilizing the unique initiating function of organolanthanide(III) complexes (Scheme 2, Fig. 1).[3] The relevant complexes include lanthanide hydrides, trialkylaluminum complexes of alkyllanthanides, and simple alkyl complexes synthesized from $LnCl(C_5Me_5)_2$ (Fig. 2). Most of them have been characterized by single X-ray analysis.[20] The results of the polymerization of MMA with the $[SmH(C_5Me_5)_2]_2$ initiator at different temperatures are summarized in Table 2. The most striking is $M_w/M_n = 1.02$—1.04, for $M_n > 60 \times 10^3$. Remarkably, the organolanthanide complexes give high conversion (polymer yield) in a relatively short period, and allow the polymerization to proceed over a wide range of reaction temperatures from −78 to 60 °C. Furthermore, syndiotacticity exceeding 95% is obtained when the polymerization temperature is lowered to −95 °C.

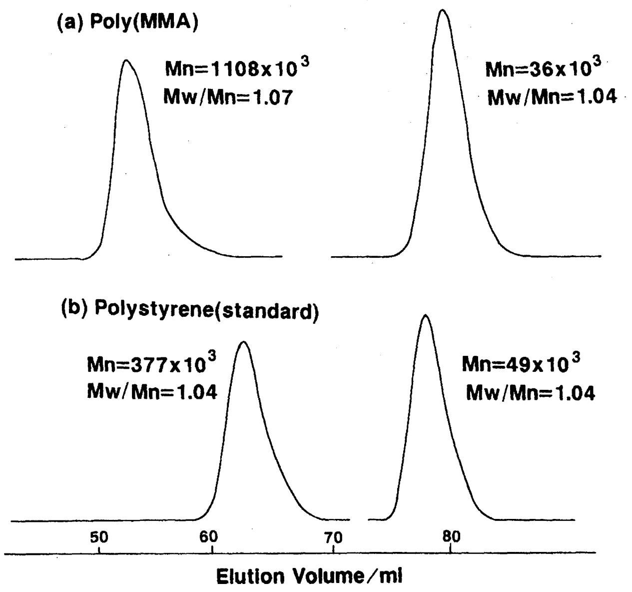


Fig. 1. GPC profiles of poly(MMA) and standard poly(styrene).

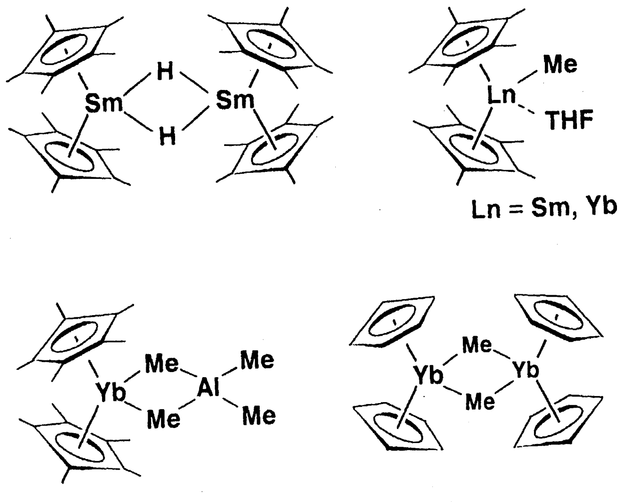
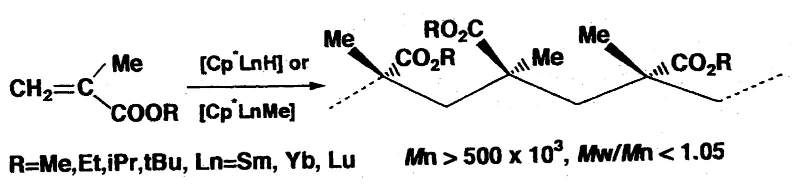


Fig. 2. Typical organolanthanide(III) initiators.

These findings show that ideal living polymerization is made possible when $[SmH(C_5Me_5)_2]_2$ or $[LnMe(C_5Me_5)_2]$ (Ln = Y, Sm, Yb, and Lu) is used as the initiator. A polymerization process can be called as living if the following four criteria are obeyed. First, the number-average molecular weight of the resulting polymer should increase linearly in proportion to the conversion (polymer yield) irrespective of the initiator concentration, with M_w/M_n remaining in the 1.03—1.04 range during the reaction (Fig. 3). Second, log $[M]_0/[M]_t$ varies linearly with time, since no growing ends should be dead. Third, the maximum efficiency of the initiator should be greater than 95%; actually neither termination nor chain transfer should take place. Fourth, homogeneous polymerization proceeds very rapidly and completes within 30 min when 200 molar amounts of monomer are fed to the initiation system.

In general, syndiotacticity increases with lowering the polymerization temperature. In the case of $[SmH(C_5Me_5)_2]_2$, it increased from 78 to 95.2% as the polymerization temperature was changed from 25 to −95 °C, but the polydispersity index remained low.[3] Extrapolating the data suggests that syndiotacticity over 98% may be obtained at −115 °C. Polymerization of MMA in both THF and toluene using the organolanthanide initiators gave syndiotactic polymers, in contrast to the fact that the RMgX initiator in toluene led to isotactic polymers.[15]



Scheme 2.

Table 2. Characterization of Monodisperse Poly(MMA) Synthesized by $[SmH(C_5Me_5)_2]_2$ Initiator

Polymerization temperature (°C)	MMA/initiator charged (mol/mol)	$M_n \times 10^3$	M_w/M_n	$\frac{rr}{\%}$	Conversion/% (react. time)
40	500	55	1.03	77.3	99 (1 h)
0	500	58	1.02	82.4	99 (1 h)
0	1500	215	1.03	82.9	93 (2 h)
0	3000	563	1.04	82.3	98 (3 h)
−78	500	82	1.04	93.1	97 (18 h)
−95	1000	187	1.05	95.3	82 (60 h)

M_n and M_w/M_n were determined by GPC using standard poly(MMA) with M_w measured by light scattering. Solvent, toluene; solvent/$[M]_0 = 5$ (vol/vol).

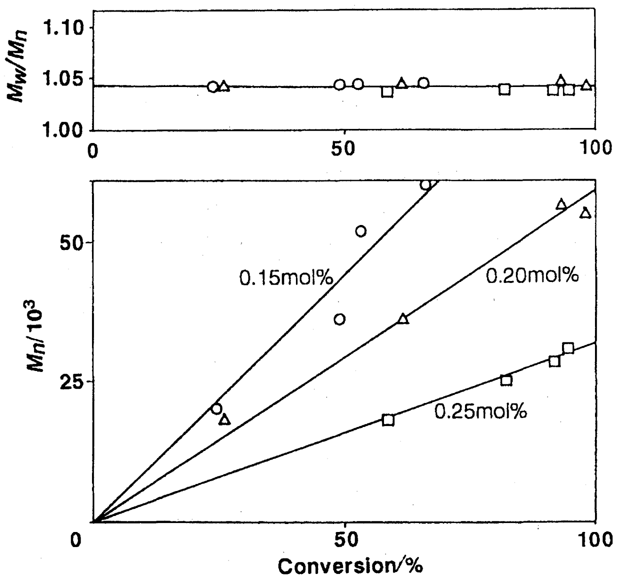


Fig. 3. M_w/M_n and M_n vs. conversion plots for poly(MMA) obtained using $[SmH(C_5Me_5)_2]_2$.

The typical initiator systems reported so far for the synthesis of highly syndiotactic poly(MMA) are bulky alkyllithium $CH_3(CH_2)_4CPh_2Li$,[21] Grignard reagent in THF,[22] and some AlR_3 complexes.[23] Although the first initiator in THF reacted rapidly with MMA at −78 °C, the M_n reached only 10000 with $M_w/M_n = 1.18$, while it gave isotactic polymers in toluene. Isobutylmagnesium bromide and 4-vinylbenzylmagnesium bromide in THF at lower temperature also gave high syndiotacticity, but M_n remained as low as 14000—18000 and the yields were quite low. When *i*BuMgBr or *t*BuMgBr was used in toluene instead of THF, the resulting poly(MMA) had a high isotacticity of 96.7% with $M_n = 19900$ and $M_w/M_n = 1.08$.[24] $AlEt_3 \cdot PR_3$ complexes gave high syndiotacticity, but not a high molecular weight.[23]

Ketene silyl acetal/nucleophilic agent systems initiate the polymerization of alkyl methacrylates. These well-known Group Transfer systems yielded living polymers with atactic sequences at relatively high temperature.[2] $Me_2C{=}C(OMe)OSiR_3$ and $R_2POSiMe_3$ can be used as initiators, and tris(dimethylamino)sulfonium bifluoride and Et_4CN are frequently used as catalysts. For example, the M_w/M_n of the resulting poly(MMA) was 1.06 for $M_n = 3800$, and 1.15 for $M_n = 6300$. In the polymerization of butyl acrylate, the molecular weight obtained was only 4800 with M_w/M_n of 2.14. Thus, we conclude that organolanthanide-initiated polymerization is superior in obtaining monodisperse high molecular weight poly(MMA) and poly(alkyl acrylate). However, the Group Transfer systems have some advantages of synthesizing poly(acrylonitrile) and poly(*N*,*N*-dimethylacrylamide), which are difficult to produce with conventional organolanthanide initiators.

For the organolanthanide system which allows living polymerization of MMA, Yasuda et al.[3] studied the dependence of M_n on the initiator concentration (Fig. 4). When the reaction was conducted at 0 °C, M_n of 530×10^3 with $M_w/M_n = 1.04$ was obtained quantitatively at an initiator concentration of 0.005 mol%. This M_n value is the largest ever reported for living polymers. However, when the reaction temperature was lowered to −78 °C, M_w/M_n increased to 1.15, due presumably to the occurence of undesirable side reactions with water or oxygen contaminants in the monomer or solvent. In order to evaluate the living nature of the polymerization, 160 molar amounts of MMA were first polymerized and a polymer of $M_n = 15 \times 10^3$ was obtained at a quantitative yield. After 30—40 min, 160 molar amounts of MMA were again added to the system, which was then kept at 0 °C.

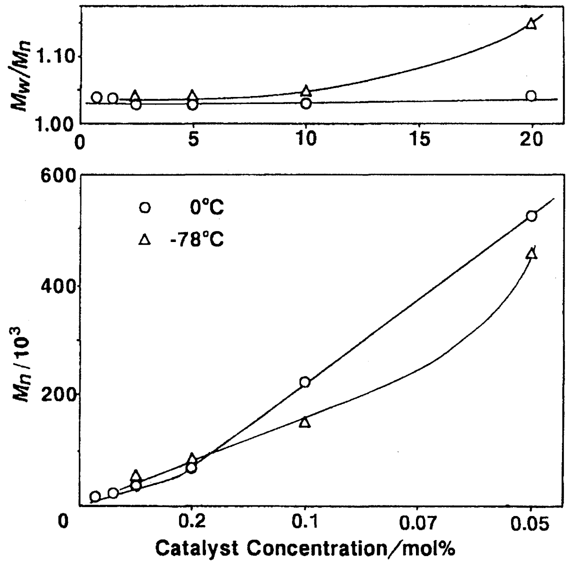
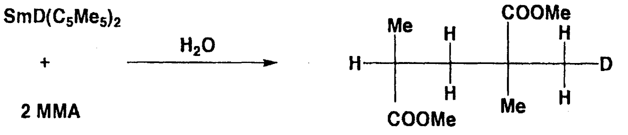


Fig. 4. M_n and M_w/M_n vs. catalyst concentration plots, initiator $[SmH(C_5Me_5)_2]_2$.

Living polymerization took place after 1 h and gave poly(MMA) of $M_n = 32\times10^3$ with $M_w/M_n = 1.03$ at 99% yield. The polymer produced after 10 h reaction had $M_n = 53\times10^3$ with $M_w/M_n = 1.03$, and the relative ratio of the GC peak was as high as 78%, indicating that only 22% of the growing ends were "dead" or dormant. Interestingly such a long life of growing ends has never been observed for other living polymeric systems. When the *t*BuMgBr or *i*BuMgBr-initiated polymerization was carried out at 0 °C, the resulting poly(MMA) showed broad polydispersity ($M_w/M_n > 2.5$). This implies the need of lower temperature for the living polymerization with the RMgX system.

These findings motivated Yasuda and co-workers[3] to isolate the 1 : 1 or 1 : 2 adduct of $[SmH(C_5Me_5)_2]_2$ with MMA in order to elucidate the initiation mechanism. They obtained the desired 1 : 2 adduct as an air-sensitive orange crystal (mp 132 °C). Upon deuterolysis it produced $DCMe(CO_2Me)CH_2CMe(CO_2Me)CH_3$ at an excellent yield (90%), suggesting that it contains either a Sm enolate or a Sm α-C bond (Scheme 3). The addition of 100 molar amounts of MMA to it yielded poly(MMA) of $M_n =$ ca.110×10^3 and $M_w/M_n = 1.03$. This result proves that the 1 : 2 adduct is a real active species. In this way, Yasuda et al. succeeded for the first time in isolating the intermediate; they were able to prove that the initiation process occurs much faster than the propagation process.

