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Organo-rare-earth-metal initiated living polymerizations of polar and nonpolar monomers

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Abstract

This review article deals with the rare-earth-metal initiated living polymerizations of polar and nonpolar monomers to give monodisperse high molecular weight polymers at high conversion. A typical example is seen in the polymerization of methyl methacrylate (MMA) with $[SmH(C_5Me_5)_2]_2$ or $LnMe(C_5Me_5)_2(THF)$ ($Ln = Sm, Y$, Lu etc.), giving high molecular weight syndiotactic polymers ($M_n > 1000{,}000$, syndiotacticity $> 95\%$) quantitatively at low temperature (-95 °C). Synthesis of high molecular weight isotactic poly(MMA) with very low polydispercity was for the first time achieved by the efficient catalytic action of $[(SiMe_3)_3C]_2Yb$. Living polymerizations of alkyl acrylates were also possible by the excellent catalysis of $LnMe(C_5Me_5)_2(THF)$ ($Ln = Sm$, Y). By taking advantages of the living polymerization ability, we attempted the ABA-type triblock copolymerization of MMA–butyl acrylate–MMA to obtain rubber-like elastic polymers. Organo-rare-earth-metal complexes such as $LnOR(C_5R_5)_2$ or $LnR(C_5R_5)_2$ conducted the living polymerizations of various lactones such as β-propiolactone, δ-valerolactone and ε-caprolactone, and also conducted the block copolymerizations of MMA with various lactones. C_1-symmetric silylene bridged bulky organolanthanide(III) complexes such as $SiMe_2[2(3),4\text{-}(SiMe_3)_2C_5H_2]_2LnCH(SiMe_3)_2$ ($Ln = La$, Sm, Y) show high catalytic 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 catalytic activity for the polymerization of ethylene, giving $M_n > 10^6$ with $M_w/M_n = 1.6$. Utilizing the high polymerization activity of rare-earth-metal complexes towards both polar and nonpolar monomers, block copolymerizations of olefins with polar monomers such as MMA and lactones were for the first time realized. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rare-earth-metal complex; Polymerization; Alkyl (meth)acrylate; Lactones; Ethylene; Olefins; Styrene; Alkylisocyanates

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1. Introduction

During the period of 1985–1988, Evans developed organo-rare-earth-metal chemistry with bulky ligands and demonstrated some curious reactions, for example, the double insertion of CO molecules into the –N=N– double bond [1]. This prominently interesting chemistry stimulates us to start the reactions of rare-earth-metal complexes with a variety of organometallics. At the end of 1989, we had succeeded in isolating a novel rare-earth-metal complex by the 1:1 reaction of a Yb(II) complex, $(C_5Me_5)_2Yb(THF)_2$, with $AlEt_3$ to give $(C_5Me_5)_2Yb{\cdot}AlEt_3(THF)$ (**1**), whose structure was determined by X-ray analysis (Fig. 1) [2]. This complex is composed of one transition metal and one main-group metal species, indicating a kind of homogeneous Ziegler–Natta catalyst. Therefore, we demonstrated the polymerizations of methyl methacrylate (MMA) and

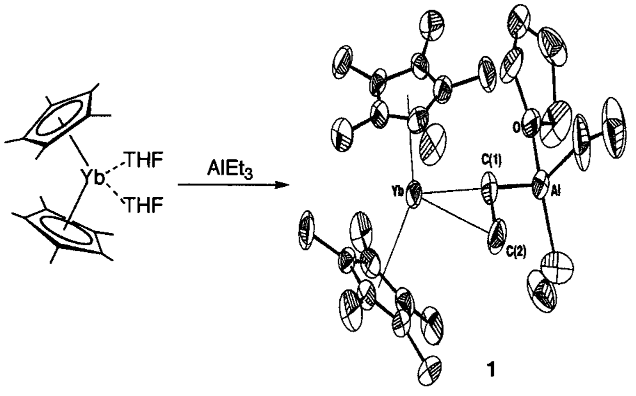

Fig. 1. Formation of $(C_5Me_5)_2Yb{\cdot}AlEt_3(THF)$.

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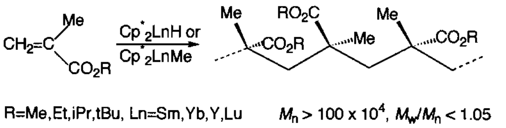
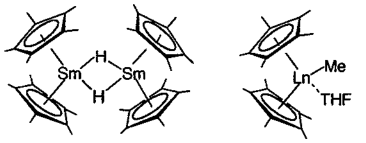


Fig. 2. Organolanthanide initiated syndiotactic polymerization of MMA.



