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Tetrahedron 59 (2003) 10409–10418

TETRAHEDRON

Isospecific polymerizations of alkyl methacrylates with a bis(alkyl)Yb complex and formation of stereocomplexes with syndiotactic poly(alkyl methacrylate)s

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Received 24 April 2003; accepted 30 July 2003

Abstract—Yb[C(SiMe$_3$)$_3$]$_2$ initiates the living polymerization of methyl methacrylate (MMA) at −78°C to give the polymer with M_n of 51.0×10^4 (M_w/M_n=1.1) and high isotacticity (97%) in a quantitative yield. Mixing of the acetone solution of resulting polymer (M_n=16.3×10^4) with the acetone solution of syndiotactic poly(MMA) (M_n=15.7×10^4) prepared by the (C$_5$Me$_5$)$_2$SmMe(THF) initiator produces desired stereocomplex in high yield bearing very high T_m whose tensile modulus is higher than the respective isotactic and syndiotactic poly(MMA)s. Yb[C(SiMe$_3$)$_3$]$_2$ also generated isotactic (98%) poly[2-(dimethylamino)ethyl methacrylate] (DMEMA), and (C$_5$Me$_5$)$_2$SmMe(THF) affords the syndiotactic (97%) polymer in high yields. The combination of isotactic poly(MMA)-*block*-poly(DMEMA) (97/3) and syndiotactic poly(MMA)-*block*-poly(DMEMA) (97/3) provides the amphiphathic stereocomplex. In sharp contrast to the catalysis of Yb[C(SiMe$_3$)$_3$]$_2$ in toluene, the addition of THF or HMPA resulted in the formation of syndio-rich poly(MMA).

1. Introduction

Novel rare earth metal initiators such as SmMe(C$_5$Me$_5$)$_2$-(THF) **1** or [SmH(C$_5$Me$_5$)$_2$]$_2$ have been found to realize the highly syndiotactic poly(MMA) (>95%) with high molecular weight (M_n>100×10^4) and low polydispersity (M_w/M_n<1.05) in a quantitative yield by the unique living polymerization.[1,2] Since this reaction proceeds in a living fashion, we could isolate the 1:4 stoichiometric reaction product between [SmH(C$_5$Me$_5$)$_2$]$_2$ and methyl methacrylate (MMA), which could be analyzed by X-ray analysis to include an eight-membered ring. By the further addition of 100 equiv. of MMA, this adduct shows the excellent catalytic activity giving a polymer of ca. M_n=10000 with extremely low polydispersity (M_w/M_n=1.02) in a quantitative yield. This sort of initiator also displays high catalytic efficiency for living polymerizations of alkyl acrylates,[3] lactones,[4] and cyclic carbonates.[5] More recently, polymerizations of MMA using trimethylsilyl- and bis-(trimethylsilyl)-substituted bis(cyclopentadienyl)-samariummethyl complexes were carried out to reduce the cost of initiator from the industrial point of view.[6]

On the other hand, the preparation method for high molecular weight isotactic poly(MMA)s has not been established until now. The molecular weights obtained so far for isotactic polymer (>96%) are only 12000–20800 by the use of BuMgBr or *t*-BuMgBr in toluene.[7,8] Therefore, we have explored a variety of metallocene complexes such as cyclopentadienyl(indenyl)SmMe-(THF) and cyclopentdienyl(fluorenyl)SmMe-(THF) for fixation of the reaction site to one direction. However, all the attempts failed, since these initiators always produce the syndiotactic polymers. Therefore, we have next examined the polymerization using a variety of non-metallocene type rare earth metal complexes. As a consequence, Yb[C(SiMe$_3$)$_3$]$_2$ was found for the first time to generate high molecular weight isotactic poly(MMA)s in high yield. Then we have explored the synthesis of stereocomplex by mixing the acetone solution of the resulting syndiotactic and isotactic poly(MMA)s. As an extension of this reaction, we are succeeded in preparation of both syndiotactic and isotactic poly[2-(dimethylamono)ethylene methacrylate] (DMEMA) using SmMe(C$_5$Me$_5$)$_2$(THF) or Yb[C(SiMe$_3$)$_3$]$_2$, respectively (Scheme 1).

Keywords: rare earth metal complexes; methyl methacrylate; 2-(dimethylamino)ethyl methacrylate; stereocomplex; dialkylytterbium complex; dialkylsamarium.

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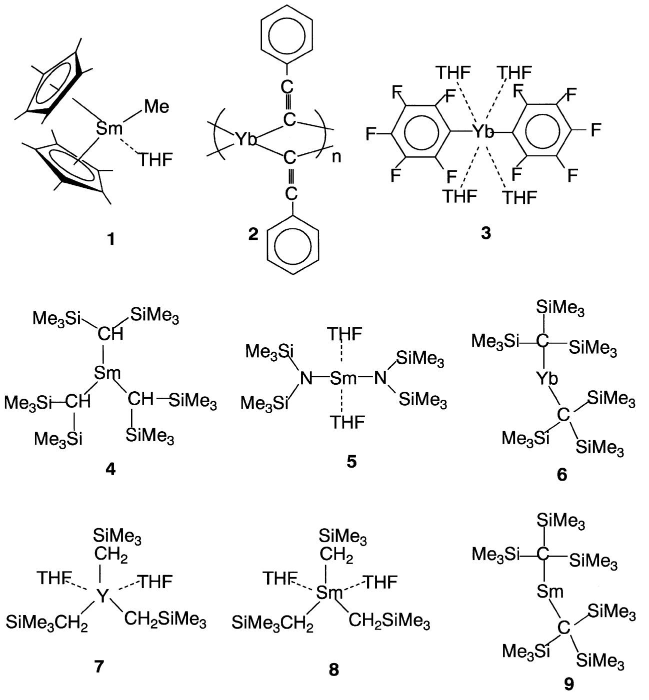
doi:10.1016/j.tet.2003.07.014



Scheme 1. Non-metallocene type initiators used for the polymerizations.

2. Results and discussion

2.1. Preparation of isotactic poly(MMA) with high molecular weight

In order to realize the isotactic poly(MMA) (isotacticity >90%) with high molecular weight (M_n>200000), we have explored the polymerizations using $Et_2Si(C_5H_4)(C_5Me_4)YH$ and (C_5H_5)(fluorenyl)SmMe(THF) for fixation of the reaction site at the less bulky (C_5H_5) direction by the assistance of bulky C_5Me_4 or fluorenyl group. However, the polymerizations always produce only syndiotactic poly(MMA)s (78 and 82%, respectively) with high molecular weights (M_n=6–8×10^4) and low polydispersities (M_w/M_n=1.15–1.27) at 0°C.

