Anionic polymerization of methyl methacrylate and *tert*-butyl acrylate initiated with the YCl$_3$/lithium amide/*n*BuLi systems

Eiji Ihara *, Naohiro Omura, Tomomichi Itoh, Kenzo Inoue *

*Department of Material Science and Biotechnology, Graduate School of Science and Engineering, Venture Business Laboratory,
Ehime University, 3 Bunkyo-cho, Matsuyama 790–8577, Japan*

Abstract

The anionic polymerization of methyl methacrylate (MMA) was initiated with a mixture of lithium amide of various secondary amines and *n*BuLi in the presence of YCl$_3$, where an Y-ate complex was formed and an amide ligand on Y attacked MMA nucleophilically. In THF at −78 °C, PMMAs with narrow molecular weight distributions were obtained in high yields. The presence of a secondary amino group derived from the initiator at the polymer chain end was confirmed by MALDI-TOF-MS analyses. The initiating system using indoline as a secondary amine was effective for block copolymerization of MMA with *tert*-butyl acrylate (*t*BA), giving poly-(MMA-*b*-*t*BA)s with narrow molecular weight distributions.
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1. Introduction

Transition metal complexes have been utilized as initiators for controlled polymerization of vinyl monomers, where propagating chain ends containing transition metal moiety play an essential role for the control with respect to molecular weight and tacticity of the resulting polymers [1]. One of the possible strategies for such polymerizations is the use of transition metal ate complexes as initiators for anionic polymerization, on the assumption that growing chain end containing transition metal moiety with an anionic charge on the metal center can affect the propagation. Following such a concept, Mardare and Matyjazewski reported anionic polymerization of methyl methacrylate (MMA) using ate complexes of Ni and Pd as initiators [2]. We have also been investigating the initiating ability of ate complexes of Mn, Fe, Co, Ni, Cr, Mo,

W, V, and Nb, generated *in situ* by the reaction of the metal halide of these elements with organolithium compounds [3]. In particular, we have found that ate complexes of Mn, Fe, Mo, and W are effective to control the molecular weight of PMMA, in conjunction with an organoaluminum compound as an additive, giving PMMAs with narrow molecular weight distributions (MWD) in high yields [3a,3b,3c]. Furthermore, when lithium amides of secondary amines were used for the generation of ate complexes of Nb, Mo, and W, the resulting ate complexes bearing the amide group as ligand on the metal center polymerized MMA stereoselectively, giving highly isotactic PMMAs [3f].

In this article, mixtures of lithium amides of various secondary amines and *n*BuLi were reacted with YCl$_3$, expecting that Y-ate complexes with the amide ligands were generated [4]. Then, the initiating ability of the system was investigated for anionic polymerization of MMA and block copolymerization of MMA with *tert*-butyl acrylate (*t*BA).

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* Corresponding author. Fax: +81 89 9278547.
  E-mail address: ihara@eng.ehime-u.ac.jp (E. Ihara).