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3, Ln=Sm,Yb

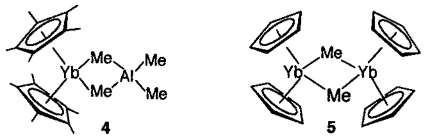

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Fig. 3. Typical initiators used for the living polymerization of MMA.

styrene as typical monomers. As a consequence, the complex **1** was found to exhibit high catalytic activity, especially for MMA, but is inert toward styrene and 1-olefins. A detailed stoichimetric reaction of **1** with MMA revealed the formation of a complicated mixture containing at least four kinds of products. However, divalent complexes are known to be readily oxidized into trivalent metal compounds by the attack of stilbene [3] and diphenylacetylene [4]. Therefore, we examined the catalysis of the trivalent complexes $(C_5Me_5)_2LnR$ (Ln = Sm, Yb, Y, Lu; R = H or Me) [5,6]. The living polymerization of MMA occurred successfully, and this kind of polymerization satisfied the following four requirements for the first time: (1) a number-average molecular weight (M_n) greater than 1×10^6; (2) a molecular weight distribution [weight − average molecular weight/number − average molecular weight (M_w/M_n)] less than 1.05; (3) a syndiotacticity greater than 95%; and (4) a conversion greater than 99% in a short period.

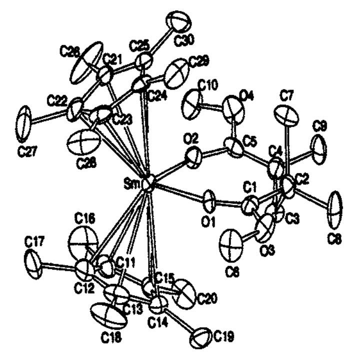
2. Highly stereospecific living polymerization of alkyl methacrylates

Although various living polymerization systems have been reported, no type of anionic [7], cationic [8], Group Transfer [9], and metal carbene initiated polymerizations [10] has ever achieved to this end. In this regard, it is remarkable that high molecular weight poly(MMA)s having an unusually low polydispersity have been synthesized by the use of organolanthanide(III) complexes (Fig. 2). The relevant complexes include lanthanide hydrides **2**, bulky alkyl lanthanide **3**, trialkylaluminum complexes of alkyllanthanides **4**, and simple alkyl complexes **5** synthesized from $LnCl(C_5Me_5)_2$ (Fig. 3). Most of them have been isolated and well-characterized by the single X-ray analysis. The most striking of $[(C_5Me_5)_2SmH]_2$ initiated polymerization of MMA is $M_w/M_n = 1.02–1.04$ for $M_n > 1 \times 10^5$. Remarkably, the $[(C_5Me_5)_2SmH]_2$ complex gives high conversion (polymer yield) in a short period, and allows the polymerization to proceed over a wide range of reaction temperatures from −78 to 60 °C. Furthermore, syndiotacticity exceeding 95% is realized when the polymerization temperature is lowered to −95 °C.

The typical initiator systems reported so far for the synthesis of highly syndiotactic poly(MMA) are bulky alkyllithium $CH_3(CH_2)_4CPh_2Li$ [11], Grignard reagent in THF [12], and some AlR_3 complexes [13]. Although the $CH_3(CH_2)_4CPh_2Li$ initiator in THF reacted rapidly with MMA at −78 °C, the M_n reached only 10,000 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 14,000–18,000 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 $M_n = 19{,}900$ and $M_w/M_n = 1.08$ [14]. $AlEt_3{\cdot}PR_3$ complexes gave high syndiotacticity, but not a high molecular weight.

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 [9]. $Me_2C{=}C(OMe)OSiR_3$ and $R_2POSiMe_3$ can be used as initiators, and tris(dimethylamino)sulfonium bifluoride ($TASHF_2$) and Et_4NCN 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 $M_n = 6300$. Thus, organolanthanide-initiated polymerization is superior regarding the obtaining of monodisperse high molecular weight poly(MMA)s.

These findings motivated us 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. After expending many efforts, we have finally obtained the desired 1:2 adduct as an air-sensitive orange crystal (m.p. 132 °C). The X-ray analysis of the adduct indicates that one of the MMA unit is linked to the metal in an enolate form while at the other end, the penultimate MMA units is coordinated to the metal through its C=O group. Thus eight membered cyclic intermediate was formed (Fig. 4). Although similar cyclic intermediates have been proposed by Bawn et al. and Cram and Copecky for the isotactic polymerization of MMA, no isolation of such active species has succeeded. On the basis of the X-ray structural data as well as the mode of polymerization, we have proposed a coordination anionic



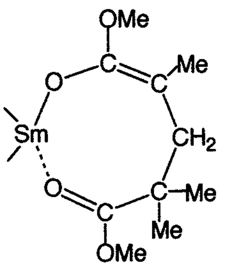


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Fig. 4. X-ray analysis of $Sm(C_5Me_5)_2(MMA)_2H$.

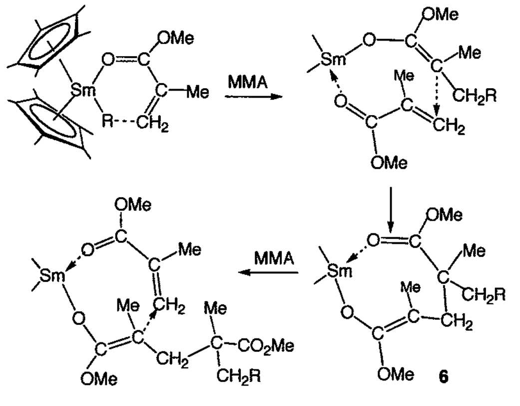


Fig. 5. Reaction mechanism for the syndiotatic polmerization of MMA.