Therefore, we have explored the catalysis of non-metallocene type rare earth metal complexes using $(perfluorophenyl)_2Yb(THF)_4$ **2**,[9] $Ln(C{\equiv}CPh)_2$ **3**,[10] $Sm[CH(SiMe_3)_2]_3$ **4**,[11] $Sm[N(SiMe_3)_2]_2(THF)_2$ **5**,[12] and $Yb[C(SiMe_3)_3]_2$ **6** (Fig. 1).[13] As a consequence, all of these complexes exhibit excellent catalysis by themselves at −78°C toward the polymerization of MMA without presence of any cocatalyst such as methylaluminoxane (MAO) or metal oxide (Table 1). $(Perfluorophenyl)_2$-$Yb(THF)_4$ and $Ln(C{\equiv}CPh)_2$ produced syndiotactic poly(MMA)s in high yields, and $Sm[CH(SiMe_3)_2]_3$ and $Sm[N(SiMe_3)_2]_2(THF)_2$ produced atactic poly(MMA)s in

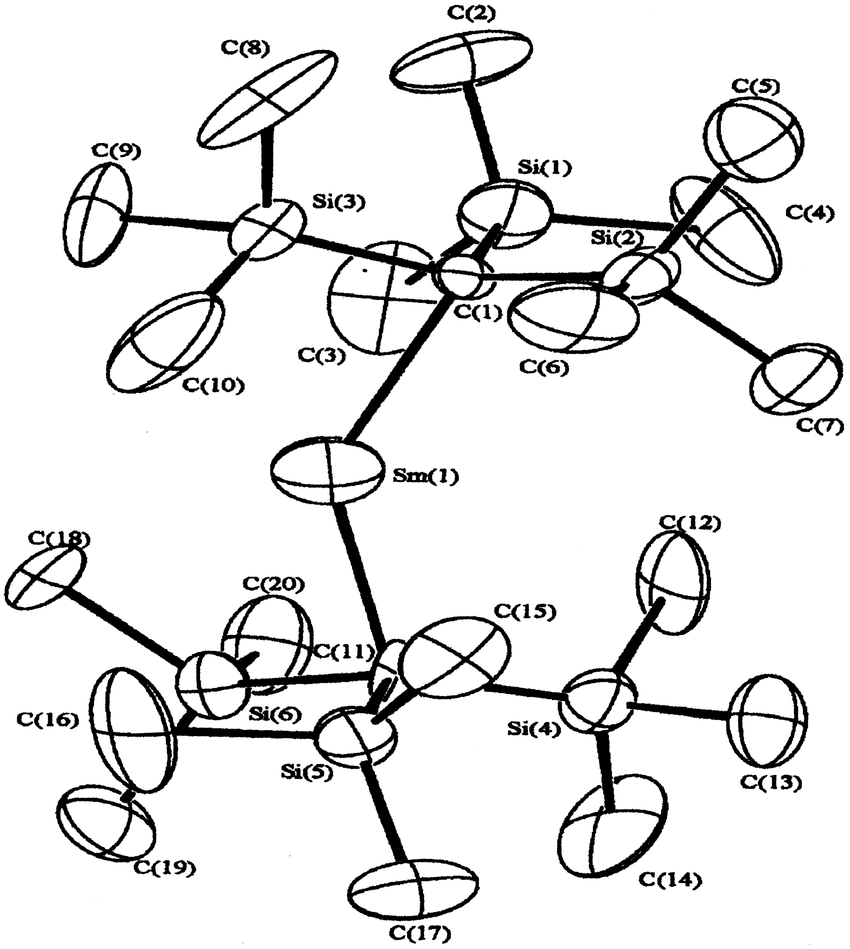


Figure 1. Molecular structure of **9**.

Table 1. Polymerizations of methyl methacrylate with non-metallocene complexes[a]

Initiator	Temperature (°C)	Time (h)	Yield (%)	$M_n/10^4$	M_w/M_n	rr	mr	mm
$(PhC{\equiv}C)_2Yb$[b] **2**	0	20	0					
	−78	6	52	7.7	1.5	83	8	9
	−78	20	100	12.1	1.5	82	8	10
$(C_6F_5)_2Yb(THF)_4$ **3**	0	20	0					
	−78	6	67	3.0	1.3	82	17	1
	−78	20	100	4.4	1.2	80	18	2
$[(Me_3Si)_2N]_2Sm(THF)_2$ **4**	0	20	0					
	−78	6	21	0.6	1.2	27	34	39
	−78	20	35	0.7	1.3	27	35	38
$[(Me_3Si)_2CH]_3Sm$ **5**	0	20	13	0.5	2.0	45	34	21
	−78	6	3	3.3	1.4	49	42	9
	−78	20	5	6.6	1.4	50	41	9
$[(Me_3Si)_3C]_2Yb$ **6**	0	20	98	15.3	1.2	9	13	78
	−78	6	75	32.7	1.2	1	2	97
	−78	20	100	51.0	1.1	1	2	97

[a] Polymerization conditions: $[M]_0/[I]_0$=1000 mol/mol, solvent toluene, toluene/$[M]_0$=2.0 vol/vol.

moderate yields. In contrast to these initiators, we have found that $Yb[C(SiMe_3)_3]_2$ produced high isotactic poly(MMA) in excellent yield as evidenced from ^1H NMR spectrum (Me, 1.18 ppm in $CDCl_3$ while that of syndiotactic polymer at 0.88 ppm). Resulting M_n is 51.0×10^4 and M_w/M_n is 1.1. To understand more precise reaction conditions, the monomer/initiator ratio was varied using a very pure complex (Table 2). When the reaction temperature was fixed to −78°C and the reaction time to 3 h, we could obtain isotactic (97%) poly(MMA) with M_n of 49.9×10^4 by using $[M]_0/[I]_0$ ratio of 2900 mol/mol. The use of decreased $[M]_0/[I]_0$ ratio of 200 mol/mol at −78°C resulted in the formation of M_n of 3.2×10^4 with high isotacticity (97%). Thus, M_n increased linearly with an increase of $[M]_0/[I]_0$ ratio suggesting the occurrence of living polymerization. To further confirm the livingness, two step polymerization was carried out, i.e. polymerization of MMA (500 equimole) first takes place for 3 h at −78°C using $Yb[C(SiMe_3)_3]_2$ as an initiator. Resulting M_n is $7.3\times10_4$ (M_w/M_n=1.1) in 100% yield, and then further addition of 500 equimole of MMA followed by the polymerization at −78°C resulted in the formation of poly(MMA) having M_n of 15.2×10^4 (M_w/M_n=1.3) in 100% yield (in total 200% yield). This behavior clearly indicates the occurrence of living polymerization.