Yasuda et al.[3c] also determined the 8-membered structure of $[SmH(MMA)_2(C_5Me_5)_2]$ by single X-ray analysis ($R_w = 0.082$) (Fig. 5), finding that one of the MMA unit is linked to the metal in an enolate form and at the other end the penultimate MMA unit is coordinated to the metal through its C=O group. Although similar cyclic intermediates have been proposed by Bawn et al.[25] and Cram and Copecky[26] for the isotactic polymerization of MMA, no isolation of such active species has succeeded. It is expected that, in the initiation step, the hydride attacks the CH_2 group of MMA, and a transient $SmOC(OCH_3){=}C(CH_3)_2$ species should be formed. Then, the incoming MMA molecule is supposed to participate in the 1,4-addition to produce an 8-membered cyclic intermediate (Fig. 6). Further addition of MMA to the 1 : 2 addition compound liberates the coordinated ester group and the 8-membered cyclic intermediate is again generated. In order to confirm the above-mentioned initiation mechanism, Yasuda et al.[3c] allowed $[Y(OCH{=}CH_2)(C_5Me_5)]_2$ to react with excess MMA (100 molar amounts) and obtained poly(MMA) of $M_n = 10200$ and $M_w/M_n = 1.03$ at high yield. However, $[Y(OMe)(C_5Me_2)_2]_2$ and $[Sm(OEt)(C_5Me_5)_2(Et_2O)]$ were completely inert for the polymerization of MMA. Other related rare earth metal complexes such as $[YMe(C_5Me_5)_2(Et_2O)]$, $[YbMe(C_5Me_5)_2(THF)]$, $[YMe(C_5H_5)_2]_2$, $[SmMe_2AlMe_2(C_5Me_5)_2]$, $[SmMe(C_5Me_5)_2(THF)]$, and $[LuMe(C_5Me_5)_2(THF)]$ also showed comparably high initiating activity, and they all allowed living syndiotactic polymerization of MMA to give the polymers with $M_n = 65$—120×10^3 and $M_w/M_n = 1.03$—1.05. The efficiency of these initiators was higher than 90%. Lowering the reaction temperature to −78 °C led to the production of syndiotactic polymers with *rr* > 90% in all cases.



Scheme 3.

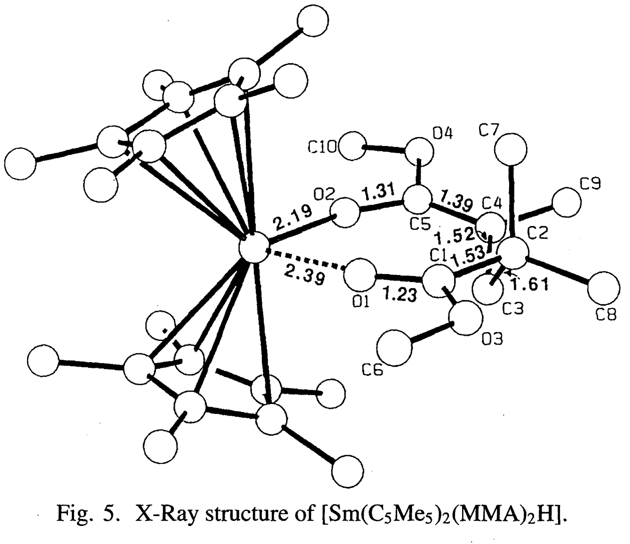


Fig. 5. X-Ray structure of $[Sm(C_5Me_5)_2(MMA)_2H]$.

The apparent rate of polymerization (the activity) increased with increasing ionic radius of the metal (Sm > Y > Yb > Lu) and decreased with increasing steric bulkiness of the auxiliary ligands ($C_5H_5 > C_5Me_5$).[3a] The former agrees with the order of ionic radii, Sm (1.11 Å) > Y (1.04 Å) > Yb (1.01 Å) > Lu (1.00 Å). More precisely, it conforms to the order of the Cp(centroid)–lanthanide bond length of $Ln(C_5Me_5)_2X$, i.e. Sm (2.72 Å) > Y (2.65 Å) > Yb (2.64 Å) > Lu (2.63 Å). This suggests that the use of $LaMe(C_5Me_5)_2$ (La = 1.17 Å) is preferable to obtain high molecular weight polymers in a short time.

On the basis of the X-ray structural data as well as the mode of polymerization, Yasuda et al.[3a] proposed a coordination anionic mechanism involving an 8-membered transition state for the organolanthanide initiated polymerization of MMA (Fig. 6). The steric control to the polymerization reaction may be ascribed to the intermolecular repulsion between C(7) and C(9) (or the polymer chain), since completely atactic polymerization occurred when the monomer was methyl or ethyl acrylate.

Recently, isotactic polymerization of MMA has also been achieved (*mm* = 94%, $M_n = 134\times10^3$, $M_w/M_n = 6.7$) by using $\{Me_2Si(C_5Me_4)[C_5H_3$-(1*S*),(2*S*),(5*R*)-neomenthyl]LaR$\}$ (R = $CH(SiMe_3)_2$ or $N(SiMe_3)_2$),[27] but $\{Me_2Si(C_5Me_4)$-$[C_5H_3$-(1*S*),(2*S*),(5*R*)-menthyl]LnR$\}$ (Ln = Lu, Sm; R = $CH(SiMe_3)_2$ or $N(SiMe_3)_2$ has been effective to produce a syndiotactic poly(MMA) (*rr* = 69%, $M_n = 177\times10^3$, $M_w/M_n = 15.7$) (Fig. 7). A possible explanation for this difference is that the menthyl complex produces a syndiotactic polymer via a cyclic 8-membered intermediate, while the neomenthyl complex produces an isotactic polymer via a nonlinear intermediate. To ascertain this idea, [*i*Pr(Cp)(2,7-*t*Bu$_2$-flu-

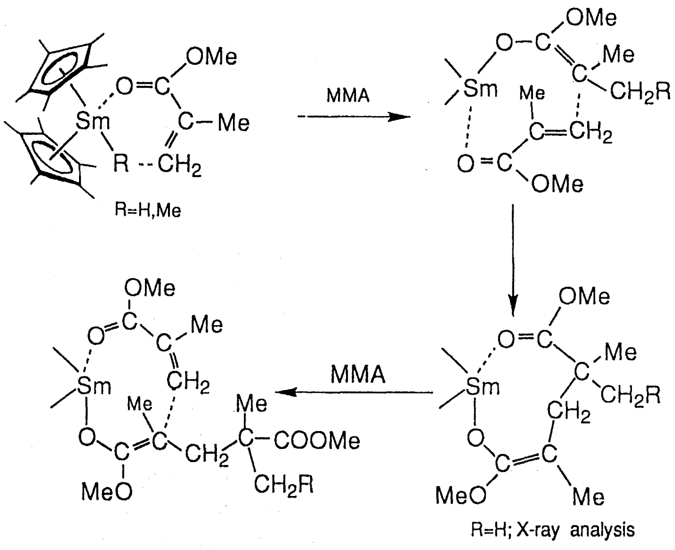


Fig. 6. Initiation mechanism for polymerization of MMA.

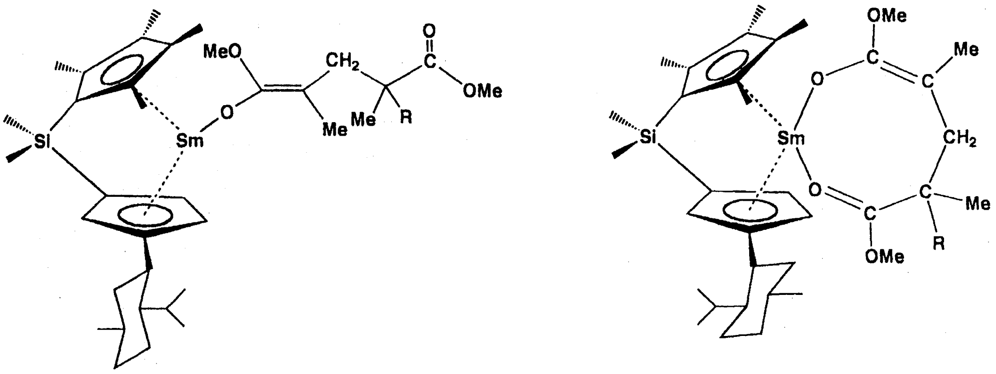


Fig. 7. Intermediates for isotactic and syndiotactic polymerization of MMA.

orenyl)YCH$(SiMe_3)_2$] was synthesized and used to perform isotactic polymerization of MMA.[28] The resulting polymer had 78—79% syndiotacticity, contrary to our expectation. Therefore, it was concluded that stereoregularity varies with subtle difference in steric bulkiness between the complexes. Actually, isotactic poly(MMA) ($mm = 97\%$, $M_n = 140000$) was obtained quantitatively when the nonmetallocene system, $[(Me_3Si)_3C]_2Yb$, was used.[29]

Boff and Novac[6] found a divalent rare earth metal complex, $[Sm(C_5Me_5)_2]$, to be a good catalyst for polymerization of MMA. The initiation started with the coupling of two coordinated MMA molecules to form Sm(III) species. The bisallyl initiator, $[Sm(\mu\text{-}\eta^3\text{-}CH_2\text{---}CH\text{---}CHCH_2)_2(C_5Me_5)_2]$, was also effective for living polymerization of MMA. In this case, MMA must add to both ends of the butadiene group. In the polymerization of MMA initiated with methyl(tetraphenylporphyrinato)aluminum, a sterically crowded Lewis acid such as methylaluminum(ortho-substituted phenolate) serves as a very effective accelerator without damaging the living character of polymerization. Thus, the polymer produced in a 3 s reaction has narrow polydispersity ($M_w/M_n = 1.09$) and sufficiently high molecular weight, $M_n = 25500$. However, ortho-nonsubstituted analogue and simple organoaluminum such as trimethylaluminum cause the occurrence of termination.[30]

The organolanthanide initiators allowed stereospecific polymerization of ethyl, isopropyl, and *t*-butyl methacrylates (Table 3). The rate of polymerization and the syndiotacticity decreased with increasing bulkiness of the alkyl group in the order Me > Et > *i*Pr ≫ *t*Bu. Butyl methacrylate was also polymerized using $Nd(octanoate)_3/Al\textit{i}Bu_3$ ($Al/Nd = 7$—10), but the molecular weight distribution and stereoregularity were not reported.[31]

In general, Ziegler–Natta catalysts such as $TiCl_4/MgCl_2/AlR_3$ and Kaminsky catalysts such as $Cp_2ZrCl_2/(AlMe_2\text{–O–})_n$ do not catalyze the polymerization of polar monomers. However, a mixture of cationic species $Cp_2ZrMe(THF)^+$ and Cp_2ZrMe_2 has been found to do so for MMA,[32] allowing syndiotactic poly(MMA) ($rr = 80\%$, $M_n = 120000$, $M_w/M_n = 1.2$—1.3) to be obtained. Recently, Soga et al.[33] reported the syndio rich polymerization of MMA catalyzed by $Cp_2ZrMe_2/B(C_6F_5)_3$ or $Ph_3CB(C_6F_5)_4/ZnEt_2$ and also the isotactic polymerization of MMA catalyzed by *rac*-Et$(ind)_2ZrMe_2/B(C_6F_5)_3/ZnEt_2$ (Scheme 4).

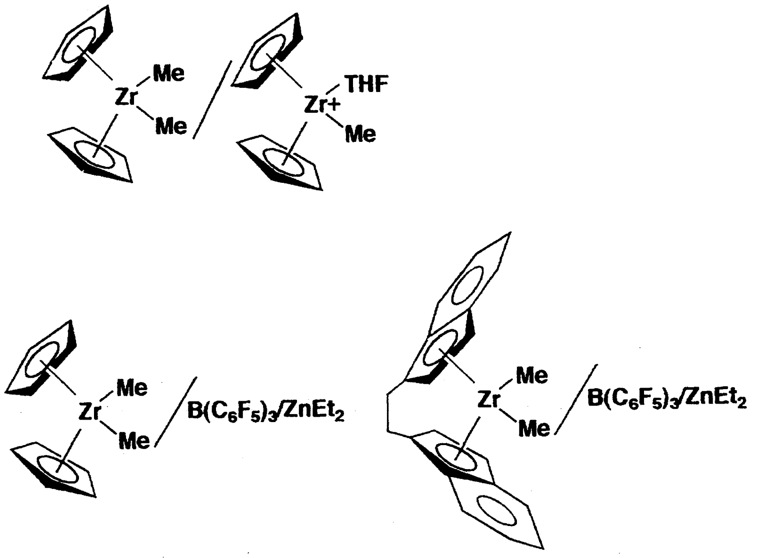
Living Polymerization of Alkyl Acylates

In general, living polymerization of alkyl acrylates is difficult because the chain transfer or termination occurs, owing

Table 3. Organolanthanide Initiated Polymerization of Alkyl Methacrylates

Initiator	Monomer	$M_n/10^3$	M_w/M_n	rr/%	Conversion/%
$[SmH(C_5Me_5)_2]_2$	MMA	57	1.03	82.4	98
	EtMA	80	1.03	80.9	98
	*i*PrMA	70	1.03	77.3	90
	*i*BuMA	63	1.42	77.5	30
$[LuMe(C_5Me_5)_2(THF)]$	MMA	61	1.03	83.7	98
	EtMA	55	1.03	81.0	64
	*i*PrMA	42	1.05	80.0	63
	*i*BuMA	52	1.53	79.5	20

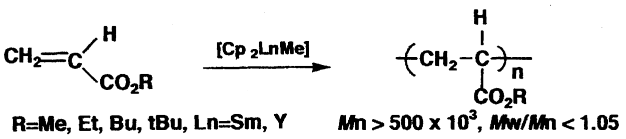
Polymerization conditions: 0 °C in toluene, initiator concentration 0.2 mol%.



Scheme 4.

to a high sensitivity of the acidic α-proton to the nucleophilic attack. Exceptions are the living polymerization of a bulky acrylic ester catalyzed by the bulky alkyllithium/inorganic salt (LiCl) system[5] as well as the Group Transfer polymerization of ethyl acrylate with ZnI_2 as the catalyst.[2] Porphyrinatoaluminum initiator systems also induced the living polymerization of *t*-butyl acrylate,[34] but the upper limit of molecular weight attained was ca. 20000.