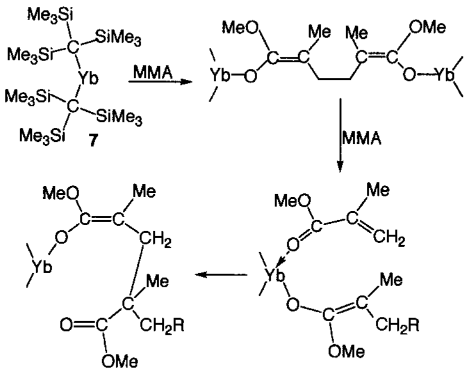


Fig. 6. Proposed mechanism for the isotactic polymerization of MMA.

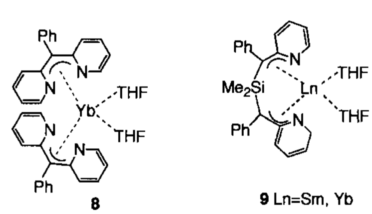


Fig. 7. Initiators useful for the isotactic polymerization of MMA.

mechanism (Fig. 5). 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 eight-membered cyclic intermediate **6** (Fig. 4). Further addition of MMA to the resulting 1:2 addition compound liberates the coordinated ester group and the eight-membered cyclic intermediate is again generated. The intermolecular repulsion between C(7) and C(9) (or the polymer chain) should be the essential factor in determining the syndiotacticity.

Recently, isotactic polymerization of MMA has also been achieved (mm = 94%, $M_n = 1.34 \times 10^5$, $M_w/M_n = 6.7$) by using $Me_2Si(C_5Me_4)[C_5H_3$-(1*S*),(2*S*),(5*R*)-neomenthyl]LaR ($R = CH(SiMe_3)_2$ or $N(SiMe_3)_2$) [15], 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 producing a syndiotactic poly(MMA) (rr = 69%, $M_n = 1.77 \times 10^5$, $M_w/M_n = 15.7$). A possible explanation for this difference is that the menthyl complex produces a syndiotactic polymer via a cyclic eight-membered ring intermediate, while the neomenthyl complex produces an isotactic polymer via a nonlinear intermediate. Therefore, it was concluded that stereoregularity varies with subtle difference in steric bulkiness between the complexes. Actually, high molecular weight isotactic poly(MMA) (mm = 97%, M_n = 220,000) was first obtained quantitatively when the nonmetallocene system, $[(Me_3Si)_3C]_2Yb$ **7**, was used as initiator [16]. We propose here the initiation mechanism for the isotactic polymerization of MMA as shown in Fig. 6. The MMA molecule always coordinates to the metal from the fixed site and the resulting coordination complex rearranges to new enolate via S_N1 reaction mechanism without formation of an eight-membered ring intermediate. Bis[(2-pyridyl)$_2$CPh]Yb(THF) complex **8** and lanthanide (Sm, Yb) complexes of bis(2-pyridylphenylmethyl)dimethylsilane **9** also speed up the isotactic polymerization of MMA (Fig. 7) in the absence of cocatalyst such as MAO or $B(C_6F_5)_3$ [17].

Boffa and Novak found a divalent rare-earth metal complex, $Sm(C_5Me_5)_2$, to be a good catalyst for polymerization of MMA [18]. The bis-allyl initiator, $[Sm(\mu\text{-}\eta^3\text{-}CH_2CHCH)(C_5Me_5)_2]_2$ was also effective for living polymerization of MMA. In this case, MMA must add to both ends of the C_6H_8 group. In the polymerization of MMA initiated with methylaluminum tetraphenylporphyrine, sterically crowded Lewis acid such as methylaluminum(ortho-substituted phenolate) serves as a very effective accelerator without damaging the living character of polymerization [19]. Thus, the polymer obtained by aluminum compound has narrow polydispersity ($M_w/M_n = 1.09$) and sufficiently high molecular weight, M_n = 25,500, but the stereoregularity is very poor.

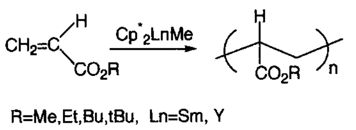


Fig. 8. Living polymerization of alkyl acrylates.

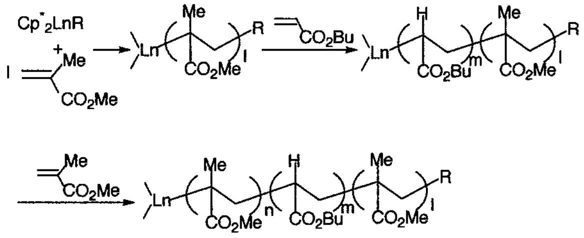


Fig. 9. ABA-type block copolymerization of MMA–BuA–MMA.

In general, Ziegler–Natta catalysts such as $TiCl_4$–$MgCl_2$–AlR_3 and Kaminsky catalysts like Cp_2ZrCl_2–$(AlMe_2\text{-}O\text{-})_n$ 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 [20], allowing syndiotactic poly(MMA) (rr = 80%, $M_n = 120{,}000$, $M_w/M_n = 1.2$–1.3) to be obtained. Recently, Soga et al. [21] reported the syndio-rich polymerization of MMA catalyzed by Cp_2ZrMe_2–$Ph_3CB(C_6F_5)_4$–$ZnEt_2$ and also the isotactic polymerization of MMA catalyzed by *rac*-$Et(ind)_2ZrMe_2$–$B(C_6F_5)_3$–$ZnEt_2$ (mm = 96.5%, $M_n = 39.3 \times 10^4$, $M_w/M_n = 1.43$).