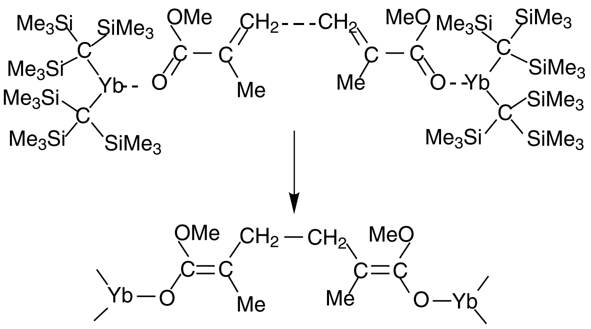
The syndiotactic polymerization of MMA proceeds via an eight-membered ring containing Sm atom as revealed by the X-ray analysis of $(C_5Me_5)_2Sm(MMA)_2H$ species.[1,2] Isotactic polymerization should occur by the enantiomorphic site control. The divalent species should be converted to trivalent species by the addition of MMA as shown in Scheme 2.

Table 2. $Yb[C(SiMe_3)_3]_2$ initiated polymerization of MMA

$[M]_0/[I]_0$	Yield (mol/mol)	M_n (%)	M_w/M_n 10^4	Tacticity		
				mm	mr	rr
200	>99	3.2	1.2	97	2	1
500	>99	7.3	1.2	97	2	1
1000	>99	16.3	1.1	97	2	1
2000	>99	32.2	1.2	97	2	1
2900	>99	49.9	1.2	97	2	1
500[a]	28	3.2	1.7	1	12	87
1000	0.8	–	–	–	–	–

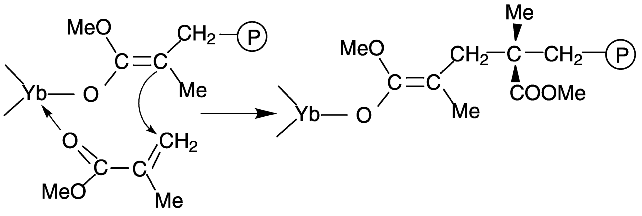
Polymerization conditions: −78°C for 3 h in toluene. [toluene]/$[M]_0$=3.0 vol/vol.

[a] −78°C for 3 h in THF.



Scheme 2. Reaction mode for initiation of MMA polymerization.

In fact, head-to-head dimer of MMA could be isolated by the hydrolysis of 1:1 reaction mixture in 67% yield. Isotactic polymer should be formed without formation of an eight-membered ring intermediate, holding the linear structure as described in Scheme 3.



Scheme 3. Reaction mechanism for initiation of MMA polymerization.

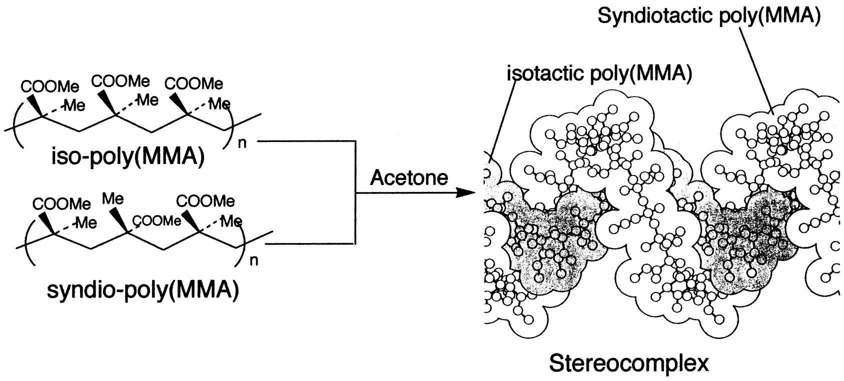
2.2. Formation of high molecular weight stereocomplex of poly(MMA)

Recently, preparation of stereocomplexes using low molecular weight isotactic and syndiotactic poly(MMA) has been reported.[14] Since we could prepare both high molecular isotactic and syndiotactic poly(MMA)s using $Yb[C(SiMe_3)_3]_2$ and $(C_5Me_5)_2SmMe(THF)$, respectively,

Table 3. Preparation of stereocomplexes between syndiotactic and isotactic poly(MMA)

Iso/syndio ratio (mol/mol)	Yield (%)	T_m (°C)	T_g (°C)
1/3	43	207	94.3
1/2	83	208	94.6
1/1	52	204	93.8
2/1	15	204	93.2

Stereocomplexes were obtained as a gel by mixing of syndiotactic poly(MMA) with isotactic poly(MMA) dissolved in acetone.



Scheme 4. Formation of high molecular weight stereocomplexes.

we explored the synthesis of high molecular weight stereocomplexes by the addition of the acetone solution of isotactic poly(MMA) to the acetone solution of syndiotactic poly(MMA). Gel formation occurred immediately after mixing these two solutions as white precipitates. The addition of isotactic poly(MMA) ($M_n=16.3\times10^4$, $M_w/M_n=1.11$) to 2 equimolar amount of syndiotactic poly(MMA) ($M_n=15.7\times10^4$, $M_w/M_n=1.01$) provides highest yield of the stereocomplex (Table 3), whose molecular structure was proposed by Challa et al. to be 9/1 double-stranded helix (isotactic polymer is surrounded by syndiotactic poly(MMA) (Scheme 4).[15,16] This product exhibits high T_m of 208°C. The 1/3 and 2/1 addition of isotactic polymer to syndiotactic polymer yielded the stereocomplex in only 43 and 15%, respectively, whose T_m are 207 and 204°C. The composition of gel is iso/syndio=ca. 1/2 regardless the 1/3 or 2/1 addition of iso/syndio polymers, as analyzed by GPC in $CHCl_3$ (stereocomplex is dissociated into respective iso- and syndiotactic polymers in $CHCl_3$). These polymers show intermediate T_g between isotactic poly(MMA) ($T_g=55$°C) and syndiotactic poly(MMA) ($T_g=130$°C). An annealing of the resulting 1/2 stereocomplex in the DSC cell at 180 and 200°C for 5 days resulted in the increase of T_m to 208 and 228°C, respectively, due to the thermodynamic phase transition (Table 4). We used four kinds of different molecular weight poly(MMA)s with either high isotactic or syndiotactic regulation to construct the stereocomplexes, i.e. syn-1: syndiotacticity 95%, $M_n=13.2\times10^4$, $M_w/M_n=1.04$, syn-2: syndiotacticity 93%, $M_n=38.2\times10^4$, $M_w/M_n=1.08$, iso-1: isotacticity 98.5%, $M_n=16.5\times10^4$, $M_w/M_n=1.20$, iso-2: isotacticity 98%., $M_n=35.7\times10^4$, $M_w/M_n=1.20$. The gel formation occurred in high conversion (89–95%) by mixing iso-1 with syn-1 or by mixing iso-2 with syn-2 in the 1/2 molar ratio, while gel formation between iso-2 and syn-1 markedly decreased. However, the gel formation between iso-2 with syn-1 in 1/4 ratio indicates high yield. In this case, isotactic polymer should be surrounded by two equimoles of the syndiotactic polymer chain.