2. Results and discussion

2.1. Polymerization of MMA initiated with YCl_3/lithium amide of secondary amine/nBuLi systems

On the assumption that an yttrium ate complex bearing four amide ligands can be generated, 4 equiv. of lithium amide of indoline was reacted with YCl_3 in THF at 0 °C–room temperature. Then, the mixture was cooled to −78 °C and 100 equiv. of MMA with respect to YCl_3 was added to examine the initiating ability of the system for anionic polymerization of MMA (Scheme 1). As a result, the polymerization proceeded efficiently, giving a PMMA with a very narrow molecular weight distribution (MWD) in a high yield (run 1 in Table 1). The reaction of 20 equiv. of MMA with the initiating system gave a low molecular weight polymer with a narrow MWD as expected, and the sample was subjected to matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analysis in order to precisely characterize the chain end structure. As shown in Fig. 1, the MS spectrum shows a main set of peaks with an interval of $m/z = 100.1$ in a relatively narrow range of molecular mass ($m/z = 1000$–4500) as expected for a narrow MWD polymer. In addition, the appearance of only one set of peaks in the spectrum indicates the high uniformity of the polymerization with respect to initiation and termination. The chain end structure can be estimated from the m/z value
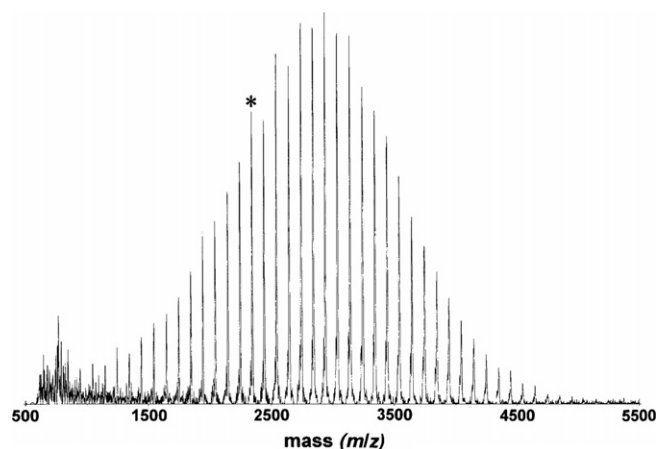

Fig. 1. MALDI-TOF-MS spectrum of PMMA obtained in run 2 in Table 1.

of the spectrum. For example, the value for the peak with * in Fig. 1 is $m/z = 2342.5$, which is close to the calculated value of 2344.73 for a Na-adduct of MMA 22-mer with the amino group derived from indoline at α- and H at ω-chain ends. The result clearly demonstrates that the polymerization was initiated by the nucleophilic attack of the amide of indoline and was quenched by the reaction of the growing end with H^+.

As illustrated in Scheme 2, when the lithium amide of indoline and nBuLi with the [lithium amide]:[nBuLi] ratio
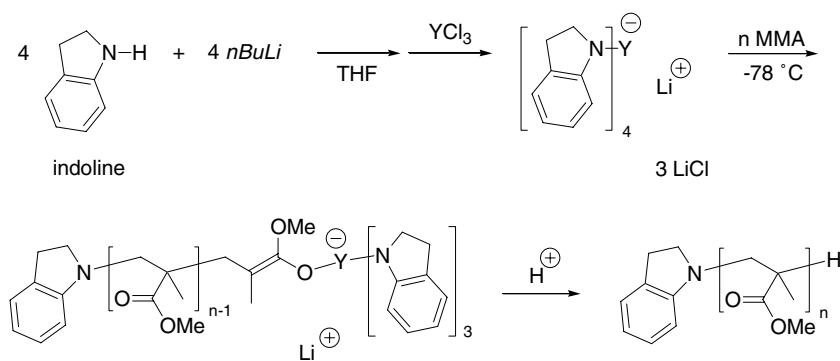
Scheme 1.

Table 1
Polymerization of MMA initiated with the YCl_3/lithium amide of indoline/nBuLi systems[a]

Run	Initiating system [lithium amide]:[nBuLi]:[YCl_3]	[MMA]/[YCl_3]	YCl_3 (mmol)	Yield (%)	M_n 10^{3b}	M_w/M_n[b]
1	4:0:1	100	0.157	91	19.2	1.03
2	4:0:1	20	0.187	100	2.2	1.07
3	3:1:1	100	0.148	92	25.0	1.04
4	2:2:1	100	0.165	92	29.2	1.03
5	1:3:1	100	0.167	92	18.8	1.04
6	1:3:1	20	0.157	100	4.5	1.08
7	0:4:1	100	0.141	44	62.8	3.43
8	2:0:1	100	0.115	No polymerization		
9	3:0:1	100	0.116	91	45.2	1.04