3. Living polymerization of alkyl acrylates

In general, the living polymerizations of alkyl acrylates are very difficult because the chain transfer or termination occurs easily, owing 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 [23] as well as the Group Transfer polymerization of ethyl acrylate with ZnI_2 as the catalyst [9]. Porphyrinatoaluminum initiator systems also induced the living polymerization of *t*-butyl acrylate [22], but the upper limit of molecular weight attained was ca. 20,000. We have 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 nonstereospecific [24] (Fig. 8). The initiator efficiency exceeded 90% except for *t*BuA. Thus, initiation occurs in a quantitative fashion. This reaction should proceed in a living manner, because the M_n of poly(BuA) initiated by $SmMe(C_5Me_5)_2(THF)$ increased linearly in proportion of the conversion, while M_w/M_n remained unchanged, irrespective of the initiator concentration. In order to establish the characteristic nature of these initiation sytems, the initiator concentration was decreased from 0.1 to 0.002 mol% and high molecular weight poly(EtA) of $M_n = 400{,}000$ with narrow molecular weight distribution ($M_w/M_n = 1.05$) was obtained.

ABA-type triblock copolymerization of MMA–BuA–MMA should give rubber-like elastic polymers, because the resulting copolymers 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. The first step of polymerization of MMA gave M_n of 15,000 with $M_w/M_n = 1.04$ and then a mixture of MMA and BuA was added to this growing end to result in the formation of the desired ABA-triblock copolymer (BuA polymerized more rapidly than MMA) (Fig. 9). Table 1 shows the typical mechanical properties of the ABA-type copolymers thus obtained. It is seen that homo–poly(MMA) has large tensile modulus and large tensile strength, but is poor in elongation and shows very large compression set. In contrast, the triblock copolymer (8:72:20) shows a 58% compression set and a large elongation (163%), indicating that this polymer is a thermoplastic elastomer. The triblock copolymer of MMA–EtA–EtMA in the ratio of 26:48:26 also showed large elongation and small compression set as well as large tensile modulus and tensile strength. Thus, elastic copolymers of methacrylate and acrylate were for the first time obtained by using living polymerization ability.

4. Block copolymerization of hydrophobic and hydrophilic acrylates

Trimethylsilyl methacrylate (TMSMA) was found to speed up the living polymerization with the $SmMe(C_5Me_5)_2(THF)$ initiator to give high molecular weight syndiotactic polymer ($M_n = 56{,}000$, rr = 92%) with very low polydispersity ($M_w/M_n = 1.09$). By utilizing this nature, we have performed the block copolymerization of TMSMA with MMA or butyl acrylate to obtain the adhesive materials upon hydrolysis of the resulting polymer [25]. Thus, block copolymerization of TMSMA (67 mmol) with MMA (124 mmol) gave after the hydrolysis thermally stable adhesive materials ($M_n = 28{,}100$, $M_w/M_n = 1.17$) in high yield (ca. 100%) for the first time (Fig. 10).

Table 1
Mechanical properties of triblock copolymers

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

5. 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. Pattern and Novak 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 [26]. When hexyl isocyanate was added to $TiCl_3(OCH_2CF_3)$ the polymerization took place at room temperature to give 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. 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 ($M_w/M_n = 2.08–3.16$) [27]. Furthermore, it was shown that butyl, isobutyl, octyl and *m*-tolyl isocyanates were polymerized using lanthanum isopropoxide as the initiator. When the reaction temperature was raised to ambient temperature, only cyclic trimers were produced at high yields. More recently, we have found that $La(C_5Me_5)_2[CH(SiMe_3)]_2$ **10** also initiates the polymerization of butyl isocyanate and hexyl isocyanate at 50–60% yields at 0 °C [28] (Fig. 11). $Sm[2,6\text{-}(i\text{PrO})_2C_6H_5]_3$ **11** also showed the good catalytic activity for polymerizations of hexyl isocyanate and butyl isocyanate at 25 °C [29].

6. Living polymerization of lactones

$AlEt_3–H_2O$ or $AlEt_3$-catalyzed polymerizations of 3-methyl-β-propiolactone and ε-caprolactone have been reported [30,31], but this polymerization generally gives a broad molecular weight distribution. We have 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 component 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 [32]. 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 and show bimodal pattern [33]. 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 to produce **12**, as is the case for the reaction of YCl_3 with ε-caprolactone, giving the first six-coordinate-mer complex, YCl_3·(ε-caprolactone)$_3$ **13** in which each caprolactone molecule is coordinated as a monodentate ligand through its carbonyl oxygen [34] (Fig. 12). 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

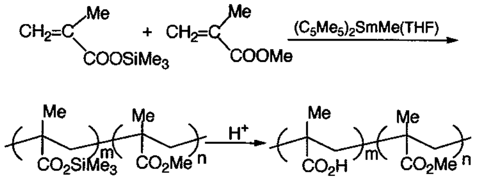


Fig. 10. Block copolymerization of MMA with TMSMA.