Ihara et al.[35] found the efficient initiating properties of $[SmMe(C_5Me_5)_2(THF)]$ and $[YMe(C_5Me_5)_2(THF)]$ for living polymerization of acrylic esters, i.e. methyl acrylate (MeA), ethyl acrylate (EtA), butyl acrylate (BuA), and *t*-butyl acrylate (*t*BuA), although the reactions were non-stereospecific (Scheme 5, Table 4). The initiator efficiency exceeded 90% except for *t*BuA. Ihara et al.[35] therefore concluded that the reactions occur in living fashion. In fact, the M_n of poly(BuA) initiated by $[SmMe(C_5Me_5)_2(THF)]$ increased linearly in proportion to the conversion, while M_w/M_n remained unchanged, irrespective of the initiator concentration. The rate of polymerization increased with increasing bulkiness of alkyl acrylates in the order BuA > EtA > MeA, but the order was reversed in the case of methacrylic ester systems, MMA > EtMA (ethyl methacrylate) > BuMA (butyl methacrylate). For MeA, the polymerization completed in 300 s at 0 °C, and both M_n and conversion increased with the polymerization time. On the other hand, the polymerization completed in 5 s at 0 °C for EtA and BuA. In order to establish the characteristic nature of these initiation systems, the initiator concentration was decreased from 0.1 to 0.002 mol% and high molecular weight poly(EtA) of $M_n = 400000$ with narrow molecular weight distribution ($M_w/M_n = 1.05$) was obtained. In a similar manner, high molecular weight poly(BuA) and poly(MeA) were synthesized successfully.



Scheme 5.

Ihara et al.,[35] who measured the life time of the growing end, found that MeA (200 mmol) in toluene underwent living polymerization with $[SmMe(C_5Me_5)_2(THF)]$ (0.2 mol% of monomer). After completion of the polymerization (1 min), they added the same amount of MeA (200 mmol) to the polymerization system but observed no polymerization taking place. In contrast, the polymerization resumed after the system had been kept for 1 min in THF, which indicated that the growing ends were completely living. When this

Table 4. Polymerization of Alkyl Acrylates Initiated by Organolanthanide Complexes

Initiator	Monomer	$M_n/10^3$	M_w/M_n	Tacticity/%			Conversion	Initiator
				rr	mr	mm	%	Efficiency/%
[SmMe(C_5Me_5)$_2$(THF)]	MeA	48	1.04	30	50	20	99	89
	EtA	55	1.04	51		49	94	86
	*n*BuA	70	1.05	28	53	19	99	91
	*t*BuA	15	1.03	27	47	26	99	79
[YMe(C_5Me_5)$_2$(THF)]	MeA	50	1.07	33	51	16	99	86
	EtA	53	1.05	47		53	96	91
	*n*BuA	72	1.04	22	51	27	98	88
	*t*BuA	17	1.03	25	45	30	99	75

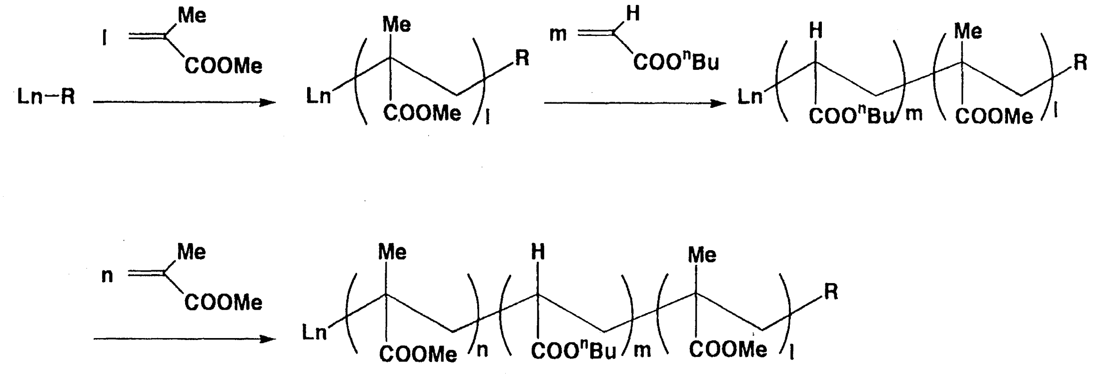
Polymerization conditions: 0 °C in toluene, initiator concentration 0.2 mol%.

polymerization system was held for a longer time, 10 min, at 0 °C, all the growing ends were dead. Thus, the final polymer formed had a rather broad molecular weight distribution.

To gain an insight into the initiation mechanism, Ihara et al.[35] examined the 1 : 2 reactions of [SmMe(C_5Me_5)$_2$(THF)] with methyl acrylate or *t*-butyl acrylate. Quenching of the reaction mixture of methyl acrylate and organolanthanide yielded $CH_3CH_2CH(CO_2Me)CH_2CH(CO_2Me)H$ at 65% yield. More efficient initiating properties were found when *t*-butyl acrylate was allowed to react with [SmMe(C_5Me_5)$_2$(THF)], yielding $CH_3CH_2CH(CO_2t\text{Bu})CH_2CH(CO_2t\text{Bu})H$ to 96% at 0 °C upon hydrolysis. Thus, the constitution of the acrylic ester dimer is essentially the same as that observed for the addition of MMA to [SmH(C_5Me_5)$_2$]$_2$. Therefore, the formation of an 8-membered intermediate is highly probable in this case too.

Ihara et al.[35] measured the tacticity at temperatures from −78 to 60 °C, but observed little change of it. This may be ascribed to the absence of steric repulsion between H(7) and H(9) atoms. The organolanthanide system was found to initiate the living copolymerization of methyl acrylate with ethyl or butyl acrylate and also that of ethyl acrylate with butyl acrylate. The monomer reactivity ratio determined by using the Fineman–Ross equation shows that the monomer reactivity ratio of methyl acrylate ($r_1 = 0.959$) is higher than that of ethyl acrylate ($r_2 = 0.597$), but similar to that of butyl acrylate (MeA $r_1 = 0.426$, BuA $r_2 = 0.578$). By contrast, the monomer reactivity ratios of alkyl acrylate ($r_2 = 19.9$—21.3) are higher than that of MMA ($r_1 = 0.008$—0.024). Although in free radical initiating system using AIBN, MMA exhibits a higher reactivity than methyl acrylate, i.e. r_1 (MMA) = 1.0, r_2 (MeA) = 0.5, the reverse was found in the case of $NaNH_2$-initiating system, r_1 (MMA) = 0.1, r_2 (MeA) = 4.5.[35c,35d] This implies that block copolymerization occurs preferentially at high conversion even when a mixture of alkyl acrylate and methyl methacrylate is used. In fact, in the random copolymerization of MMA with BuA (charged ratio 1 : 1), the BuA component in the resulting copolymer is higher than 88% (almost BuA component) when the conversion reaches 50%.

ABA type triblock copolymerization of MMA/BuA/MMA should give rubber-like elastic polymers. The resulting copolymer should have two vitreous outer blocks, where the poly(MMA) moiety (hard segment) associates with the nodules, and the central soft poly(BuA) elastomeric block provides rubber elasticity. Ihara et al.[35] were the first to synthesize an AB type block copolymer, with MMA (190 molar amounts of initiator) polymerized by [SmMe(C_5Me_5)$_2$(THF)] and then BuA (290 molar amounts of initiator) polymerized to the poly(MMA) end. It consisted of 52 MMA and 48 BuA with $M_n = 47000$ and $M_w/M_n = 1.04$. When the BuA was first polymerized and MMA was then polymerized after the system had been held for 5 min, the resulting polymer had a lower molecular weight $M_n = 21700$ and a higher polydispersity $M_w/M_n = 1.19$. This result may be due to partial deactivation of the growing end during the standing of the system. Thus, BuA was added at once after MMA was polymerized for 30 min, and after BuA was polymerized for 2 min, MMA was again added (Scheme 6). The first step gave poly(MMA) with $M_n = 15000$ and $M_w/M_n = 1.04$, the second step gave poly(MMA)-block-poly(BuA) with $M_n = 36000$ and $M_w/M_n = 1.05$ (MMA/BuA = 43/57), and the final step gave poly(MMA)-block-poly(BuA)-block-poly(MMA) with $M_n = 144000$ and $M_w/M_n = 1.09$ (MMA/BuA/MMA = 13/125/72). Thus, the MMA block was elongated longer than expected, which may be attributed to partial deactivation of the growing end of poly(MMA)-block-poly(BuA). So Ihara et al. added a mixture of MMA and BuA at once to the growing end of poly(MMA) (BuA polymerized more rapidly than MMA), and found that this treatment allowed living triblock copolymerization to proceed preferentially and produced various triblock copolymers.[35] Table 5 shows the typical mechanical properties of the copolymer thus obtained. It is seen that homo-poly(MMA) has large tensile modulas and large tensile strength, but is poor in elongation and Izod impact strength. Furthermore, homo-poly(MMA) shows no decrease in compression set (typical rubber shows ca. 20%). In contrast, the triblock copolymer (8 : 72 : 20) shows a 58% compression set, and its Izod impact strength is in the range "not break" (> 400 J m^{-1}), while its hardness is lowered to 20 JISA. Its most interesting property is a large elongation (163%). By contrast for the triblock copolymers composed of MMA/BuA/MMA in 6 : 91 : 3 and 25 : 51 : 24 ratios, the compression set increases to 97 or 101%, which indicates that these polymers are not elastic. The elonga-



Scheme 6.

Table 5. Mechanical Properties of Triblock Copolymers

Copolymer	Tensile modulas MPa	Tensile strength MPa	Elongation %	Izod impact strength J m^{-1}	Compression set/% (70 °C, 22h)
Poly(MMA)	610	80	21	18	100
poly(MMA/BuA/MMA) (20 : 47 : 33)	75	27	83	383 (N.B)	101
poly(MMA/BuA/MMA) (25 : 51 : 24)	46	22	81	390 (N.B)	103
poly(MMA/BuA/MMA) (8 : 72 : 20)	0.8	0.7	163	400 (N.B)	58
poly(MMA/BuA/MMA) (6 : 91: 3)	0.2	0.1	246	410 (N.B)	97
poly(MMA/EtA/EMA) (26 : 48 : 26)	119	22	276	34	62

N.B: not break.

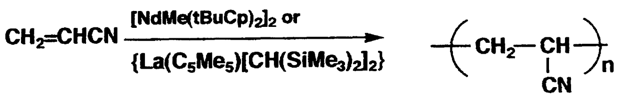
tion of the 25 : 51 : 24 triblock copolymer is 81%, and that of 6 : 91 : 3 copolymer is 246%. Thus a suitable composition ratio is required to get elastic triblock copolymers.

Polymerization of Acrylonitrile

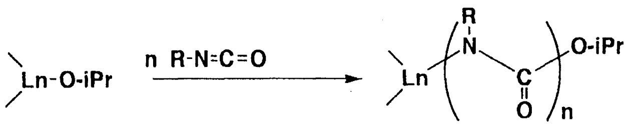
Ren et al.[36] carried out polymerization of acrylonitrile using $[NdMe(t\text{BuCp})_2]_2$ to obtain M_n of 2.5—8.2×10^4 at 10—28% yield, and showed that the product was atactic (*rr* = 26—30%, *rm* = 41—46%, *mm* = 27—30%) (Scheme 7). Hue et al.[10] found a bulky phenoxy complex, $\{Sm[O\text{–}C_6H_2\text{-}2,6\text{-}(t\text{Bu})_2\text{-}4\text{-Me}]_2\}$, is active for atactic polymerization of acrylonitrile at 60 °C in toluene and $M_n = 2.1\times10^4$ was obtained when the conversion reached 72%. According to a recent work by Tanaka et al.[38] $\{La[CH(SiMe_3)_2]_2(C_5Me_5)\}$ has a good catalytic activity for polymerization of acrylonitrile (Scheme 7). However, the product was very poor in stereoregularity (*rr* = 26—29%, *mr* = 42—46%, *mm* = 25—32%), as was the case with such anionic type catalysts as BuLi and *t*BuMgCl.[39]

Polymerization of Alkyl Isocyanates

Polyisocyanates have attracted much attention owing to their liquid crystalline properties, stiff-chain solution characteristics, and induced optical activities associated with the helical chain conformation (Scheme 8). Pattern and Novak[40] discovered that such titanium complexes as $[TiCl_3(OCH_2CF_3)]$ and $[TiCl_2(C_5H_5)(OCH_2CF_3)]$ initiate the living polymerization of isocyanates, giving polymers with narrow molecular weight distribution. When hexyl isocyanates was added to $[TiCl_3(OCH_2CF_3)]$, the polymerization took place at room temperature, with M_n increasing linearly with the initial monomer-to-initiator mole ratio or the monomer conversion ($M_w/M_n = 1.1$—1.3) over a wide range. Recently, Fukuwatari et al.[41] found lanthanum isopropoxide to serve as a novel anionic initiator for the polymerization of hexyl isocyanate at low temperature (−78 °C), which led to very high molecular weight ($M_n > 10^6$) and rather narrow molecular weight distribution ($M_w/M_n = 2.08$—3.16). Other



Scheme 7.