Table 4. Effect of annealing temperature on T_m

Iso/syndio ratio (mol/mol)	Annealing temperature (°C)	T_m (°C)
1/2	180	210
1/2	200	228

Heated for 5 days.

Mechanical properties of the stereocomplex are examined using the isolated gel. In order to prepare rigid films, we dissolved the gel to $CHCl_3$ followed by the addition of acetone (2/1 vol/vol ratio) and then the solution was gradually evaporated to precipitate the film samples. Table 5 shows the result of mechanical properties for iso-1/syn-1, iso-2/syn-2 stereocomplexes together with homopoly(syn-1) and homopoly(iso-1). Syn-1 exhibits high tensile strength and high tensile modulus, while iso-1 has high elongation. The stereocomplex composed of iso-1/syn-1 shows a little smaller tensile modulus, whereas iso-2/syn-2 stereocomplex revealed higher tensile modulus (131.2 kgf/mm^2) than syn-2 homopolymer (116.1 kgf/mm^2). Tensile strengths of stetreocomplexes indicate the intermediate value between iso-1 and syn-1 polymers, while the elongation was lower than the homopolymers. Thus, stereocomplexes exhibit rigid structure with high tensile modulus and high tensile elongation.

Table 5. Mechanical properties of stereocomplexes and homopoly(MMA)

Polymers	Tensile modulus (kgf/mm^2)	Tensile strength (kgf/mm^2)	Elongation (%)
Iso-1	30.2	8.0	435.2
Syn-1	116.1	42.9	42.9
Iso-1/syn-1	96.3	35.6	12.4
Iso-2/syn-2	131.2	30.7	9.8

Film samples were prepared by evaporation of acetone/$CHCl_3$ (1/2 vol/vol) mixture.

2.3. Preparation of high molecular weight syndiotactic and isotactic poly[2-(dimethylamino)ethyl methacrylate]

As an extension of the present studies, we have explored the polymerization of 2-(dimethylamino)ethyl methacryrate (DMEMA) using $SmMe(C_5Me_5)_2(THF)$ and

Table 6. Polymerizations of 2-(dimethylamono)ethyl methacrylate with $Cp^*_2SmMe(THF)$

$[M]_0/[I]_0$ (mol/mol)	Temperature (°C)	Time (h)	Yield (%)	M_n	M_n 10^4	Tacticity		
						mm	mr	rr
100	25	0.5	100	1.1	1.18	1	21	78
200	0	1	100	1.9	1.08	1	13	86
300	−78	5	99	3.0	1.14	0	3	97
600	−78	5	99	5.3	1.20	0	3	97
1200	−78	5	98	9.4	1.22	0	3	97

Polymerization conditions, solvent toluene, toluene/$[M]_0$=3.0 vol/vol.

$Yb[C(SiMe_3)_3]_2$ as initiators. Resulting polymers exhibit high molecular weights and are soluble in water freely. Due to growing concerns on environmental protections, water-soluble polymers have undergone a fast development. Cationic polyelectrolites are now a center of growing interest in view of their various applications in areas such as flocculation, adhesives, emulsion and dispersion stabilizer.[17,18] In this regard, the anionic polymerization of DMEMA, the quaternization of which is straightforward, has been considered to be promising. To our best knowledge, the only preceding report on its anionic polymerization has been published by Nazarov and Jerome, who used butyllithium[19] and diphenylmethyllithium/LiCl,[20] respectively, as initiators. The polymerizations of DMEMA were also reported using living radical initiators.[21,22] We wish to report here its polymerizations and copolymerizations with rare earth metal compounds.

The polymerization of DMEMA proceeded expectedly by using $(C_5Me_5)_2SmMe(THF)$ to provide for the first time highly syndiotactic polymers with high molecular weight and low polydispersity (Table 6). The polymerization completes in 4 h at −78°C giving polymers quantitatively with M_n of 9.2×10^4 in the case of $[M]_0/[I]_0$=1200 mol/mol. Syndiotactcity reached 97%. The use of higher polymerization temperatures resulted marked decrease of syndiotacticity.

Isotactic poly(DMEMA) was also available using $Yb[C(SiMe_3)_3]_2$ as an initiator. The M_n was measured in water (see Section 4). The polymer yield reached 99% when we used $[M]_0/[I]_0$ ratio of 200 mol/mol at −78°C (Table 7). However, increasing polymerization temperature to 25°C lacks the catalytic activity, presumably due to the thermal instability of the intermediate because of the formation of unstable alkyl complex. Thus, isotacticity of 97% was realized at −78°C.

The attempt to construct the stereocomplex by mixing the water solution of isotactic and syndiotactic poly(DMEMA)s failed, because of the formation of water-insoluble fraction (yellow powder) only in very low yield (2 wt%).

Therefore, block copolymerizations of DMEMA with MMA were carried out with $(C_5Me_5)_2SmMe(THF)$ or $Yb[C(SiMe_3)_3]_2$ (Table 8). The use of excess MMA (MMA/DMEMA=96/4) resulted in high yield of block copolymers composed of 97/3 ratio (Scheme 4). The mixing of the acetone solutions of the resulting isotactic and syndiotactic block copolymers immediately generates the stereocomplex as a gel (Table 9). Resulting polymer serves as a novel amphipathic molecule toward both organic solvent and water. The formation of stereocomplex was confirmed by observing the high temperature of T_m [homo iso- and syn-poly(MMA) do not show T_m values]. Resulting

Table 7. Polymerizations of 2-(dimethylamino)ethyl methacrylate with $Yb[C(SiMe_3)_3]_2$

$[M]_0/[I]_0$ mol/mol	Temperature (°C)	Time (h)	Yield (%)	M_n	M_n 10^4	Tacticity		
						mm	mr	rr
200	25	1	11	1.5	4.53	16	21	63
200	0	1	34	1.6	3.85	21	30	49
200	−78	5	99	3.0	1.35	98	1	1
500	−78	5	89	8.7	1.74	98	2	0
1000	−78	5	45	12.5	2.11	98	2	0

Polymerization conditions, solvent toluene, toluene/$[M]_0$=5.0 vol/vol.