[a] Polymerization conditions: −78 °C for 14 h (runs 1, 3–5, 7–9) or 3 h (runs 2,6) in 10 mL of THF.
[b] Estimated by GPC calibrated by PMMA standards.
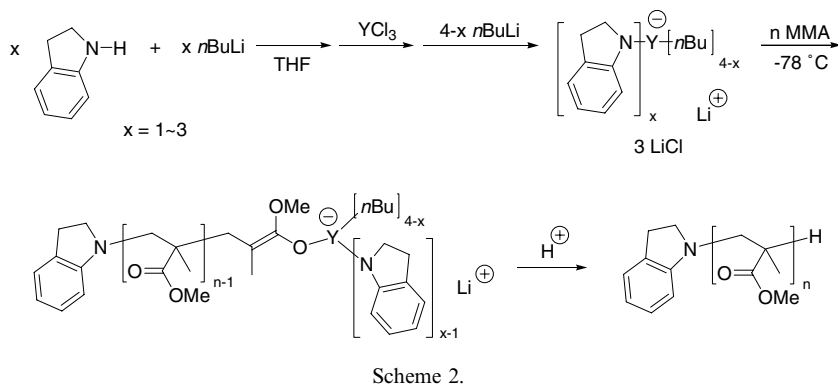
Scheme 2.

of 3:1, 2:2, and 1:3 were successively added to YCl₃ ([YCl₃] × 4 = [lithium amide] + [nBuLi]), the resulting initiating system was able to afford narrow MWD PMMAs by the reaction with 100 equiv. of MMA (Scheme 2 and runs 3–5 in Table 1). Considering the systems generated from the reaction mixtures with such compositions of lithium amide and nBuLi could generate a mixture of ate complexes with various ligand compositions of the amide and nBu groups, it is interesting to note that narrow MWD PMMAs were obtained. Because the system generated from 4 equiv. of nBuLi and YCl₃ did not give a narrow MWD PMMA as shown in run 7 in Table 1 and even the system from [lithium amide]:[nBuLi] = 1:3 gave narrow MWD PMMAs (runs 5 and 6), we can reasonably assume that Y-ate complexes having the amide and nBu groups with a composition expected from the [lithium amide]:[nBuLi] ratio were mainly formed in the initiating systems. As shown in run 8, a mixture of 2 equiv. of the lithium amide with YCl₃ did not polymerize MMA as expected. On the other hand, a mixture of 3 equiv. of the lithium amide with YCl₃ gave a narrow MWD PMMA, whose M_n value was much higher than those of PMMAs in runs 1, 3–5. The result suggests that a small amount of the Y-ate complex with four amide ligand would be generated by the reaction of 3 equiv. of the lithium amide with YCl₃.

MALDI-TOF-MS analysis of the sample obtained in run 6 in Table 1 revealed the presence of the amino group and H at α- and ω-chain end, respectively. Thus, on the presumed structure of the Y-ate complex with amide and nBu ligands, the amide group preferentially attacked MMA to initiate the polymerization.

Although we did not have any direct evidence, we suppose that the mixtures of the lithium amide and nBuLi reacted with YCl₃ to generate Y-ate complexes bearing amide and nBu groups as ligands (whereas it might be possible that nBu–Y would be transformed into H–Y via β-H elimination, we tentatively assume that the nBu remains on the Y center without any evidence throughout this study). The amide group on Y initiated the MMA polymerization, leaving an anionic Y-ate complex as a propagating chain end as illustrated in Schemes 1 and 2. The presence of Y-containing moiety would contribute to the stabilization of the growing chain end, which led to the formation of nar-

row MWD PMMAs. In addition, as the MS analyses of the ω-chain ends indicated, the growing end can survive in the reaction mixture until MeOH was added to quench the polymerization.

It was reported that 3 equiv. of a substituted phenyl anion reacted with SmCl₃ to give a Sm-ate complex bearing four rather sterically bulky ligands, which was isolated and characterized by X-ray analysis [5] (Scheme 3). Although the Sm-ate complex was not effective as an initiator for MMA polymerization [5], the example showed the high tendency of the rare earth elements to form ate complexes by the reaction with organolithium compounds.