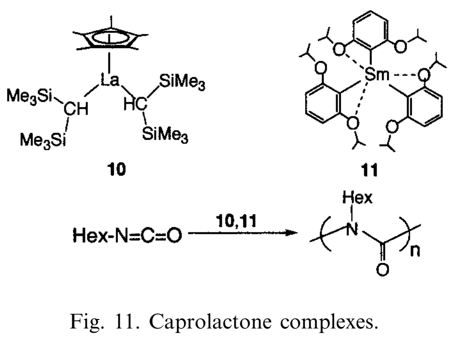
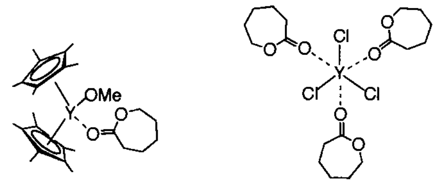


Fig. 11. Caprolactone complexes.



12 **13**

Fig. 12. Living polymerization of alkyl isocyanate.

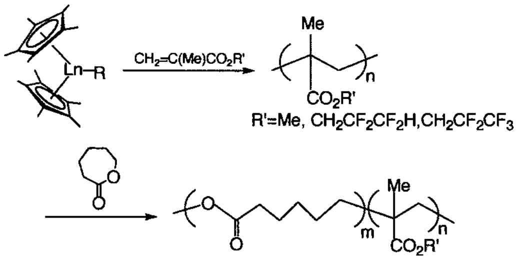


Fig. 13. Copolymerization of alkyl methacrylates with caprolactone.

group to produce Ln[O(CH$_2$)$_5$C(O)OR](C$_5$Me$_5$)$_2$(ε-caprolactone). In the (C$_5$Me$_5$)$_2$SmMe initiator system, the reaction is started by the attack of ε-caprolactone or δ-valerolactone to M–R group to result in the formation of an acetal which was followed by ring opening. This process has been confirmed by ^{13}C-NMR studies of the stoichiometric reaction products.

Anionic block copolymerizations of alkyl methacrylates with lactones proceeded smoothly to give copolymers with $M_w/M_n = 1.11–1.23$ when the monomers were added in this order [35]. However, when the order of addition was reversed, no copolymerization took place, i.e. no addition of MMA to the polylactone active end occurred (Fig. 13).

7. 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 [36]. 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 ligands, as shown in Fig. 14 [37]. 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 utilizing 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 two trimethylsilyl groups are located at 2,4- and 3,4-position of each Cp ring. Both were converted to alkyl derivatives (**14** from C$_1$ complex) when they were allowed to react with bis(trimethylsilyl)methyllithium. The Cp′–Sm–Cp′ angle of the racemic-type precursor is 107°, which is about 15° smaller than that of nonbridged SmMe(C$_5$Me$_5$)$_2$(THF).

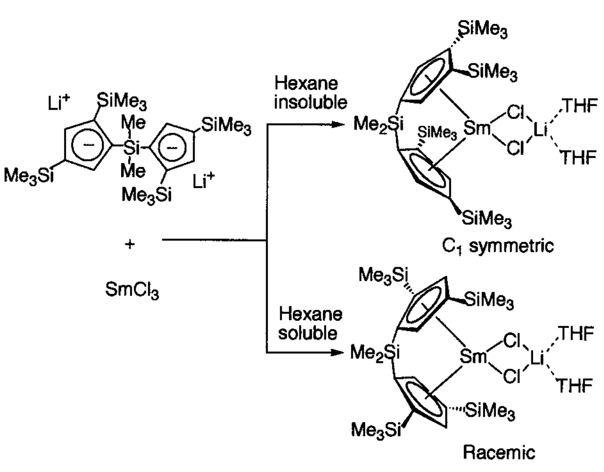


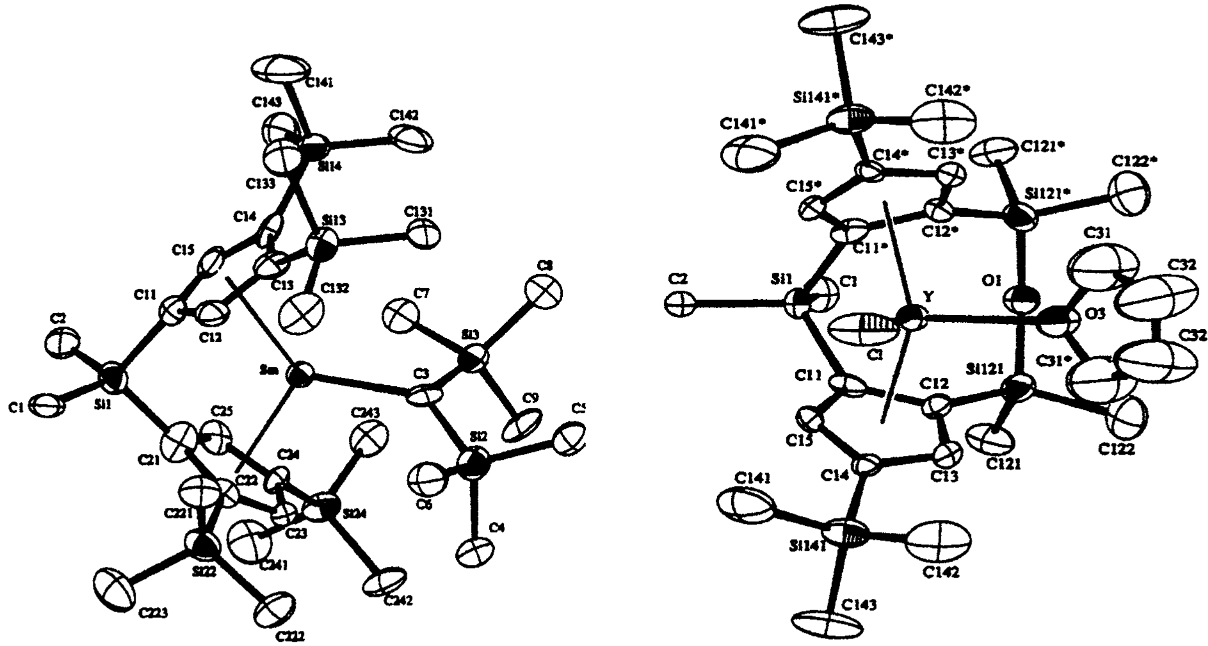
Fig. 14. Synthesis of organo-lanthanides (III) complex.