Table 8. Block copolymerization of DMEMA with MMA

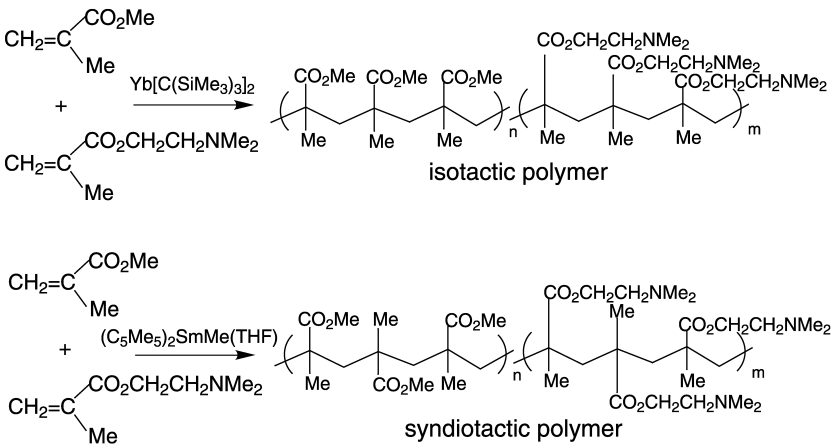
Initiator	$[M]_0/[I]_0$ (mol/mol)	Feeded ratio DMEMA/MMA	Yield (%)	Composition DMEMA/MMA	M_n	M_n 10^4	Tacticity		
							mm	mr	rr
Cp^*_2SmMe	200	4/96	99	3/97	9.5	1.16	0.1	6.2	93.7
$Yb[C(SiMe_3)_2]_2$	200	4/96	99	3/97	9.4	1.28	92.4	5.1	2.5

Polymerization conditions, DMEMA was polymerized for 0.5 h followed by the polymerization of MMA for 3 h at −78°C. Polymerization conditions; solvent toluene.

Table 9. Stereocomplex between isotactic poly(MMA-*co*-DMEMA) and syndiotactic poly(MMA-*co*-DMEMA)

Polymer	Iso/syn ratio, feeded ratio	Iso/syn, found	Yield (%)	T_m (°C)	T_g (°C)
iso-Poly(MMA-*co*-DMEMA)/syn-poly(MMA-*co*-DMEMA)	1.0/2.0	1.0/2.0	85	198	110
iso-Poly(MMA-*co*-DMEMA)/syn-poly(MMA)	1.0/2.0	1.0/2.1	78	196	113

Acetone solution of isotactic poly(MMA-*co*-DMEMA) was mixed with syndiotactic poly(MMA-*co*-DMEMA).



Scheme 5. Block copolymerizations of MMA with DMEMA.

stereocomplexes exhibit no solubility in acetone and THF, but are soluble freely in $CHCl_3$ (Scheme 5).

2.4. Polymerizations of MMA with $Ln(CH_2SiMe_3)_3$

To compare with the catalysis of divalent $Ln[C(SiMe_3)_3]_2$, those of trivalent $Ln(CH_2SiMe_3)_3$ was studied using Y and Sm complexes. $Y(CH_2SiMe_3)_3(THF)_2$ **7** and $Sm(CH_2SiMe_3)_3(THF)_2$ **8** were prepared according to the known method.[23] The polymerization was carried out in both toluene and THF (Table 10). The complex **7** produced iso-rich polymer at ambient temperature, while the atactic polymerization preferred by lowering the reaction temperature in toluene. The reason is not clear at present. Similar trend was observed using complex **8** as an initiator. In contrast to the behavior in toluene, the polymerizations in THF generate syndio-rich polymers especially at low temperatures using complex **7**. Similar behavior was also observed using the complex **8**. This is presumably due to the occurrence of chain control by the coordination of strong donor. Nearly the same result was obtained by the addition of HMPA (hexamethylphosphorous triamide) to $Yb[C(SiMe_3)_3]_2$, i.e. $Yb[C(SiMe_3)_3]_2$/HMPA (1:5 molar ratio) affords the syndio-rich poly(MMA) in 99% yield at −78°C by stirring for 10 h, whose M_n is 38.5×10^4 ($M_w/M_n=2.5$), and tacticity is mm/mr/rr=2/27/71.

2.5. Polymerization of other monomers with $Yb[C(SiMe_3)_3]_2$ or $Sm[C(SiMe_3)_3]_2$

$(C_5Me_5)_2SmMe(THF)$ has high catalytic activity for polymerizations of ε-caprolactone (CL) as reported previously.[4] $Yb[C(SiMe_3)_3]_2$ also showed high catalytic activity for polymerizations of ε-caprolactone at ambient temperature. This system yielded the polymer ($M_n=6.6\times10^4$, $M_w/M_n=1.58$) after 2 h in quantitative yield, when we used $[M]_0/[I]_0$ ratio of 500 mol/mol. However, we failed random or block copolymerization of DMEMA with CL, due to the preferred polymerization of ε-caprolactone in 35–37% yield at 0°C, although the block copolymerization proceeds in high yield (91%) between MMA and CL (MMA was first polymerized at −78°C for 3 h followed by the copolymerization with CL at 25°C for 3 h in toluene). M_n is 2.6×10^4 ($M_w/M_n=1.25$) when we employed $[M]_0/[I]_0$ ratio of 150 mol/mol and MMA/CL ratio of 50/50 mol/mol. Resulting MMA/CL ratio in the block copolymer is 52/48 mol/mol.

Table 10. Polymerizations of MMA with $Ln(CH_2SiMe_3)_3$ in toluene and THF

Initiator	Solvent	Temperature (°C)	Yield (%)	M_n	M_n 10^4	Tacticity		
						mm	mr	rr
$Y(CH_2SiMe_3)_3$	Toluene	−78	99	18.2	1.65	29	43	28
		0	69	7.5	2.52	64	24	12
		25	55	4.1	3.15	70	20	10
	THF	−78	99	14.1	1.60	2	26	72
		0	88	5.6	1.55	7	34	59
		25	45	3.4	1.47	10	36	54
$Sm(CH_2SiMe_3)_3$	Toluene	−78	99	13.3	1.72	40	37	23
		0	99	5.6	1.98	73	18	9
		25	55	3.7	2.35	75	19	6
	THF	−78	99	10.5	1.85	1	15	84
		0	72	7.9	1.76	5	29	66
		25	33	4.5	1.72	6	33	61

$[M]_0/[I]_0$ ratio=200 mol/mol, solvent/[M]=2.0 vol/vol.