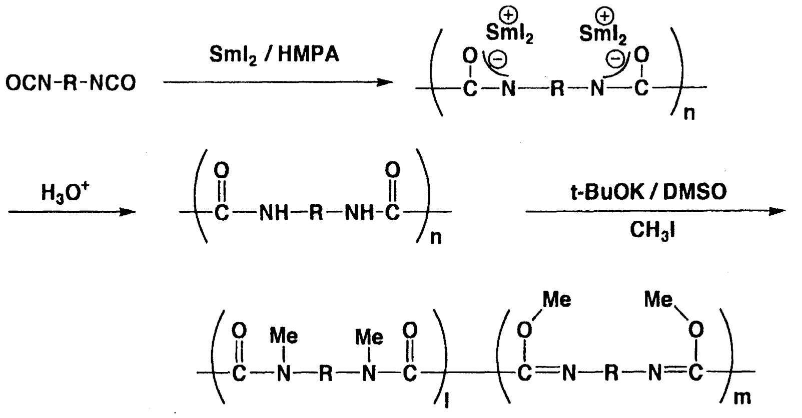
Scheme 8.

lanthanum alkoxides such as $[Sm(OiPr)_3]$, $[Yb(OiPr)_3]$, and $[Y(OiPr)_3]$ also induced the polymerization of hexyl isocyanate. Furthermore, it was shown[41] that butyl, isobutyl, octyl and *m*-tolyl isocyanates were polymerized using lanthanum isopropoxide as the 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 at high yields. In an unpublished work, Tanaka et al.[11] showed that $La(C_5Me_5)_2[CH(SiMe_3)]_2$ also initiates the polymerization of butyl isocyanate and hexyl isocyanate at 70—80% yields in THF.

More recent reports showed that the selective reductive homocoupling polymerization of aromatic diisocyanates via one electron transfer promoted by samarium(II) iodide in the presence of hexamethylphosphoramide $[PO(NMe_2)_3]$ (HMPA) can produce poly(oxamide)s in nearly quantitative yield (Scheme 9). The polymers obtained were insoluble in common organic solvents. The alkylation of poly(oxamide)s with methyl iodide or alkyl bromide in the presence of potassium *t*-butoxide gave readily soluble alkylated polymers in good yield. In either case, the alkylation was almost complete, and both N- and O-alkylations proceeded. The ratio of N- and O-methylations was found to be 64 : 36 by ^{1}H NMR, and that of N- and O-allylation was 3 : 1 by ^{13}C NMR analysis. The SmI_2(HMPA) initiated polymerization system was applied to a variety of diisocyanates including bis(2,6-diisocyanatophenyl)methane, 2,6-diisocyanatotoluene, 2,6-naphthyl diisocyanate, and *o*-toluidine diisocyanate, giving polymers whose molecular weight were 2000—9000. TGA measurements on them showed T_{d10} values in the range 248—320 °C.[42,43]

Living Polymerization of Lactones

$AlEt_3$—H_2O or $AlEt_3$-catalyzed polymerization of 3-methyl-β-propiolactone and ε-caprolactone has been reported,[44,45] but this polymerization generally gives a broad molecular weight distribution. Yamashita et al.[46] explored the polymerization of various lactones including β-propiolactone (PL), 3-methyl-β-propiolactone (MePL), δ-valerolactone (VL) and ε-caprolactone (CL) initiated by single organolanthanides, and found that VL and CL led to the living polymerization, yielding polymers with $M_w/M_n = 1.05$—1.10 at quantitative yields (Table 6). For ε-caprolactone, M_n obtained with the $[SmMe(C_5Me_5)_2(THF)]$ or $[SmH(C_5Me_5)_2]_2$ system increased with increasing conversion, but M_w/M_n remained constant, irrespective of the conversion. For β-propiolactone, the use of $YOR(C_5Me_5)_2$ was more favorable. On the other hand, divalent organolanthanide complexes can initiate the polymerization of lactones, but the resulting polymers had rather broad molecular weight distributions.[47] $[Nd(acac)_3{\cdot}3H_2O]/AlR_3$ and $[Nd(naphthenate)_3]/AlR_3$ initiators were effective for the ring opening polymerization of ε-caprolactone, but no data for molecular weight distribution were reported.[48] $[Ln(OiPr)_3]$ (Ln = La, Pr, Nd, Gd, and Y) also catalyzed the polymerization of CL, but the polydispersity index was larger ($M_w/M_n = 1.2$—2.4) than that obtained with $[LnMe(C_5H_5)_2(THF)]$.[49] Furthermore, $[Sm(2,6\text{-}tBu_2\text{-}4\text{-}Me\text{-}C_6H_2)_2(THF)_4]$ initiated the polymerization of CL to form a polymer with



Scheme 9.

Table 6. Living Polymerization of Lactones with Organolanthanide Complexes

Initiator	Monomer	$M_n/10^3$	M_w/M_n	Conversion/%
$[SmMe(C_5Me_5)_2(THF)]$	VL	75.2	1.07	80.1 (7 h)
	CL	109.4	1.09	92.0 (7 h)
$[SmH(C_5Me_5)_2]_2$	VL	65.7	1.08	90.5 (7 h)
	CL	71.1	1.19	28.7 (5 h)
$[YOMe(C_5H_5)_2]_2$	CL	162.2	1.10	87.5 (5 h)
	PL	60.5	3.1	94.5 (5 h)

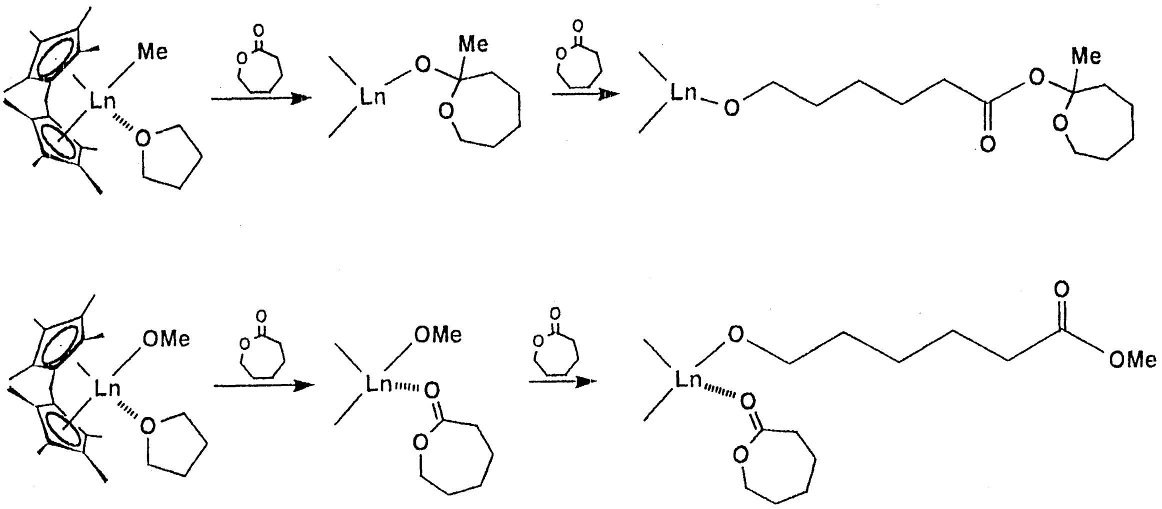
PL propiolactone, VL varelolactone, CL caprolactone. Polymerization, 0 °C in toluene.

M_n of 15—16×10^4 and M_w/M_n of 1.650.

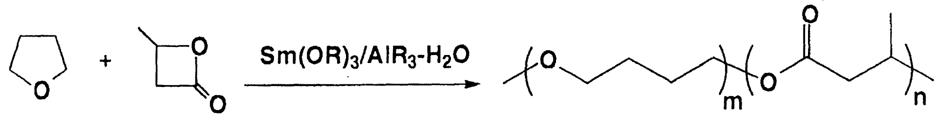
At the early stage of the polymerization of lactone with [Ln(OR)(C_5Me_5)$_2$], one mole of ε-caprolactone may coordinate to the metal, as is the case for the reaction of YCl_3 with ε-caprolactone, giving the first six-coordinate mer complex, YCl_3·(ε-caprolactone)$_3$ in which each ε-caprolactone molecule is coordinated as a monodentate ligand through its carbonyl oxygen.[51] The polymerization starts with the coordination of ε-caprolactone to form the 1 : 1 complex [Ln(OR)(C_5Me_5)$_2$(ε-caprolactone)], and in its propagation step the alkoxide attacks the C=O group to produce {Ln[O-(CH_2)$_5$C(O)OR](C_5Me_5)$_2$(ε-caprolactone)}. In the [SmMe-(C_5Me_5)$_2$] initiator system, the reaction is initiated by the attack of ε-caprolactone or δ-valerolactone to result in the formation of an acetal; ring opening follows. This process has been confirmed by ^{13}C NMR studies of the stoichiometric reaction products (Scheme 10).

The above organolanthanide complexes are less effective to obtain high molecular weight polymers of 3-methyl-β-propiolactone. However, random copolymerization of 3-methyl-β-propiolactone with THF occurred upon initiation with the [Sm(O*i*Pr)$_3$]/$AlEt_3$–H_2O system (1 : 5—1 : 10), although the $AlEt_3$–H_2O system was completely inert to the polymerization of tetrahydrofuran (THF).[52] The polymers produced were 43/57—24/76 in the lactone/THF ratio and had M_n of 10000—200000 and M_w/M_n of 1.08—1.26 (Scheme 11). In this system, some cationic initiator is supposed to be formed when the two components are mixed.

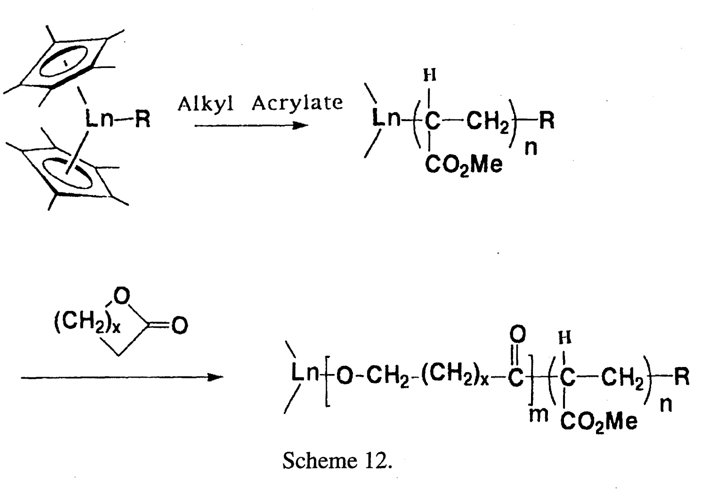
Anionic block copolymerizations of MMA with lactones proceeded smoothly to give copolymers with M_w/M_n = 1.11—1.23 when the monomers were added in this order. However, when the order of addition was reversed, no copolymerization took place,[3c] i.e. no addition of MMA to the polylactone active end occurred (Scheme 12).



Scheme 10.



Scheme 11.



Scheme 12.

Polymerization of Tetrahydrofuran

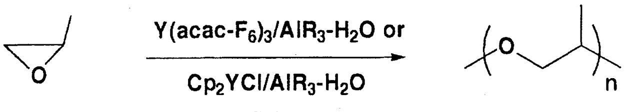
The ring opening polymerization of tetrahydrofuran (THF) was first reported by Meerwein,[53] who used the trialkyloxonium salt as the initiator. Recently, Jin et. al.[54] found that the [Ln(CF_3COO)$_3$]/AlH*i*Bu$_2$/propylene oxide (1/4/1) system allows THF to polymerize at high yield (50—55%). Nomura et al.[55] succeeded in quantitative one-pot transformation of the cationic growing centers of telechelic poly(THF) into anionic ones by using samarium(II) iodide/HMPA. The transformed poly(THF) macrodianion initiated the polymerization of *t*-butyl methacrylate (*t*BuMA) with quantitative initiation efficiency; a unimodal triblock copolymer of *t*BuMA and THF were obtained (Scheme 13). According to Nomura et al.,[56] the transformed poly(THF) macroanion is active for the living polymerization of CL producing an ABA-type triblock copolymer of CL with THF (Scheme 14).

Stereospecific Polymerization of Oxirans

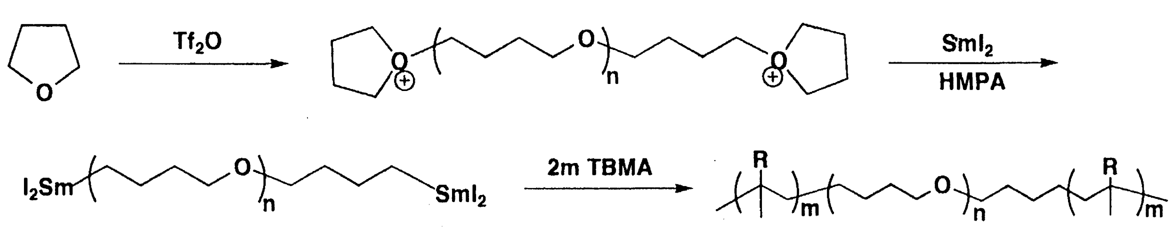
Such organolanthanide(III) complexes as [LnMe(C_5Me_5)$_2$] or [LnH(C_5Me_5)$_2$] do not initiate the polymerization of oxirans, but more complex systems like Ln(acac)$_3$/AlR_3/H_2O and Ln(2-EP)$_3$/AlR_3/H_2O [2-EP; bis(2-ethylhexyl)phosphate] do this with good initiation activity.[57] High molecular weight poly(ethylene oxide) is one of the common water-soluble polymers which are useful as adhesives, surfactants, plasticizers, and dispersants as well as for sizing. Poly(ethylene oxide) of $M_n = 2.85\times10^6$ was obtained with the [Y(2-EP)$_3$]/Al*i*Bu$_3$/H_2O system at the ratio of $Y/Al/H_2O = 1/6/3$. The initiator activity depended upon the molar ratio of the components. Polymerization of propylene oxide was reported to proceed with the Ln(acac)$_3$/AlEt$_3$/H_2O system, and it was found that light rare earth elements (Y, La, Pr, Nd, and Sm) produced very high molecular weight poly(propylene oxide) at $Al/Ln = 6$ in a short period of time (2 h) in toluene.[58] It was also found that the [Nd(acac-F_3)$_3$]/AlR_3/H_2O (Ln = Y, Nd) systems[59] gave isotactic poly(propylene oxide), while the [LnClCp$_2$]/AlR_3/H_2O, [Sm(O*i*Pr)$_3$]/AlR_3/H_2O or [Y(2-ethylhexanoate)$_3$]/AlR_3/H_2O system produced relatively low molecular weight isotactic species of this polymer (Scheme 15).