Meso-type ligands were synthesized by forcing two trimethylsilyl groups to be located at the 4-position of the Cp ligand with introduction of two bridges (complex **15**). 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 (Fig. 15). The *meso*-type alkyl complex was synthesized in a similar manner.

Interestingly, only C$_1$-type complexes can initiate the polymerization, implying that the catalytic activity varies with the structure of the complex. The polymerization of ethylene with (C$_5$Me$_5$)$_2$SmH in the presence of PhSiH$_3$ formed PhH$_2$Si 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 PhH$_2$Si 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) [38].

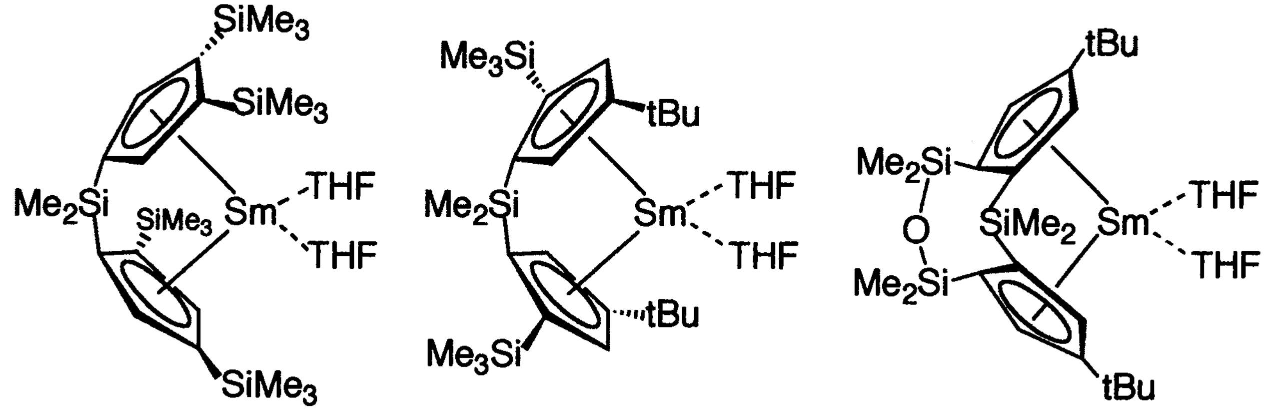
Racemic, *meso*, and C$_1$-symmetric *divalent* organolanthanide complexes (Fig. 16) can be synthesized by allowing the dipotassium salt of the corresponding ligand to react with SmI$_2$ [39] (Fig. 16). The *meso*-type complex **18** has the highest activity (47 g mol^{-1} h atm) for the polymerization of ethylene, but the molecular weights of the resulting polymers are the lowest (M_n = 10,000–40,000). On the other hand, the *racemic* (**17**) and C$_1$-symmetric (**16**) complexes produce much higher molecular weight polyethylene (M_n = 35–

1×10^6) but the activity is rather low (6–14, 1.1–1.6 g mol^{-1} h, respectively). Particularly, the very high molecular weight polyethylene obtained 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) $M_n = 24{,}600$, $M_w/M_n = 1.85$; 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 structure. The poly(1-alkene) obtained revealed highly isotactic structure (> 95%) when examined by ^{13}C-NMR. The dihedral angles of Cp′–Ln–Cp′ of *racemic* and *meso*-type divalent complexes were 115.8 and 116.5°, respectively; these values are much smaller than those of $(C_5Me_5)_2SmMe(THF)$ (136.7°) [40] and $Sm(C_5Me_5)_2$ (140.1°). Therefore, it can be concluded that the complexes having smaller Cp′–Ln–Cp′ angles exhibit 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 *cis–trans* ratio of 55/45 (Fig. 17).



14 **15**

Fig. 15. Three valent organo-lanthanide complexes.



C_1 symmetric Racemic Meso

16 **17** **18**

Fig. 16. Typical divalent organolanthanide initiators.

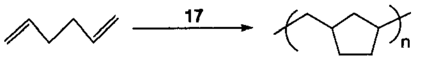


Fig. 17. Ring-closing polymerization of 1,5-hexadiene.