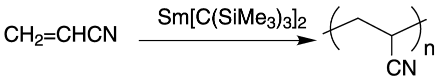
Relating complex, $Sm[C(SiMe_3)_3]_2$, exhibits less activity for polymerizations of MMA as compared with $Yb[C(SiMe_3)_3]_2$. The exact molecular structure of $Sm[C(SiMe_3)_3]_2$, which was prepared from SmI_2 and $(SiMe_3)CK$ (see Section 4) was determined by X-ray analysis (Fig. 1). Resulting complex is Sm(II) species, containing no donor molecules. The Sm–C bonds are 2.58 Å and the C–Sm–C angle is 143.4°. The polymerization of MMA using $[M]_0/[I]_0$ ratio of 200 mol/mol at 0–25°C for 2 h gave only 8–17% yield. At these temperatures, 74–65% of isotacticities and M_n of 43×10^4 ($M_w/M_n=1.14$) were observed.

However, the catalysis of $Sm[C(SiMe_3)_3]_2$ toward the polymerizations of acrylonitrile is much higher than $Yb[C(SiMe_3)_3]_2$ (Table 11, Scheme 6). The polymer yield reaches 55% when the polymerization was carried out in the bulk state. The resulting M_n is $2.5–2.8\times10^4$ and molecular weight distributions were relatively narrow. In sharp contrast to alkyllanthanide complexes, metallocene type rare earth metal complexes such as $(C_5Me_5)_2SmMe(THF)$ or $[(C_5Me_5)_2SmH]_2$ are completely inert toward the polymerizations of acrylonitrile.

Table 11. Polymerization of acrylonitrile with $Sm[C(SiMe_3)_3]_2$

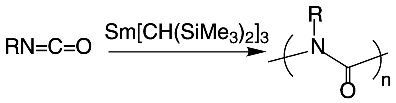
$[M]_0/[I]_0$ (mol/mol)	Temperature (°C)	Time (h)	Yield (%)	M_n 10^4	M_w/M_n
200	25	4	21	2.6	1.68
200	0	4	35	2.5	1.49
200	−78	4	55	2.9	1.38

Polymerization was conducted in the bulk state.



Scheme 6. Polymerizations of alkyl isocyanates.

Although metallocene type rare earth metal complexes also show no catalytic activity for polymerizations of alkyl isocyanate, $Sm[CH(SiMe_3)_2]_3$[11] revealed moderate activities toward the polymerizations of hexyl isocyanate and butyl isocyanate at −40 to −78°C, due to the presence of strong inductive effect of alkyl group (Scheme 7). Table 12 summarizes the polymerizations of alkyl isocyanates. When the polymerizations were carried out at temperatures higher than 0°C, an alkyl isocyanate converted into cyclic trimer quantitatively by holding the solution for 2 h. The polymer yield increases to 57 to 62% by the addition of THF to toluene at −78°C. M_n was 10.4×10^4 ($M_w/M_n=1.4–1.5$) and sometimes M_n reached 116×10^4.



Scheme 7. Polymerizations of acrylonitrile.

Table 12. Polymerizations of alkyl isocyanates with $Sm[CH(SiMe_3)_2]_3$

Monomer	Temperature (°C)	Time (h)	Toluene/THF (mL)	Yield (%)	M_n 10^4	M_w/M_n
HexylNCO	−40	15	15.0/0.0	39	5.2	3.65
	−78	15	15.0/0.0	11	116.2	1.78
	−78	12	7.0/0.8	57	10.4	1.57
BuNCO	−40	15	15.0/0.0	43	3.5	9.71
	−78	12	7.0/0.8	62	9.8	1.45

Polymerization conditions; initiator concentration 1.0 mol% of monomer.

3. Conclusion

The isotactic living polymerization of MMA was realized using $Yb[C(SiMe_3)_3]_2$ as a novel initiator at −78°C, giving the polymer with M_n of 51.0×10^4 ($M_w/M_n=1.1$) and high isotacticity (97%). Mixing of the acetone solution of the isotactic poly(MMA) ($M_n=16.3\times10^4$) with the acetone solution of syndiotactic poly(MMA) ($M_n=15.7\times10^4$) generates a stereocomplex bearing very high T_m in high yield, whose tensile modulus is higher than respective isotactic and syndiotactic homopoly(MMA)s. $Yb[C(SiMe_3)_3]_2$ also produced highly isotactic (98%) poly[2-(dimethylamino)ethyl methacrylate] (DMEMA), and $(C_5Me_5)_2SmMe(THF)$ affords highly syndiotactic (97%) polymer in quantitative yields. The mixing of isotactic poly(MMA)-*block*-poly(DMEMA) (97/3) and syndiotactic poly(MMA)-*block*-poly(DMEMA) (97/3) provides the desired stereocomplex. $MCH_2SiMe_3(THF)_2$ (M=Y, Sm) conducts the syndiotactic polymerizations of MMA at ambient temperature while the atactic polymerization preferred by lowering the reaction temperature. The catalysis of $Sm[C(SiMe_3)_3]_2$ toward the polymerization of acrylonitrile is higher than $Yb[C(SiMe_3)_3]_2$ $Sm[CH(SiMe_3)_2]_3$ revealed a moderate activity for polymerization of hexyl isocyanate.

4. Experimental

4.1. General methods

All the operations were performed under argon by using standard Schlenk techniques. Tetrahydrofuran (THF) and toluene were dried first over CaH_2 for 1 week, then over Na metal, and distilled before use. Commercially available MMA (Aldrich) was dried over CaH_2 for 10 days, then distilled, and further dried over molecular sieves 4A for more than 5 days. $SmCl_3(THF)_2$ was gifted from Rhodia, France. ^1H NMR spectra were recorded on a JEOL JMN-LA400 spectrometer. Chemical shifts were calibrated with $CHCl_3$ in $CDCl_3$ at 7.26 ppm. Elemental analysis was performed on a Perkin–Elmer-2400 Series II CHNS/O analyzer. Number-average molecular weight (M_n) and molecular weight distributions (M_w/M_n) of polymers were determined by gel permeation chromatography (GPC) on a Tosoh SC-8010 high-speed liquid chromatograph equipped with a differential refractometer with $CHCl_3$ as an eluent at 40°C (flow rate, 1.0 mL). The columns used were TSK gel G5000H, G4000H, G3000H, and G2000H. Molecular weights were determined with a universal curve plotted with polystyrene standards, the M_w value of which were determined by a light scattering method. GPC analysis of poly(DMEMA) was carried out in MeOH/0.1N NaCl aqueous solution (50/50) including 0.5% of triethylamine using Shodex OH-pak SB-805, SB-804, and SB-803 columns at 40°C. The M_n and M_w/M_n were calibrated using poly(ethylene oxide) (M_n=660000 and 25000) and poly(ethylene glycol) (M_n=1470) dissolved in MeOH/0.1N NaCl solution (50/50). GPC analysis of poly(acrylonitrile) was operated on a Tosoh CO-800 instrument using 0.01 M LiCl/DMF solution and HXL-1 and GMHXL2 columns at 35°C. M_n and M_w/M_n were calibrated with polystyrene standards. The glass-transition temperature (T_g) and melting point (T_m) were measured on a Seiko SSC-5100 DSC-22C apparatus. The polymer samples were scanned from −100 to 120°C at a heating rate of 10°C min^{-1} under a nitrogen stream. The T_m and heat of fusion at melting point ($-\Delta H_m$) were determined in the first heating, whereas T_g was determined on the second heating.