Random copolymerization of propylene oxide with ethylene oxide proceeded smoothly with the [Nd(2-EP)$_3$]/AlEt$_3$/H_2O system at 80 °C.[60] From the copolymerization composition curve, the monomer reactivity ratios were evaluated to be r_1 (EO) = 1.60 and r_2 (PO) = 0.45. The conversion increased with an increase in the Al/Nd ratio and saturated at a molar ratio of 16. The ^{13}C NMR spectrum of the random copolymer clearly indicated the existence of the propylene oxide–ethylene oxide linkages in the polymer chains. Since the [Nd(2-EP)$_3$]/AlEt$_3$/H_2O system generates a growing poly(propylene oxide) chain having a very long life, block copolymerization with ethylene oxide can be achieved successfully. The [Ln(acac)$_3$]/Al*i*Bu$_3$/H_2O (1 : 8 : 4) systems, especially in the case of Nd derivative, also initiated the polymerization of epichlorohydrin (EPH) to yield a polymer of $M_V = 16.5\times10^5$ with 21% crystallinity, and a remarkable solvent effect was observed.[61] Toluene is used preferably, while aliphatic hydrocarbons are not suitable because poly(epichlorohydrin) precipitates from the solvent during the polymerization. The relative monomer reactivities evaluated for the propylene oxide (PO)-allyl glycidyl ether (AGE) system were r_1 (PO) = 2.0 and r_2 (AGE) = 0.5, and those for the epichlorohydrin–AGE system were r_1 (EPH) = 0.5 and r_2 (AGE) = 0.4.[61] This combination of monomer reactivity ratios indicates that the polymerization with [Ln(acac)$_3$]/Al*i*Bu$_3$/H_2O follows a coordinated anionic mechanism, but that with the Al*i*Bu$_3$/H_2O system follows a cationic polymerization mechanism. The ability to produce high molecular weight polymers is in the order $Nd > La = Sm > Pr = Dy = Y > Gd = Yb > Eu$.

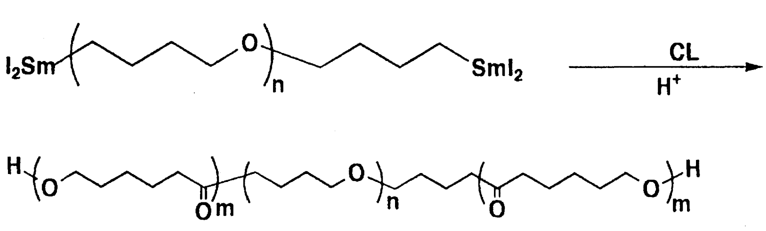
Although the copolymerization of propylene oxide with



Scheme 15.



Scheme 13.



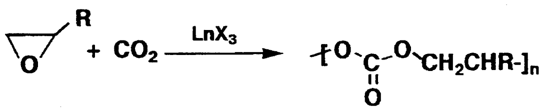
Scheme 14.

CO_2 takes place effectively with the organozinc-additives or the tetraphenylporphyrin–AlCl system,[62] the copolymerization of epichlorohydrine with CO_2 does not occur with these catalysts. Shen et al.[63] showed that a rare earth metal catalyst such as the Nd(2-EP)$_3$/Al*i*Bu$_3$ (Al/Nd = 8) system was very effective for the copolymerization of epichlorohydrine with CO_2 (30—40 atm) at 60 °C (Scheme 16). The content of CO_2 in the copolymer reached 23—24 mol% when 1,4-dioxane was used as solvent.

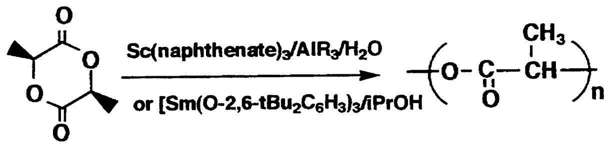
The ZnEt$_2$/H$_2$O,[64] AlEt$_3$/H$_2$O,[65] and Cd salt[66] systems are well-known initiators for the polymerization of propylene sulfide. Shen et al.[67] examined this polymerization with the [Ln(2-EP)$_3$]/Al*i*Bu$_3$/H$_2$O system and found that high molecular weight polymers were produced at a low concentration of Nd (6.04×10^{-3} mol dm^{-3}) in the ratio of Nd/Al/H$_2$O = 1/8/4. The polymerization activity decreased in the order Yb = La > Pr > Nd = Eu > Lu > Gd > Dy > Ho > Er. The ^{13}C NMR spectrum indicated that β-cleavage occurs preferentially over the α-cleavage and the ratio of these ring openings changes little with the initiator system and the polymerization temperature used. The polymers obtained were amorphous according to DSC and XRD analyses. Shen et al.[68] also showed that chloromethylthiirane-(2-chloro-3-methyl-2-butene sulfide) can be polymerized to high molecular weight polymers ($[\eta]\times10^2$ dl g^{-1} = 4—5) by the use of [Nd(P$_{204}$)$_3$]/AlR$_3$ (P$_{204}$ = [CH$_3$(CH$_2$)$_3$(CH$_2$CH$_3$)-CHCH$_2$O]$_2$P(O)O–) in 1 : 12 ratio. Conversions were higher than 80%. This monomer had not been induced to form high molecular weight polymers so far by using any kind of catalyst.

Polymerization of Lactide

Shen et al.[69] succeeded in producing the ring opening polymerization of DL-lactide (racemic species) using [Nd(naphthenate)$_3$]/Al*i*Bu$_3$/H$_2$O (1 : 5 : 2.5), [Nd(P$_{204}$)$_3$]/Al*i*Bu$_3$/H$_2$O, [Nd(P$_{507}$)$_3$]/Al*i*Bu$_3$/H$_2$O (P$_{507}$ = (*i*C$_8$H$_{17}$O)$_2$P(O)O–) and [Nd(naphthenate)$_3$]/Al*i*Bu$_3$/H$_2$O systems, obtaining the polymers whose molecular weights were $M_n = 3.1—3.6\times10^4$ and the conversions were larger than 94%. When the [Ln(naphthenate)$_3$]/Al*i*Bu$_3$/H$_2$O system was used, nearly the same results were obtained irrespective of the metals used (La, Pr, Nd, Sm, Gd, Ho, and Tm). Divalent [Sm(2,6-*t*Bu$_2$-4-Me-phenyl)$_2$(THF)$_4$] was also found to be active for the polymerization of DL-lactide at 80 °C in toluene, giving M_n of $1.5—3.5\times10^4$.[70] A more recent finding is that the Ln(O-2,6-*t*Bu$_2$-C$_6$H$_3$)$_3$/*i*PrOH (1 : 1—1 : 3) system initiates a smooth homo-polymerization of L-lactide, CL, and VL and gives relatively high molecular weights ($M_n > 24\times10^3$) with low polydispersity indices (M_w/M_n = 1.2—1.3) (Scheme 17).[10] Ring-opening polymerization of DL-lactide was also carried out by using Ln(O*i*Pr$_3$)$_3$ as the catalyst 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%).[71] However, the molecular weight distribution is not clear at present. A kinetic study[10] showed that the rate of polymerization is first order in both monomer and initiator. The block copolymerization of CL with L-lactide proceeded effectively and gave a polymer with a very narrow molecular weight distribution (M_w/M_n = 1.16). On the other hand, the addition of CL to the living poly(L-lactide) end led to no success.



Scheme 16.



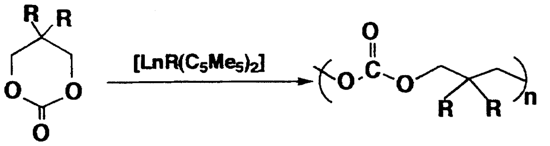
Scheme 17.

Polymerization of Cyclic Carbonates

Living polymerization of trimethylene carbonate (TMC) and 2, 2- dimethyltrimethylene carbonate readily occurred in toluene at ambient temperature when [SmMe(C$_5$Me$_5$)$_2$(THF)] or [YMe(C$_5$Me$_5$)$_2$(THF)] was used as the initiator, and yielded polymers having M_n of $3—5\times10^4$ and very low polydispersity, M_w/M_n = 1.0—1.1 (Scheme 18).[72] However, no detailed studies on such initiation and propagation mechanisms have as yet been made. Block copolymerization of trimethylene carbonate with ε-caprolactone was realized using Ln(ethyl acetoacetate)$_2$(O-*i*Pr) (Ln = Y, Nd) as the initiator.[73] 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 $4—5\times10^4$ and M_w/M_n of 1.2—1.4.

Stereospecific Polymerization of Olefins

Bulky organolanthanide(III) complexes such as LnH(C$_5$Me$_5$)$_2$ (Ln = La, Nd) were found to catalyze with high efficiency the polymerization of ethylene.[74] 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 Me$_2$Si bridged Cp ligand, as shown in Fig. 8. The reaction of the dilithium salt of this ligand with anhydrous SmCl$_3$ produced a mixture of two stereo-isomeric complexes. 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-positions of the Cp rings, while the other has a C_1 symmetric structure in which



Scheme 18.

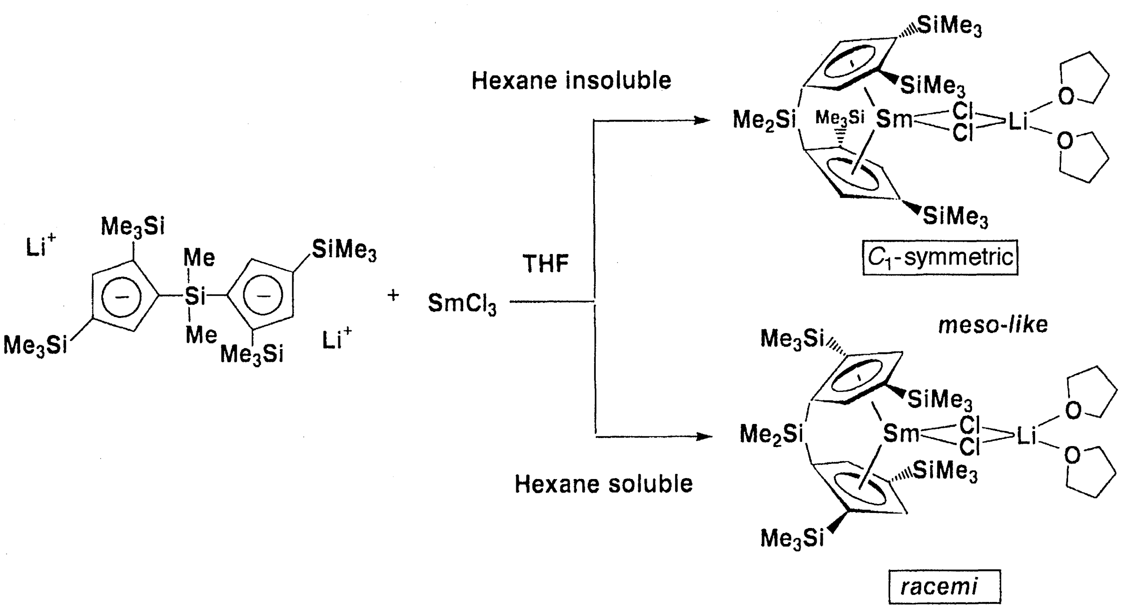


Fig. 8. Formation of organolanthanide(III) complexes.

two trimethylsilyl groups are located at 2,4- and 3,4-position of each Cp ring. Both were converted to alkyl derivatives when they were allowed to react with bis(trimethylsilyl)-methyllithium.[75] The Cp′-Sm-Cp′ angle of the racemic-type precursor is 107°, which is about 15° smaller than that of non-bridged $SmMe(C_5Me_5)_2(THF)$.