The η^5-complex, bis(Me$_3$Si-fluorenyl)Sm(THF)$_2$ **19**, readily convert to the η^6-complex, bis(Me$_3$Si-fluorene-AlEt$_3$)Sm **20**, in quantitative yield, and the η^6-complex **20** changes again to η^5-complex by the addition of THF [41]. Complex **20** shows relatively high catalytic activity (7556 g mol^{-1} h^{-1} atm^{-1}) for polymerization of ethylene in high yield ($M_n = 53{,}000$, $M_w/M_n = 1.98$) (Fig. 18).

8. Polymerization of styrene

Recent studies showed that the single component initiator [(tBuCp)$_2$LnMe]$_2$ (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 [(tBuCp)$_2$NdMe]$_2$, though stereoregularity was very poor (Fig. 19) [42]. Styrene polymerization was also performed successfully using the single component initiators, [(Me$_3$Si)$_2$N]$_2$Sm(THF)$_2$, [(Me$_3$Si)$_2$CH]$_3$-Sm, and La(C$_5$Me$_5$)[CH(SiMe$_3$)$_2$]$_2$(THF) at 50 °C in toluene without addition of any cocatalyst. The resulting polymers had $M_n = 1.5–1.8 \times 10^4$ and $M_w/M_n = 1.5–1.8$, and show atactic property [28]. 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$_5$Me$_5$)]–(AlMe–O–)$_n$ (syndiotacticity > 95%) [43].

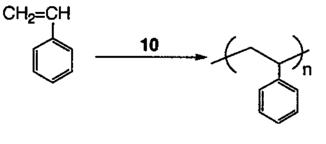
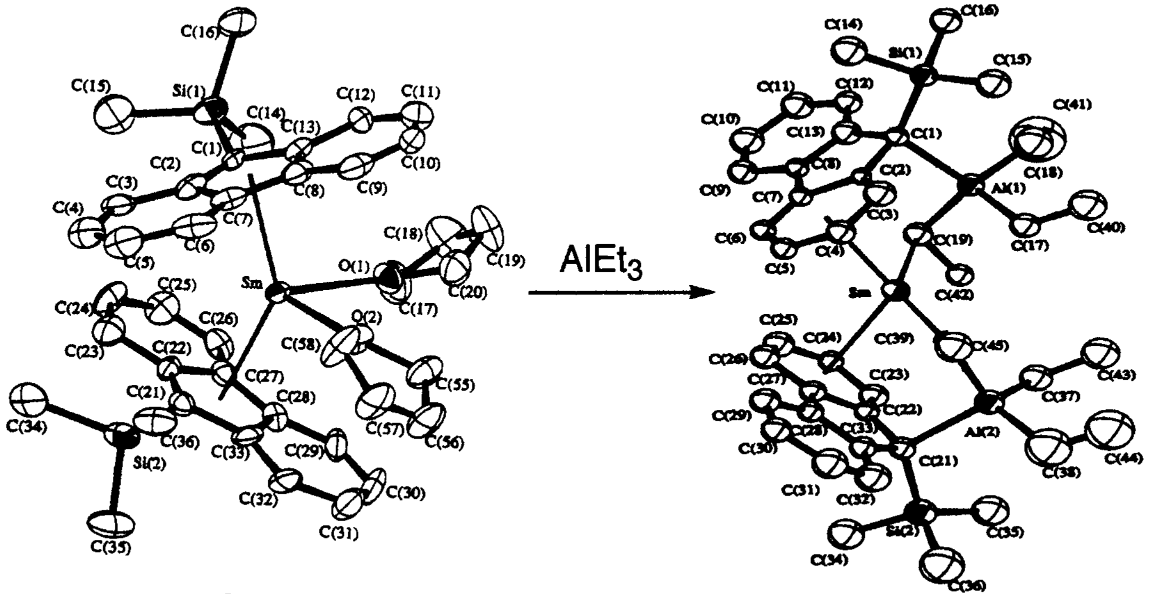


Fig. 19. Styrene polymerization by La(C$_5$Me$_5$)[CH(SiMe$_3$)$_2$]$_2$.

9. Block copolymerization of olefins with polar monomers

Block copolymerizations of ethylene or propylene with polar monomers are yet to be attained in polyolefin engineering. The success of this type of block copolymerization should give hydrophilic polymeric materials having remarkably high adhesive, dyeing, and moisture absorbing properties. The following is the first example of a well-controlled AB-type block copolymerization using the unique dual catalytic function of LnR(C$_5$Me$_5$)$_2$ (Ln = Sm, Yb, Lu; R = H, Me) complexes toward polar and nonpolar olefins [44]. Ethylene was copolymerized with MMA first by the homopolymerization of ethylene (17–20 mmol) with SmMe(C$_5$Me$_5$)$_2$(THF) or [SmH(C$_5$Me$_5$)$_2$]$_2$ (0.05 mmol) at 20 °C in toluene under atmospheric pressure, and then sequential addition of MMA (10 mmol). The initial step proceeded very rapidly, completed in 2 min, and gave a polymer of M_n = ca. 10,100 with $M_w/M_n = 1.42–1.44$. However, the second step was rather slow, with the reaction taking 2 h at 20 °C. The polymer



19 **20**

Fig. 18. η^5–η^6 Conversion of bis(fluorenyl)Sm complex by the reaction of AlEt$_3$.