4.1.1. Preparation of tris(trimethylsilyl)methane. To $CHBr_3$ (58.1 g, 20 mL, 230 mmol) in THF (450 mL) was added 90 mL of Me_3SiCl (77.1 g, 710 mmol) and the mixture was cooled to −78°C. BuLi dissolved in hexane (800 mmol) was slowly added to the mixture taking over 2 h, and then warmed to 25°C. The reaction mixture was quenched with dilute HCl aqueous solution, and the organic layer was dried over Na_2SO_4. The yellow solution was filtered and distilled under vacuum (80°C/2 mm Hg) to give 38.5 g (166 mmol) of tris(trimethylsilyl)methane as a colorless liquid in 72% yield. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.08 (s, $SiMe_3$), 0.35 (s, CH) ppm.

4.1.2. Preparation of tris(trimethylsilyl)methyl iodide. MeLi in diethyl ether (200 mmol) was dropwise added to 56 mL of $(Me_3Si)CH$ (46.3 g, 199 mmol) in THF (300 mL) at 0°C and the mixture was refluxed for 12 h. To the reaction mixture was added dropwise at −78°C 1,2-diiodoethene (58 g, 200 mmol) dissolved in THF (60 mL). The mixture was stirred at 25°C for 1 h, washed with $Na_2S_2O_3$ aqueous solution, and the organic layer was dried over Na_2SO_4. After the evaporation of the solution to dryness, the residue was extracted with hexane (300 mL). The solution was evaporated to give white–yellow powder of title compound (59.9 g, 165 mmol) in 83% yield. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.24 (s, $SiMe_3$) ppm.

4.1.3. Preparation of tris(trimethylsilyl)methyllithium(Et_2O)$_2$. $(SiMe_3)_3CI$ (65.0 g, 181 mmol) in diethyl ether (210 mL) was dropwise added to a suspension of Li powder (3.14 g, 453 mmol) in diethyl ether (30 mL) at −78°C with vigorous magnetic stirring. The reaction mixture was slowly warmed to room temperature, stirred for 4 h, and centrifuged using glass tube bearing two gateways. The supernatant liquid was filtered through a glass wool to afford a pale yellow ether solution of the title compound in 99% yield. A portion of this solution was treated with 0.1N HCl aq. solution and 0.1N NaOH solution using phenolphthalein as indicator. ^1H NMR (C_6D_6, 400 MHz) δ 3.00 (q, 8H, OCH_2CH_3), 0.89 (t, 12H, CH_2CH_3), 0.40 (s, 27H, $SiCH_3$); ^{13}C NMR (C_6D_6, 100 MHz) δ 66.1 (OCH_2CH_3), 15.0 (OCH_2CH_3), 7.7 ($SiCH_3$), 3.4 (LiCSi) ppm.

4.1.4. Preparation of tris(trimethyl)methylpotassium(Et_2O). *t*-BuOK (12.6 g, 112 mmol) in diethyl ether (150 mL) was added to $LiC(SiMe_3)_3$ (107 mmol) dissolved in diethyl ether (50 mL), and the reaction mixture was refluxed for 20 h. The solution was evaporated to dryness, and the resulting residue was washed with hexane and extracted with benzene (80 mL) at 60°C. The extract was concentrated and cooled to 0°C to afford colorless crystals in 11% yield (3.1 g, 11.5 mmol). ^1H NMR (C_6D_6, 400 MHz) δ 2.99 (q, 4H, OCH_2CH_3), 0.89 (t, 6H, CH_2CH_3), 0.45 (s, 27H, $SiCH_3$) ppm.

4.1.5. Preparation of ytterbiumdiiodide. To a solution of NH_4I (2.54 g, 17.5 mmol) in NH_3 (50 mL) at −78°C was added slowly powdered Yb metal (1.6 g, 9.2 mmol). After stirring at −78°C for 1 h, the cooling bath was removed to allow NH_3 boil away. The resulting green–yellow residue was dried under vacuum at 180°C to afford YbI_2 as yellow powder in 89% yield (3.5 g, 8.2 mmol).

4.1.6. Preparation of bis[tris(trimethylsilyl)methyl]-methylytterbium. To a suspension of YbI_2 (1.15 g, 2.7 mmol) in benzene (40 mL) was added at room temperature a solution of $(Me_3Si)_3CK$ (1.46 g, 5.4 mmol) in benzene (50 mL). After stirring the mixture for 48 h at 25°C, all volatiles were removed by evaporation and the resulting residue was extracted with hexane (40 mL). The solution was concentrated and cooled to −20°C to afford red crystals (plate) of title compound in 54% yield (0.93 g, 1.5 mmol). ^1H NMR (C_6D_6, 400 MHz) δ 0.032 (s, $SiCH_3$) ppm.

4.1.7. Preparation of bis[tris(trimethylsilyl)methyl]-samarium. To a suspension of SmI_2 (1.09 g, 2.7 mmol) in benzene (40 mL) was added at room temperature a solution of $(Me_3Si)_3CK$ (1.46 g, 5.4 mmol) in benzene (50 mL). After stirring for 48 h at 25°C, all volatiles were removed by evaporation and the resulting residue was extracted with hexane (40 mL). The solution was concentrated and cooled to −20°C to afford black needle crystals of title compound in 36% yield (0.48 g, 1.0 mmol). ^1H NMR (C_6D_6, 400 MHz) δ −0.42 (s, $SiCH_3$) ppm.

4.1.8. Preparation of tris(trimethylsilyl)methyl-yttrium(THF)$_2$. Anhydrous yttrium trichloride (1.47 g, 7.6 mmol) was suspended in THF (90 mL) and stirred at 55°C for 30 min. The solution was evaporated to dryness and the resulting $YCl_3(THF)_2$ was suspended in hexane (60 mL) and cooled to −78°C. The hexane solution (60 mL) of Me_3SiCH_2Li (23.0 mmol) was added at once to the hexane solution. The mixture was stirred at 0°C for 3 h, and the filtration gave a white precipitate, which was then extracted with hexane (10 mL×2). LiCl was filtered off, and the solution was concentrated and cooled to −25°C to provide the title complex in 34% yield. ^1H NMR (C_6D_6) δ 0.26 (d, 6H, YCH_2), 0.34 (S, 27H, $SiCH_3$), 1.46 (m, 8H, THF), 3.64 (m, 8H, THF) ppm. Anal. for $C_{20}H_{41}O_2Si_3Y$, calcd C 49.35; H 8.49. Found C 49.20; H 8.61.