Table 2 shows the MMA polymerization results using a variety of secondary amines in the YCl₃/lithium amide/nBuLi systems. In all runs, narrow MWD PMMAs were obtained although the initiation efficiency was rather low in some cases. Except for polymerizations using nBu₂NH and iBu₂NH as amines (runs 18, 20, 22, and 24) where peaks were not observed in the MALDI-TOF-MS analyses, the incorporation of the corresponding secondary amino group at α-chain end and the presence of H at ω-chain end were confirmed by MALDI-TOF-MS analyses for the samples obtained in runs 2, 4, 6, 8, 10, 12, 14, and 16. Thus, these initiating systems can provide a highly efficient method to prepare narrow MWD PMMAs bearing various amino groups at α-chain ends (Scheme 4).

It has been reported that the presence of excess inorganic salt such as LiCl in organolithium-initiated anionic polymerization can stabilize the growing chain end to realize living polymerization of alkyl methacrylates and alkyl acrylates [6]. Because in our YCl₃/lithium amide/nBuLi systems, 3 equiv. of LiCl always exists in the polymerization systems, we examined the effect by conducting
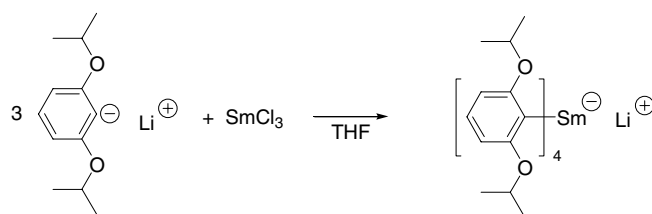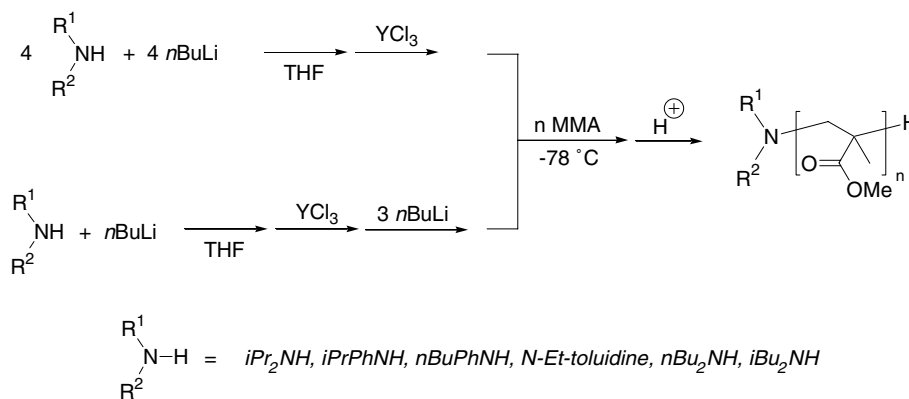

Scheme 3.

Table 2
Polymerization of MMA initiated with the YCl$_3$/lithium amide of secondary amine/nBuLi systems[a]

Run	Initiating system		[MMA]/[YCl$_3$]	YCl$_3$ (mmol)	Yield (%)	M_n 10^{3}[b]	M_w/M_n[b]
	Amine	[lithium amide]:[nBuLi]:[YCl$_3$]					
1	iPr$_2$NH	4:0:1	100	0.228	65	13.3	1.03
2	iPr$_2$NH	4:0:1	20	0.202	100	4.5	1.04
3	iPr$_2$NH	1:3:1	100	0.149	65	34.3	1.04
4	iPr$_2$NH	1:3:1	20	0.212	100	3.4	1.06
5	iPrPhNH	4:0:1	100	0.117	94	59.0	1.06
6	iPrPhNH	4:0:1	20	0.152	100	5.7	1.18
7	iPrPhNH	1:3:1	100	0.109	85	16.3	1.09
8	iPrPhNH	1:3:1	20	0.206	100	5.6	1.25
9	nBuPhNH	4:0:1	100	0.116	100	12.6	1.05
10	nBuPhNH	4:0:1	20	0.214	100	8.0	1.03
11	nBuPhNH	1:3:1	100	0.205	100	17.7	1.08
12	nBuPhNH	1:3:1	20	0.211	100	4.0	1.06
13	N-Et-Toluidine	4:0:1	100	0.165	71	17.2	1.07
14	N-Et-Toluidine	4:0:1	20	0.162	100	5.7	1.16
15	N-Et-Toluidine	1:3:1	100	0.160	73	18.6	1.09
16	N-Et-Toluidine	1:3:1	20	0.201	100	3.9	1.20
17	nBu$_2$NH	4:0:1	100	0.114	78	35.8	1.09
18	nBu$_2$NH	4:0:1	20	0.188	100	3.2	1.16
19	nBu$_2$NH	1:3:1	100	0.181	100	30.6	1.07
20	nBu$_2$NH	1:3:1	20	0.168	100	11.1	1.09
21	iBu$_2$NH	4:0:1	100	0.146	100	55.4	1.05
22	iBu$_2$NH	4:0:1	20	0.231	100	11.9	1.05
23	iBu$_2$NH	1:3:1	100	0.111	100	35.8	1.10
24	iBu$_2$NH	1:3:1	20	0.201	100	8.8	1.09