Meso type ligands were synthesized by forcing two trimethylsilyl groups to be located at the 3-position of the ligand with introduction of two bridges (Fig. 9). Actually, the complexation of this ligand with YCl_3 yielded a *meso* type complex, and the structure of the complex was determined by X-ray analysis. The meso type alkyl complex was synthesized in a similar manner.[75]

Table 7 summarizes the results of ethylene polymerization with these organolanthanide(III) complexes. Interestingly, only C_1 type complexes can initiate the polymerization (Scheme 19), implying that the catalytic activity varies with the structure of the complex. The X-ray structure of the C_1 symmetric complex is given in Fig. 10, where the C′p-Sm-Cp′ angle is seen to be 108°, a very small dihedral angle. The polymerization of ethylene with $[SmH(C_5Me_5)_2]_2$ in the presence of $PhSiH_3$ produced PhH_2Si capped polyethylene ($M_n = 9.8\times10^4$, $M_w/M_n = 1.8$), and the copolymerization of ethylene with 1-hexene or styrene gave PhH_2Si capped copolymer (comonomer content 60 and 26 mol%, respectively; $M_n = 3.7\times10^3$, $M_w/M_n = 2.9$ for ethylene-1-hexene copolymer, $M_n = 3.3\times10^3$ for ethylene–styrene copolymer) (Scheme 20).[76]

Table 8 shows the results of polymerization of α-olefins catalyzed with trivalent complexes. When a more bulky tBuMe$_2$Si group instead of the Me_3Si group was introduced into the yttrium complex, the racemic complex was formed exclusively.[75c] However, this alkyl complex didn't react with olefins, and hence it was converted to a hydride complex by

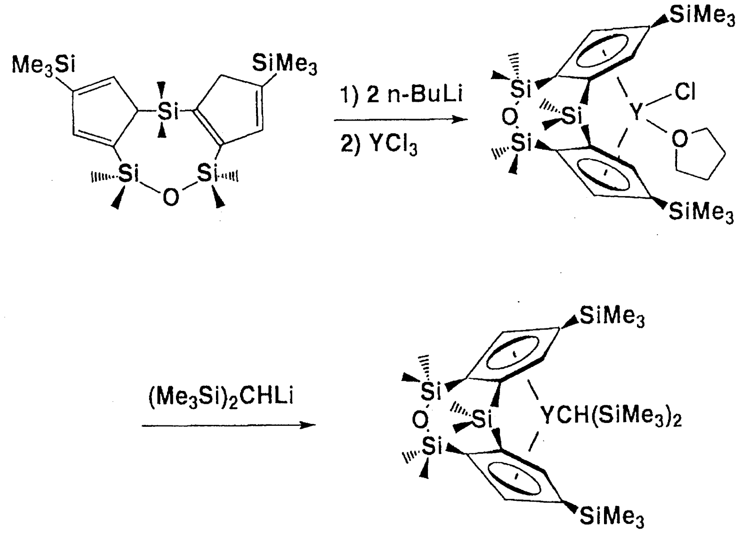
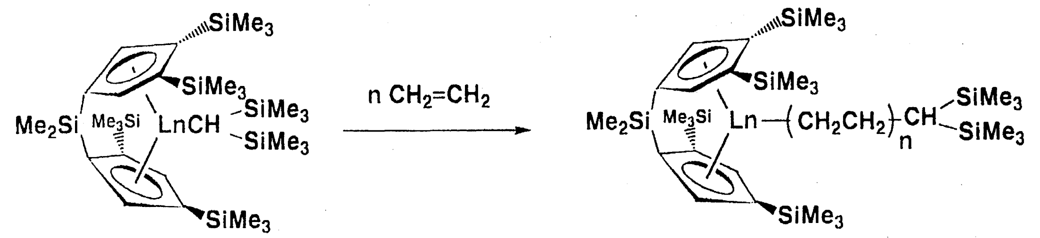


Fig. 9. Preparation of *meso* $[Me_2Si(SiMe_2OSiMe_2)(3\text{-}SiMe_3\text{-}C_5H_2)_2YCl(THF)]$.

Table 7. Ethylene Polymerization by Organolanthanide(III) Complexes

Initiator	$M_n/10^4$	M_w/M_n	Activity ($g\,mol^{-1}\,h^{-1}$)
$[(C_5Me_5)_2SmCH(SiMe_3)_2]$		No polymerization	
$[SiMe_2[2,4\text{-}(SiMe_3)_2C_5H_2]_2SmCH(SiMe_3)_2]$ (*racemi*)		No polymerization	
$[SiMe_2(Me_2SiOSiMe_2)(4\text{-}SiMe_3\text{-}C_5H_2)YCH(SiMe_3)_2]$ (*meso*)		No polymerization	
$[SiMe_2[2(3),4\text{-}(SiMe_3)_2C_5H_2]_2SmCH(SiMe_3)_2]$ (C_1)	41.3	2.19	3.3×10^4
$[SiMe_2[2(3),4\text{-}(SiMe_3)_2C_5H_2]_2YCH(SiMe_3)_2]$ (C_1)	33.1	1.65	18.8×10^4

Initiator concentration, 0.2 mol%. Ethylene was introduced by bubbling at atmospheric pressure.



Scheme 19.

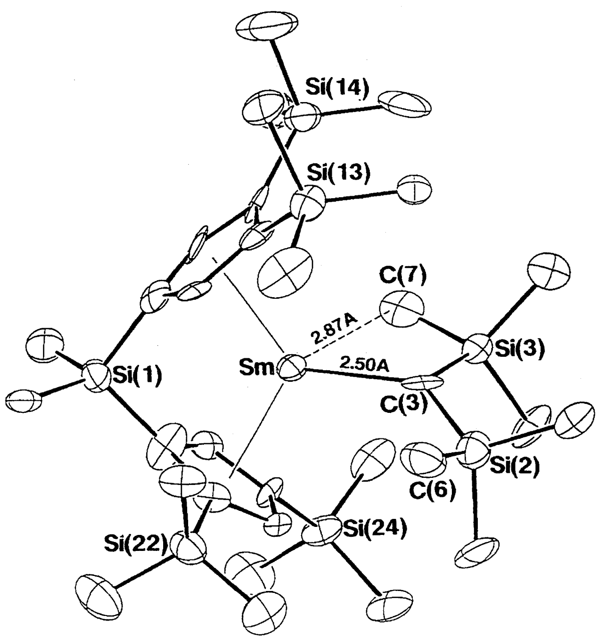


Fig. 10. X-Ray structure of C_1 symmetric $\{Me_2Si[2(3),4\text{-}(SiMe_3)_2C_5H_2]_2SmCH(SiMe_3)_2\}$.

$$PhSiH_3 + CH_2{=}CH_2 \xrightarrow{[SmH(C_5Me_5)_2]} PhSiH_2(CH_2CH_2)_nH$$

Scheme 20.

reaction with H_2. The complex obtained was reactive to various olefins and produced polymers at high yield. Poly(α-olefin) thus obtained was highly isotactic with an mmmm content > 95%, when examined by ^{13}C NMR at 34.91 ppm. It also initiated the polymerization of 1,5-hexadiene, yielding poly(methylene-1,3-cyclopentene) exclusively,[75] whose M_n ($M_n = 13.5\times10^4$) was much higher than that obtained with the Kaminsky type catalyst ($M_n < 40000$) (Scheme 21).[77] The conversions of poly(1-pentene) and poly(1-hexane) were also much higher than those obtained by $[rac\text{-}Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}tBu\text{-}C_5H_2)_2YH]$[78] or $[ScH(C_5Me_4)SiMe_2\text{-}N\text{-}tBu)(PMe_3)]_2$.[79]

Racemic, *meso*, and C_1 symmetric divalent organolanthanide complexes can be synthesized by allowing the dipotassium salt of the corresponding ligand to react with SmI_2.[80] Figures 11 and 12 show their structures determined by ^1H NMR and X-ray analyses. Table 9 shows the results from the olefin polymerization with divalent samarium complexes (Scheme 22). 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 polyethylene but the activity is rather low. Particularly, the very high molecular weight polyethylene ($M_n > 100\times10^4$) ob-

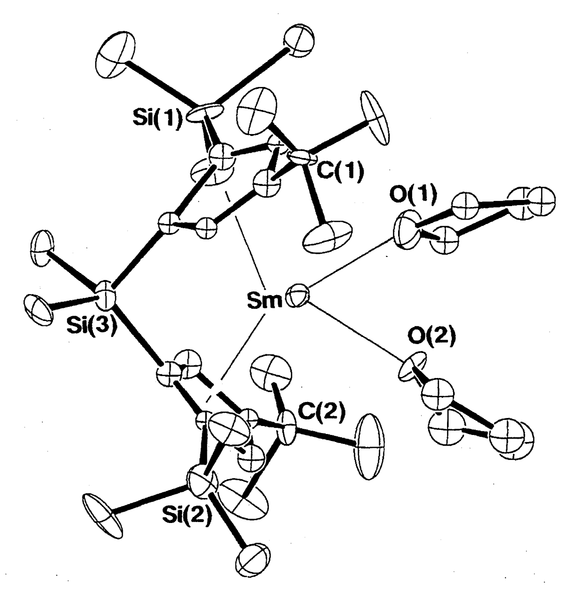
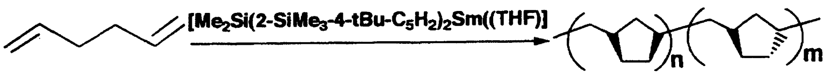


Fig. 11. X-Ray structure of *racemic* $[Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}tBu\text{-}C_5H_2)_2Sm(THF)_2]$.

Table 8. Polymerization of 1-Pentene and 1-Hexene

Monomer	Initiator	$M_n/10^3$	M_w/M_n
1-Pentene	$[Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}t\text{Bu-}C_5H_2)_2Sm(THF)_2]$	13	1.63
	$[Me_2Si[2(3),4\text{-}(SiMe_3)_2C_5H_2]_2YCH(SiMe_3)_2]$	16	1.42
	$[Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}t\text{Bu-}C_5H_2)_2YH]_2$	20	1.99
1-Hexene	$[Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}t\text{Bu-}C_5H_2)_2Sm(THF)_2]$	19	1.58
	$[Me_2Si[2(3),4\text{-}(SiMe_3)_2C_5H_2]_2YCH(SiMe_3)_2]$	64	1.20
	$[Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}t\text{Bu-}C_5H_2)_2YH]_2$	24	1.75

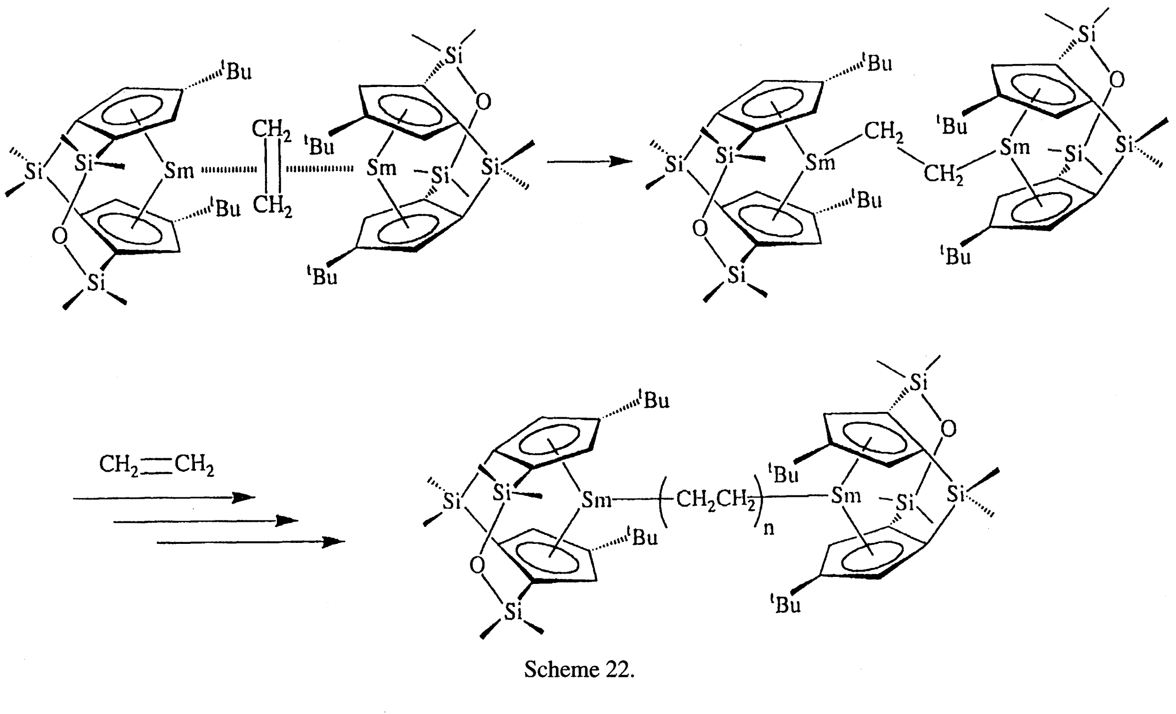
Initiator concentration, 0.2 mol% of monomer. Solvent, toluene, toluene/monomer = 5 (wt/wt).



Scheme 21.

Table 9. Ethylene Polymerization by Divalent Samarium Complexes

Initiator	Time/min	$M_n/10^4$	M_w/M_n	Activity (g mol^{-1} h^{-1})
$[(C_5Me_5)_2Sm(THF)_2]$	1	2.28	1.25	43
	3	2.46	2.28	41
Racemi	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	>100.0	1.64	1.1



Scheme 22.

tained with C_1 complex deserves attention. For the polymerization of α-olefins, only the racemic divalent complex showed good activity at 0 °C in toluene: poly(1-hexene) $M_n = 24600$, $M_w/M_n = 1.85$; poly(1-pentene) $M_n = 18700$, $M_w/M_n = 1.58$. Thus, we see that the reactivity of divalent organolanthanide complexes depends on their structure. The poly(1-alkene) obtained revealed highly isotactic structure (> 95%) when examined by ^{13}C NMR (Fig. 13). The dihedral angles of Cp′-Ln-Cp′ of racemic and meso type divalent complexes were 117 and 116.7°, respectively; these values are much smaller than those of $Sm(C_5Me_5)_2(THF)$ (136.7°)[81] and $Sm(C_5Me_5)_2$ (140.1°).[82] Therefore, it can be concluded that the complexes having smaller Cp′-Ln-Cp′ angles are more active for the polymerization of ethylene and α-olefins. 1,5-Hexadiene was polymerized smoothly by the catalytic action of [*rac*-$Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}t\text{Bu-}C_5H_2)_2Sm(THF)_2$] to give poly(methylene-1,3-cyclopentane) at a ratio of *cis*/*trans* = 55/45.[75c]

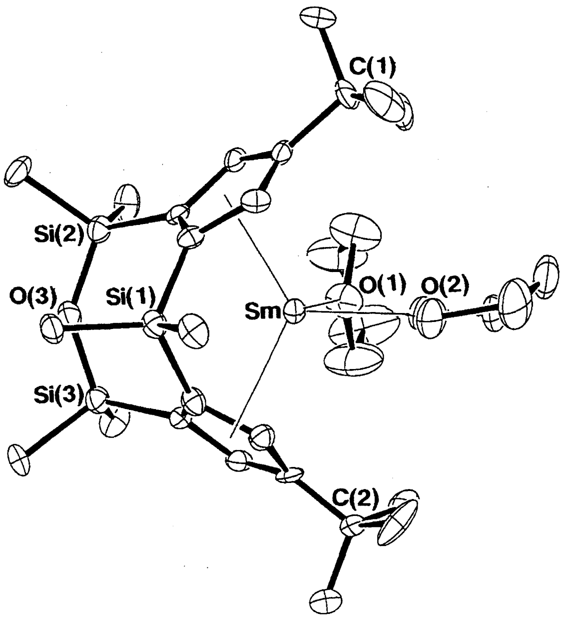


Fig. 12. X-Ray structure of *meso* $[Me_2Si(SiMe_2OSiMe_2)(3\text{-}t\text{Bu-}C_5H_2)_2Sm(THF)_2]$.