4.1.9. Preparation of tris(trimethylsilyl)methyl-samarium(THF)$_2$. $SmCl_3(THF)_2$ (1.35 g, 7.6 mmol) was suspended in hexane (60 mL) and cooled to −78°C. The hexane solution (60 mL) of Me_3SiCH_2Li (23.0 mmol) was added to the hexane suspension. The mixture was stirred at 0°C for 3 h. LiCl was removed by centrifugation, and the solution was concentrated and cooled to −25°C to provide

Table 13. Crystal data and data collection for **9**

Chem form	$C_{20}H_{54}Si_6Sm$	F_{000}	1280.00
Formula weight	613.56	μMo Kα	19.87 cm^{-1}
Color	Black	Temperature	23.0°C
Cryst dimension (mm^3)	0.23×0.20×0.15	Scan-type	$\omega-2\theta$
Crystal system	Monoclinic	$2\theta_{max}$	50.0
Lattice parameters		No of reflections	5127
a (Å)	9.010(4)	Struct. Solution	Direct method (SHELEX86)
b (Å)	23.666(7)	Refinement	Full-matrix least squares
c (Å)	15.691(5)	No of observation	4647
β	95.20(4)°	No of variables	244
V ($Å^3$)	3332.3(2)	GOF	1.64
Space group	$P2_1/n$ (#14)	R	0.118
Z	4	R_w	0.187
D_{calcd}	1.223 g/cm^3		

the title complex in 25% yield. ^1H NMR (C_6D_6) δ 0.24 (d, 6H, YCH_2), 0.33 (s, 27H, $SiCH_3$), 1.44 (m, 8H, THF), 3.64 (m, 8H, THF) ppm. Anal. for $C_{20}H_{41}O_2Si_3Sm$, calcd: C 43.82; H 7.54. Found C 43.67; H 7.78.

4.1.10. X-Ray structure determination. A black needle crystal of **9** was sealed in a glass capillary under argon. The X-ray data were collected at 23°C on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation. No empirical absorption correction was applied. The basic crystallographic parameters are listed in Table 13. Cell constants and the orientation matrix for data collection, obtained from a least-square refinement using the setting angles of 25°, carefully centered reflections in the range $23.41<2\theta<28.77°$ correspond to a primitive monoclinic cell with dimensions. The standard reflections were monitored at every 150 reflections and did not show any significant change. The structure was solved by the direct method and expanded using Fourier techniques. Some non-hydrogen atoms were anisotropically refined, while the rest were isotropically refined. Hydrogen atoms were included but not refined. All the calculations were performed by the use of Crystal Structure crystallographic software package.

4.1.11. Stoichiometric reaction of $Yb[C(SiMe_3)_3]_2$ with MMA. The 1:1 reaction of $Yb[C(SiMe_3)_3]_2$ (1.73 g, 10 mmol) with MMA (1 mL, 10 mmol) takes place at −78°C for 3 h, and the resulting mixture was hydrolyzed with water at 0°C. The organic layer was extracted with hexane (80 mL) and distilled in vacuo to give $MeO(CO)CH(Me)CH_2CH_2CH(Me)(CO)OMe$ in 67% yield. ^1H NMR (C_6D_6) δ 1.18 (d, 6H, Me), 1.88 (m, 4H, CH_2), 2.22 (m, 2H, CH), 3.62 (s, 6H, OMe) ppm. EIMS (relative ratio) m/z 170 (M^+, 6), 139 (M^+-OMe, 25), 11 ($M^+-COOMe$, 15), 108 ($M-2OMe$, 100).

4.1.12. Polymerization of MMA with $Yb[C(SiMe_3)_3]_2$. To a stirred mixture of MMA (3.0 mL, 30 mmol) and toluene (9 mL) cooled to −78°C was added $Yb[C(SiMe_3)_3]_2$ (5.1 mg, 0.03 mmol) dissolved in toluene (1 mL). A mixture was stirred for 3–12 h at a fixed temperature to conduct the polymerization. Resulting polymer was poured into excess methanol to induce the precipitation of the polymer, which was then dried in vacuo.

4.1.13. Block copolymerization of MMA with DMEMA. Block copolymerization of MMA (0.96 mL, 9.6 mmol) with DMEMA (0.07 mL, 0.4 mmol) was carried out using $Yb[C(SiMe_3)_3]_2$ (8.6 mg, 0.05 mmol) or $(C_5Me_5)_2SmMe(THF)$ (29.0 mg, 0.05 mmol) as initiators. Toluene (5 mL) was used as solvent and the polymerization was conducted at −78°C for 3 h. Resulting polymer was poured into excess methanol to precipitate the polymer, which was then dried in vacuo.

4.1.14. Formation of stereocomplex. The acetone solution (10 mL) of isotactic poly(MMA) or poly(MMA-*co*-DMEMA) (0.5 g) was mixed with the acetone solution (10 mL) of syndiotactic poly(MMA) or poly(MMA-*co*-DMEMA) (1.0 g) at ambient temperature. Immediately after mixing, the gel formation occurred. Resulting gel was dried in vacuo. Annealing of the stereocomplexes was carried out at 180 and 200°C for 3–7 days at the DSC cell in an Ar stream. Then the DSC measurement took place after cooling the sample to ambient temperature.

4.1.15. Polymerization of ε-caprolactone with $Sm[C(SiMe_3)_3]_2$. To a stirred mixture of ε-caprolactone (1.11 mL, 10 mmol) and toluene (10 mL) cooled to −78°C was added $Sm[C(SiMe_3)_3]_2$ (43.2 mg, 0.1 mmol) dissolved in toluene (2 mL). A mixture was stirred at 25°C for 2 h to conduct the polymerization. Resulting polymer was poured into excess methanol to precipitate the polymer.

4.1.16. Polymerization of acrylonitrile with $Sm[C(SiMe_3)_3]_2$. To acrylonitrile (1.4 mL, 20 mmol) dissolved in toluene (5 mL) cooled to −78°C was added $Sm[C(SiMe_3)_3]_2$ (43.2 mg, 0.1 mmol) in toluene (2 mL). A mixture was stirred at a fixed temperature for 4 h to conduct the polymerization. Resulting polymer was poured into excess methanol to precipitate the polymer, which was then dried in vacuo.

5. Supporting information available. Crystallographic data for the structural analysis of **9** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 215993. Copies of these informations may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We are indebted to a Grant-in-Aid for Scientific research (Grant No. 14350488) from the Ministry of Education, Culture, Sports, Science and Technology.

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