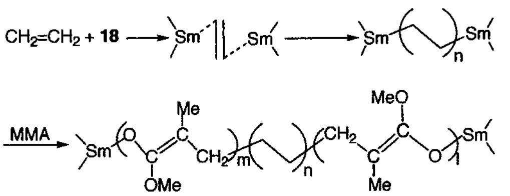


Fig. 20. ABA-type block copolymerizations of ethylene with MMA.

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 100:1–100:103 if the M_n of the initial polyethylene was fixed to ca. 10,300. ^{1}H- 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) to polyethylene blocks, however, decreased as the M_n of the prepolymer increased, especially when it exceeded ca. 12,000 at which value polyethylene began precipitating as fine colorless particles. It is noteworthy that smooth-block copolymerization of ethyl or methyl acrylate to the growing polyethylene chain ($M_n = 6600–24,800$) can be realized by the sequential addition of the two monomers.

The above work was extended 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 (100:1–100:89) 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, $M_n = 35,000$) and block copoly(ethylene–ε-caprolactone) (100:11, $M_n = 12,000$) 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.

ABA-type triblock copolymerizations of MMA–ethylene–MMA and ε-caprolactone–ethylene–ε-caprolactone were realized using divalent organolanthanide complex **18** following Fig. 20 [45].

Block copolymerizations of higher olefins such as 1-pentene or 1-hexene with polar monomers like MMA or ε-caprolactone [47] (Figs. 21 and 22) were first obtained using dinuclear 3-valent lanthanide hydride **21**, **22** [46]. The order of the addition should follow the addition of olefins first and then the addition of polar monomers. The crude product is composed of two kinds of polymers as evidenced by GPC analysis and the extraction of the products using hot hexane gives rise to the remaining of the block copolymers which shows the the unimodal pattern by GPC. The ratio of olefin to polar monomer unit can be varied at a will

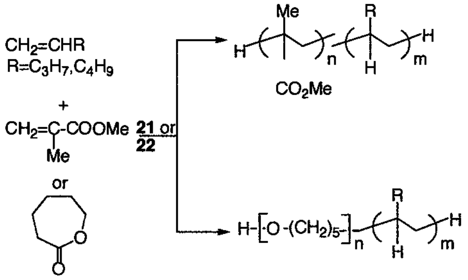
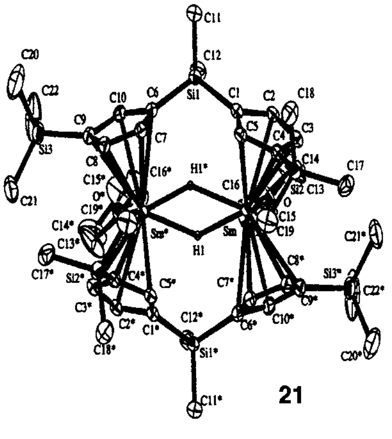


Fig. 22. Block copolymerization of olefins with polar monomers.



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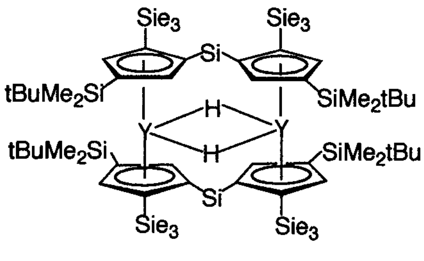

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Fig. 21. Trivalent organo-hydrolanthanides.

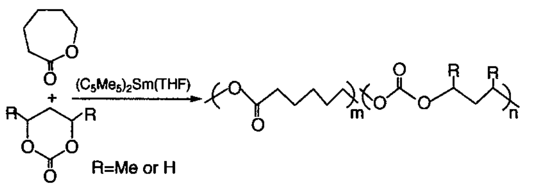

Fig. 23. Syntheses of biodegradable copolymers.

from 5/1 to 1/5 by adjusting the feed ratios of two monomers.

10. Syntheses of biodegradable polymers

Lanthanide tris(2,6-di-*t*Bu-phenolate) shows efficient catalytic activities for polymerization of ε-caprolactone and L-lactide in the presence of suitable amount of *i*PrOH to give high molecular weight polymers with extremely low molecular weight distribution in high yield at 22 °C [48]. In a similar manner, the copolymerizations of ε-caprolactone with chiral cyclic carbonates such as 1-Me–trimethylenecarbonate and 1,3-Me_2–trimethylenecarbonate using $Sm(C_5Me_5)_2Me$-(THF) produce the desired copolymers with high molecular weights and low polydispersities (Fig. 23). The polydispersity is especially low compared with the polymers obtained by conventional initiators. The polymers composed of ca. 18/82 ratio showed the maximum biodegradability as examined by activated sludge and enzymes (cholesterol esterase, lipoprotein lipase) [49]. As a consequence, the copolymer composed of ε-caprolactone with *racemic* 1-Me- or 1,3-Me_2–trimethylenecarbonate (17/83–19/82 ratio) showed excellent biodegradability. A similar result was obtained by the copolymerization of L-lactide with 1-Me–trimethylenecarbonate [50].

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