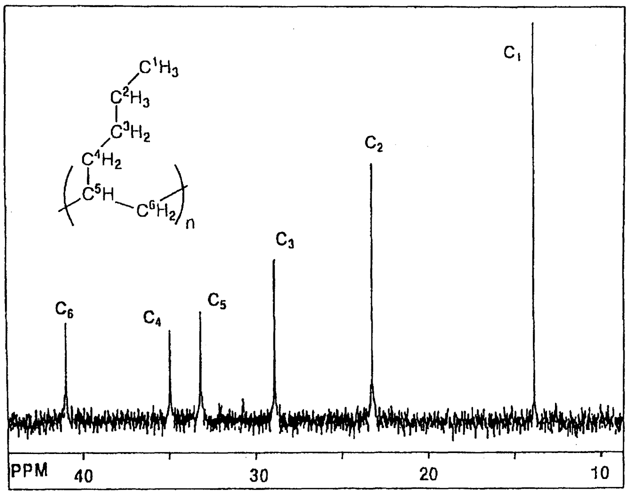


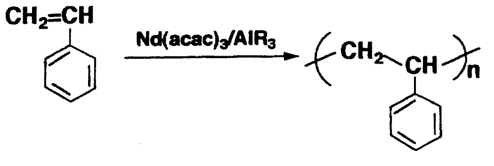
Fig. 13. ^{13}C NMR spectrum of isotactic poly(1-hexene).

Polymerization of Styrene

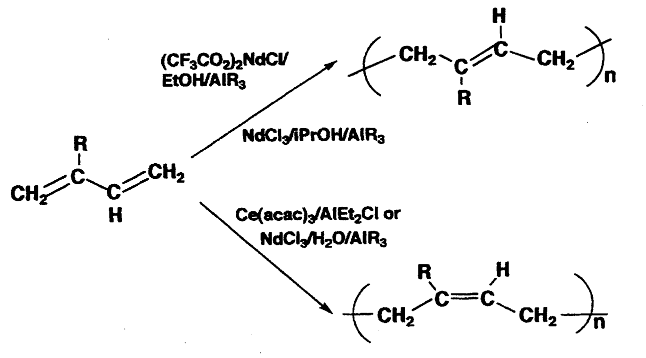
Styrene polymerization was performed by using binary initiator systems such as $[Nd(acac)_3]/AlR_3$ or $[Nd(P_{507})_3]/AlR_3$. Syndio-rich polystyrene was obtained at a ratio of Al/Nd = 10—12 (Scheme 23).[83] More recently, it was shown that the $[Gd(OCOR)_3]/i\text{Bu}_3Al/Et_2AlCl$ catalytic system initiates the copolymerization of styrene with butadiene, but gives only atactic polystyrene.[84] The $[Sm(Oi\text{Pr})_3]/AlR_3$ or $[Sm(Oi\text{Pr})_3]/AlR_2Cl$ (Sm/Al = 1—15) catalytic system also initiates the polymerization of styrene to give a high molecular weight polymer ($M_n = 300000$), low in polydispersity but atactic in stereoregularity.[85] The cationic polymerization of styrene using $[Ln(CH_3CN)_9(AlCl_4)_3(CH_3CN)]$ was also examined,[86] 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[87] showed that the single component initiator $[(t\text{BuCp})_2LnCH_3]_2$ (Ln = Pr, Nd, Gd) initiated the polymerization of styrene at relatively high temperature, 70 °C, with a conversion of 96% and the M_n of 3.3×10^4 for $[(t\text{BuCp})_2NdCH_3]_2$,[87] though stereoregularity was again very poor. The activity varied greatly with the lanthanide element; catalytic activity increased in the order Nd > Pr > Gd ≫ Sm, Y (the Sm and Y complexes showed practically no activity). Therefore, the reaction is supposed to follow the radical initiation mechanism. Styrene polymerization was also performed successfully using the single component initiators, $[(Me_3Si)_2N]_2Sm(THF)_2$, $[(Me_3Si)_2CH]_3Sm$, and $La(C_5Me_5)[CH(SiMe_3)_2]_2(THF)$ at 50 °C in toluene without addition of any cocatalyst. The resulting polymers had $M_n = 1.5—1.8\times10^4$ and $M_w/M_n = 1.5—1.8$, and show atactic property.[38] Thus no success has yet been achieved in synthesizing syndiotactic polystyrene with rare earth metal complexes, in contrast to the synthesis of highly syndiotactic polystyrene with $[TiCl_3(C_5Me_5)]/(AlMe\text{–}O\text{–})_n$ (syndiotacticity > 95%).[88,89]

Stereospecific Polymerization of Conjugate Dienes

Organolanthanide(III) based binary initiator systems were used by Yu et al.[90] for stereospecific polymerization of 1,3-butadiene and isoprene. Typically, the polymerization of 1,3-butadiene catalyzed by $C_5H_5LnCl_2{\cdot}THF/AlR_3$ yielded polymers with a *cis*-1,4-content as high as 98% (Scheme 24). The polymerization activity decreased in the order Nd > Pr > Y > Ce > Gd and $i\text{Bu}_2AlH > i\text{Bu}_3Al > Et_3Al > Me_3Al$, while the viscosity of the polymer decreased in the order $Et_3Al > i\text{Bu}_3Al > i\text{Bu}_2AlH$. Although the $NdCl_3/i\text{Bu}_3Al$ system exhibited practically no initiating activity, the use of $NdCl_3/i\text{PrOH}$ instead of the solvent-free metal chloride brought about high polymerization activity and high stereoregularity in the *cis*-1,4-polymerization of 1,3-butadiene.[91] The M_n of the polymer increased linearly with increasing



Scheme 23.



Scheme 24.

conversion and reached 1530×10^3 at 85% conversion when $NdCl_3\cdot i$PrOH/$AlEt_3$ (1 : 10) was used in heptane at −70 °C, but M_w/M_n (1.8—2.5) showed no change with conversion. The number N of polymer chains per metal atom was 1.09—1.43 at −70 °C, and increased to 2.0—3.0 when the polymerization temperature was raised to 0 °C. Most noteworthy is a very high *cis*-content realized at −70 °C, which amounted to 99.4%. This indicates the existence of the *anti*-π-allyl-Nd species rather than the *syn*-π-allyl-Nd species in the polymerization system. The *cis*-1,4-content of poly(1,3-butadiene) increased as the $AlEt_3$ concentration was lowered.91)

The arene organolanthanide system, $[Nd(C_6H_6)(AlCl_4)_3]/Al\textit{i}Bu_3$ (Al/Nd = 30), also induces the catalytic polymerization of isoprene to give *cis*-1,4 polymers in 92—93% selectivity at low conversion (17—36%). Both of the $[Nd(C_6Me_6)(AlCl_4)_3]/Al\textit{i}Bu_3$ (1 : 30) and $NdCl_3/AlCl_3/Al\textit{i}Bu_3$ (1 : 3 : 30) systems showed no catalytic activity for the polymerization of isoprene.92) The random copolymerization of isoprene with 1,3-butadiene went smoothly with the use of the $[Nd(C_6H_6)(AlCl_4)_3]/Al\textit{i}Bu_3$ system and gave an isoprene/1,3-butadiene (1 : 4) copolymer at high yield, but no data for M_w/M_n and M_n were reported.93) The β-CH_3-π-allyl)$_2LnCl_5Mg_2(TMEDA)_2/AlR_3$ and (allyl)$_4$Li systems also initiate the 1,4-polymerization of isoprene in 50% stereoregularity at high conversion.93) Highly selective *cis*-1,4-polymerizations of conjugated dienes were obtained by the use of homogeneous $[NdCl(CF_3COO)_2\cdot EtOH]/AlEt_3$ (1 : 7) initiator system, i.e. 97.5% *cis*-selectivity for butadiene and 96.7% for isoprene. Although bimetallic species like $[(CF_3COO)EtNd(\mu\text{-}Cl)(\mu\text{-}H)AlEt_2]$ are proposed as active ones, their exact structure is still unknown.94) The molecular structure of dimer complexes, $[(CF_3C)(\mu_2\text{-}O)_2(\mu_3\text{-}O)_4YAlEt_2(2THF)]_2$ and $[(CF_3)(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3NdAlEt_2(2THF)]_2$, generated during the reaction between $[NdCl(CF_3COO)_2]$ and $AlEt_3$, has recently been elucidated by X-ray analysis. However, these complexes are considered to be byproducts because they give polymers of low stereoregularity at low yield.95)

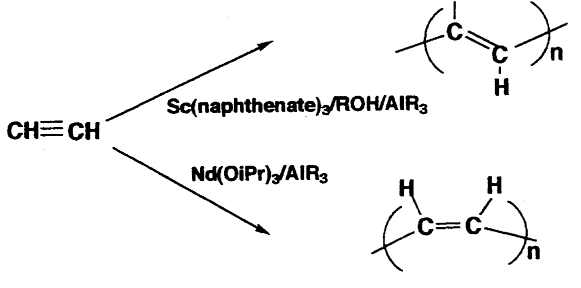
Block copolymerization of 1,3-butadiene with isoprene (32 : 68—67 : 33) giving high *cis*-1,4-polymers have also been successfully made with the Ln(naphthenate)$_3$/Al*i*Bu$_3$/$Al_2Et_3Cl_3$ system at temperatures from −78 to 33 °C. Noteworthy is the relatively long life time of this initiator. Thus it was possible to copolymerize isoprene 1752 h after the polymerization of 1,3-butadiene. The $[(\textit{i}PrO)_2HLn_2Cl_3HAlEt_2]$ species (Ln = Gd, Dy, Er, and Tm)96) prepared from either Ln(*i*PrO)$_3$/Et_2AlCl/Et_3Al or (*i*PrO)$_2$LnCl/Et_3Al also can initiate the *cis*-1,4-polymerization of 1,3-butadiene and isoprene. The most probable structure of this complex as evidenced by X-ray analysis is [(*i*PrO)HLnEt(Cl)AlHEt(Cl)LnCl(O*i*Pr)]. The polymerization activity decreased in the order Gd > Dy > Er > Tm and the *cis*-content ranged from 92 to 95% in the case of Gd derivatives. Random copolymerization of 1,3-butadiene with isoprene was also performed using $[Nd(C_6H_6)(AlCl_4)_3]/AlR_3$ (Al/Nd = 30) in benzene. Both monomers were incorporated in the copolymer selectively with *cis*-1,4-butadiene 96.1—96.4% and *cis*-1,4-isoprene 97.5—98.3%. The conversion increased with increase in the polymerization temperature from 0 (10%) to 80 °C (80—100%).97)

Some rare earth metal-based initiators induce the *trans*-1,4-polymerization of conjugated dienes at high yield. The $[Ce(acac)_3]/AlEt_2Cl$ system as well as the $CeCl_3/AlEt_2Cl$ and $GdCl_3/AlEt_3$ systems were most effective to carry out this type of polymerization for isoprene with high selectivity (91—97%).98) The marked difference in the selectivity between the $[Ce(acac)_3]/AlEt_3$ and the $[LnCl_2(C_5H_5)]/AlR_3$ or $[LnCl(\textit{i}PrO)_2]/AlR_3$ initiator systems may be due to a specific action of small amounts of water present in the system. Actually, metal compound hydrates like $NdCl_3\cdot6H_2O$, $PrCl_3\cdot6H_2O$, and $[UO_2(C_2H_3O_2)_2\cdot6H_2O]$ can initiate the *trans*-polymerization in the presence of AlR_3.99) Prolonged aging of the initiator system decreased the activity significantly, presumably owing to an irreversible self-reaction of the intermediate generated from the organolanthanide and water. A precise recent study101) on the effect of water has revealed that a maximum conversion was attainable at an $H_2O/AlEt_2Cl$ ratio of 1.1—1.2, which produces $(AlEt\text{–}O\text{–})_n(AlCl\text{–}O)_m$ species. However, the molecular weight was independent of the amount of water added to $AlEt_2Cl$.

1,3-Butadiene–styrene copolymerization was attempted using the $L_3LnRX\text{–}AlR_3$ system.100) Especially, $(CF_3COO)_3Nd/C_5H_{11}Br/Al\textit{i}Bu_3$ (1 : 3 : 15) was found to be active for this type of copolymerization, with the *cis*-content of butadiene amounting to 97.8% and the styrene content to ca. 32%. However, for the system of isoprene/styrene, the *trans*-1,4-polyisoprene copolymer was produced exclusively.

Stereospecific Polymerization of Acetylene Derivatives

polyacetylene (PA) is one of the simplest conjugated polymers; it is useful for manufacturing light weight high energy density plastics for storage batteries, solar energy cells, etc. Acetylene can be polymerized to give high *cis* PA film with $[Ti(O\textit{i}Bu)_4]/AlEt_3$101) or $[Co(NO_3)_2]/NaBH_4$102) at temperatures lower than −78 °C. Recently, it has been reported that [Ln(naphthenate)$_3$]/AlR_3/Donor (1 : 10 : 2—3) (Donor = acetone, ether, and ethyl acetate) systems also can initiate stereoregular cis polymerization of acetylene at 30 °C, which leads to silvery metallic film (Scheme 25).103,104) The polymer yield increased with increasing polymerization temperature from −15 to 45 °C. A *cis*-polyacetylene with 95% selectivity was



Scheme 25.

obtained when the Al/Ln ratio was adjusted to ca. 5. The polymerization activity decreased in the order Y = Ce > Nd = Tb > Pr > La > Lu > Gd > Tm = Er > Ho = Yb = Eu > Sm > Dy. The *trans* content of the film amounted to 100% when the temperature was raised to 180 °C. The elements leading to PA film with a *cis* content exceeding 95% are La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Y. The electrical conductivity of the films was 294×10^{-8} S cm^{-1} for La, 181×10^{-8} S cm^{-1} for Nd, 194×10^{-8} S cm^{-1} for Gd, 490×10^{-8} S cm^{-1} for Tb, and 184×10^{-8} S cm^{-1} for Tm. Differential scanning calorimetry revealed two exothermic peaks at 200 and 380 °C and an endothermic peak at 460 °C. These peaks were attributed to *cis–trans* isomerization, hydrogen migration, and chain decomposition, respectively.[104)]

[Sc(naphthenate)$_3$]/ROH/AlR$_3$ (1/2/7) has been found to exhibit an activity similar to the lanthanide series catalyst.[105)] The *cis* PA film obtained with it showed an electrical conductivity of 14.4 S cm^{-1} when the polymer was doped with I_2 at a ratio of $(CHI_{0.04})_n$. The TEM measurement suggested the formation of fibrils of about 20—30 nm in size.

The [Ln(P$_{204}$)$_3$]/AlR$_3$ system also exhibited good activity for the polymerization of acetylene when Al/Ln ratio was 5.[105)] The polymerization was conducted by the conventional method, and polymers with silverly metallic appearance were obtained. The addition of an oxygen-containing donor was effective for enhancing the polymerization rate and the *cis*-content. The effects were especially marked for P$_{204}$ (PO/Nd = 1.1). The activity decreased in the order Nd = Tb > Ce > Pr = Y > La > Er > Ho > S = Eu > Yb = Ln > Gd > Tm > Dy and the *cis*-content decreased in the order Pr (95%) > Ln = Tb = Dy (92%) > Er = Y = Sm = Gd (87—89%). The polymerization activities of [Nd(P$_{507}$)$_3$], [Nd(P$_{204}$)$_3$], and [Nd(P$_{215}$)$_3$] {P$_{215}$ = $[C_6H_{13}CH(CH_3)O]_2P(O)O$} were compared and found to increase in this order, the result is consistent with the basicities of the ligands (P$_{507}$H = pK_a 4.10, P$_{204}$H = pK_a 3.32, P$_{215}$H = pK_a 3.22). The M–C bond is supposed to weaken as the electrondonating ability of the ligand increases. The [Nd(*i*PrO)$_3$]/AlEt$_3$ (Al/Nd = 10) system[106)] was also shown to be a good initiator for the polymerization of acetylene. The soluble fraction obtained was considered to be *trans*-polyacetylene; it was shown to have a molecular weight of 277—540. Its ^{1}H NMR spectrum revealed methyl groups at $\delta = 0.826$ and terminal vinyl groups at $\delta = 4.95$.

Phenylacetylene was polymerized to give a polymer of high *cis* configuration by the use of the [Ln(naphthenate)$_3$]/AlEt$_3$ system,[107,108)] with the activity decreasing in the order Gd > Ln > Nd = Ce > Ho > Sm > Dy = Eu > Er > Pr > La > Y = Tm > Yb, and the *cis*-content exceeding 90%. It had M_n and M_w of 2×10^5 and 4×10^5, respectively, and was crystalline according to XRD and SEM measurements. Its softening point was in the range 215—230 °C. Other terminal alkynes such as 1-hexyne, 1-pentyne, 3-methyl-1-pentyne, 4-methyl-1-pentyne, and 3-methyl-1-butyne were found to polymerize quantitatively in the *cis*-fashion with the [Ln(naphthenate)$_3$]/AlR$_3$/C$_2$H$_5$OH (Ln = Sc, Nd) or [Ln(P$_{204}$)$_3$]/AlR$_3$/C$_2$H$_5$OH (1 : 7 : 3) system. The highest molecular weight M_n obtained was 16.8×10^4 for poly(1-pentyne). Trimethylsilylacetylene was oligomerized to $H(Me_3SiC{=}CH)_nCH_2CHMe_2$ (n = 2—3) by the use of LnX$_3$(Donor)/Al*i*Bu$_3$ (Ln = Gd, Pr, Nd, Tb, Dy, Lu; X = Cl, Br).[109,110)] The catalytic dimerization of terminal alkynes using [LnCH(SiMe$_3$)$_2$(C$_5$Me$_5$)$_2$] (Ln = Y, La, and Ce) has been reported recently. Here the dimer was a mixture of 2,4-disubstituted 1-buten-3-yne and 1,4-disubstituted 1-buten-3-yne for phenylacetylene and (trimethylsilyl)acetylene, but it was only a 2,4-disubstituted dimer for alkylacetylene.[111)] Selective formation of 2,4-disubstituted 1-buten-3-ynes has already been achieved with the [TiCl$_2$(C$_5$Me$_5$)$_2$]/RMgX catalyst.[112)]

Block Copolymerization of Ethylene with Polar Monomers

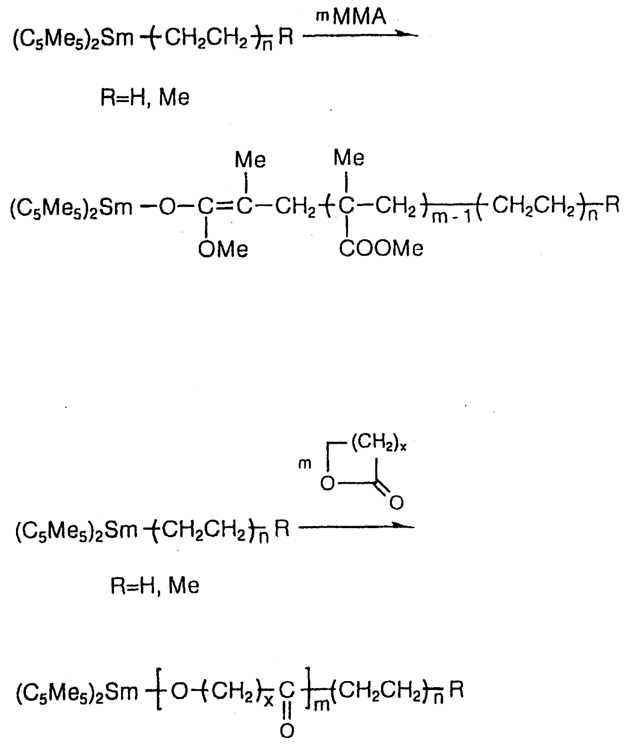
Block copolymerization of ethylene or propylene with polar monomers is yet to be attained in polyolefin engineering. The success of this type of block copolymerization should give hydrophilic polymeric materials having remarkably high adhesing, dyeing, and moisture adsorbing properties. The following is the first example of a well-con-

Table 10. Block Copolymerization of Ethylene with Polar Monomers

Polar monomer	Polyethylene block[a)] $M_n/10^3$	M_w/M_n	Polar polymer block[b)] $M_n/10^3$	M_w/M_n	Unit ratio
MMA	10.3	1.42	24.2	1.37	100 : 103
	26.9	1.39	12.8	1.37	100 : 13
	40.5	1.40	18.2	1.90	100 : 12
MeA	6.6	1.40	15.0	1.36	100 : 71
	24.5	2.01	3.0	1.66	100 : 4
EtA	10.1	1.44	30.8	2.74	100 : 85
	24.8	1.97	18.2	3.84	100 : 21
VL	10.1	1.44	7.4	1.45	100 : 20
	24.8	1.97	4.7	1.97	100 : 5
CL	6.6	1.40	23.9	1.76	100 : 89
	24.5	2.01	6.9	2.01	100 : 7

a) Determined by GPC using standard polystyrene. b) Determined by ^{1}H NMR. Polymerization was carried out at 0 °C.

trolled block copolymerization using the unique dual catalytic function of $[LnR(C_5Me_5)_2]$ (Ln = Sm, Yb, and Lu; R = H, Me) complexes toward polar and nonpolar olefins.[113] Ethylene was copolymerized with MMA first by the homopolymerization of ethylene (17—20 mmol) with $[SmMe(C_5Me_5)_2(THF)]$ or $[SmH(C_5Me_5)_2]_2$ (0.05 mmol) at 20 °C in toluene under atmospheric pressure, and then sequential addition of MMA (10 mmol) (Table 10). The initial step proceeded very rapidly, completed in 2 min, and gave a polymer of M_n = ca. 10100 and $M_w/M_n = 1.42$—1.44. However, the second step was rather slow, with the reaction taking 2 h at 20 °C (Scheme 26). The polymer obtained was soluble in 1, 2-dichlorobenzene and 1,2,4-trichlorobenzene at 100 °C but insoluble in THF and $CHCl_3$. This fact indicates quantitative conversion to the desired linear block copolymer. Repeated fractionation in hot THF did not change the molar ratio of the polyethylene and poly(MMA) blocks, though poly(MMA) blended with polyethylene can easily be extracted with THF. With the copolymerization, the elution maximum in GPC shifted to a higher molecular weight region, with its initial unimodal pattern unchanged. The relative molar ratio of the polyethylene and poly(MMA) blocks was controllable at will in the range of 100 : 1 to 100 : 103 if the M_n of the initial polyethylene was fixed to ca. 10300. ^1H and ^{13}C NMR spectra for the copolymers as well as their IR absorption spectra were superimposable onto those of the physical mixtures of the respective homopolymers. The molar ratio of the poly(MMA) and polyethylene blocks, however, decreased as the M_n of the prepolymer increased, especially when its exceeded ca. 12000 at which value polyethylene began precipitating as fine colorless particles. It is noteworthy that smooth block copolymerization of ethyl acrylate or methyl acrylate to the growing polyethylene chain (M_n = 6600—24800) can be realized by the sequential addition of the these monomers.

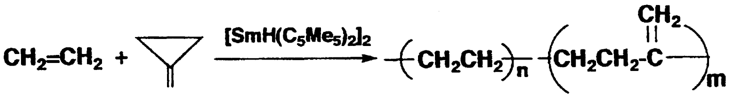


Scheme 26.

Yasuda et al.[114] extended the above work to the block copolymerization of ethylene with lactones. δ-Valerolactone and ε-caprolactone were incorporated to the growing polyethylene end at ambient temperature and the expected AB type copolymers (100 : 1 to 100 : 89) were obtained in high yield. Reversed addition of the monomers (first MMA or lactones and then ethylene) induced no block copolymerization at all, even in the presence of excess ethylene, and only homo-poly(MMA) and homo-poly(lactone) were produced.

The treatment of the resulting block copoly(ethylene/MMA) (100 : 3, M_n = 35000) and block copoly(ethylene/ε-caprolactone) (100 : 11, M_n = 12000) with dispersed dyes (Dianix AC-E) made them deeply dye with three primary colors, though polyethylene itself was inert to these dyes. Hence, these copolymers can be said to have a very desirable chemical reactivity.

More recently, Yang et al.[114] have examined a new approach in which a reactive functional group was introduced into polyolefins using methylenecyclopropane (Scheme 27). Thus, ethylene (1.0 atm) was copolymerized with methylenecyclopropane (0.25—2.5 mL) using $[LnH(C_5Me_5)_2]_2$ (Ln = Sm, Lu) in toluene at 25 °C, and it was shown that 10—65 of *exo*-methylenes were incorporated per 1000 $-CH_2-$ units. The resulting polymer had a M_w of 66—92×10^3. Yet its M_w/M_n was larger than 4.



Scheme 27.

Conclusions

This article has reviewed recent developments in the rare earth metal initiated polymerization of polar and nonpolar monomers. Most monomers including alkyl methacrylates, alkyl acrylates, alkyl isocyanates, lactones, lactide, cyclic carbonates, ethylene, 1-olefin, conjugated diene, and acetylene derivatives can be polymerized effectively with the help of the versatile function of rare earth metal initiators, except for such monomers as isobutene, vinyl ether, and 3- or 4-vinyl pyridine. The polymerization of them by a single component initiator generally proceeds in living fashion and produces high molecular weight polymers ($M_n > 400000$) of very narrow molecular weight distribution ($M_w/M_n < 1.05$) at high conversion. Thus as a problem to be solved next we face isotactic and syndiotactic polymerizations leading to polymers high enough in molecular weight and narrow enough in its distribution. Such stereospecific polymerization at high temperature is especially important for alkyl (meth)acrylate, styrene and 1-olefins from the industrial point of view. Sophisticated designs of ligands should be attempted for this purpose. Although binary and ternary initiator systems are still in use for a variety of polymerization, it is desirable in the near future to replace them by single component catalysts.

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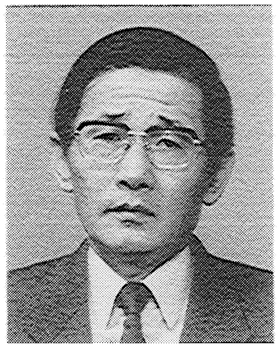

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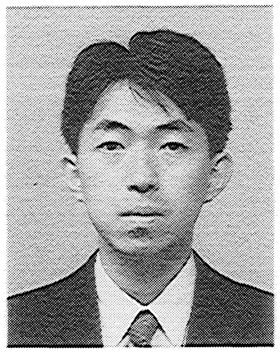

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