[a] Polymerization conditions: −78 °C for 3 h ([MMA]/[YCl$_3$] = 20) or 14 h ([MMA]/[YCl$_3$] = 20) in 10 mL of THF.
[b] Estimated by GPC calibrated by PMMA standards.

Scheme 4.

MMA polymerization with lithium amides as an initiator in the presence of 3 equiv. of LiCl in THF at −78 °C (Table 3). As a result, these lithium amide/LiCl systems also gave narrow MWD PMMAs. However, the MWD values are slightly larger than those of PMMAs obtained with YCl$_3$, which difference would be ascribed to the higher stabilizing effect of the Y-ate complex systems on the growing end.

The stabilizing effect of the Y-containing growing end is more obvious for the polymerization at 0 °C. Compared to the polymerization at 0 °C without YCl$_3$ as listed in runs 8–14 in Table 3, PMMAs obtained with YCl$_3$ had much narrower MWDs and the yield were significantly higher as shown in Table 4.

2.2. Block copolymerization of MMA with t-butyl acrylate initiated with YCl$_3$/lithium amide of secondary amine/nBuLi systems

Compared to MMA, anionic polymerization of alkyl acrylates is more difficult to control, basically because of the presence of acidic Hs at the main chain of the resulting poly(alkyl acrylate)s. Although some initiating systems have been reported to be effective for controlling the polymerization [7], control of the anionic polymerization of alkyl acrylates is still a challenging objective. When the YCl$_3$/lithium amide/nBuLi systems using indoline as a secondary amine were reacted with *tert*-butyl acrylate (tBA) in

Table 3
Polymerization of MMA initiated with the lithium amide of secondary amine/LiCl systems[a]

Run	Initiating system		Temperature (°C)	Yield (%)	M_n 10^{3b}	M_w/M_n[b]
	Amine	nBuLi (mmol)				
1	iPr$_2$NH	0.960	−78	100	2.5	1.08
2	iPrPhNH	0.960	−78	100	3.6	1.24
3	nBuPhNH	0.960	−78	100	2.3	1.29
4	Indoline	0.960	−78	100	2.8	1.11
5	N-Et-Toluidine	0.960	−78	100	3.1	1.24
6	nBu$_2$NH	0.960	−78	100	4.6	1.11
7	iBu$_2$NH	0.960	−78	100	5.9	1.04
8	iPr$_2$NH	0.760	0	66	1.2	4.02
9	iPrPhNH	0.760	0	73	2.4	2.09
10	nBuPhNH	0.760	0	71	4.1	1.66
11	Indoline	0.760	0	77	3.4	2.01
12	N-Et-Toluidine	0.760	0	75	2.7	2.47
13	nBu$_2$NH	0.760	0	61	2.3	3.59
14	iBu$_2$NH	0.760	0	47	1.4	3.70

[a] Polymerization conditions: 1 h in 20 mL of THF. [amine] = [nBuLi], [LiCl]:[lithium amide] = 3:1.
[b] Estimated by GPC calibrated by PMMA standards.

Table 4
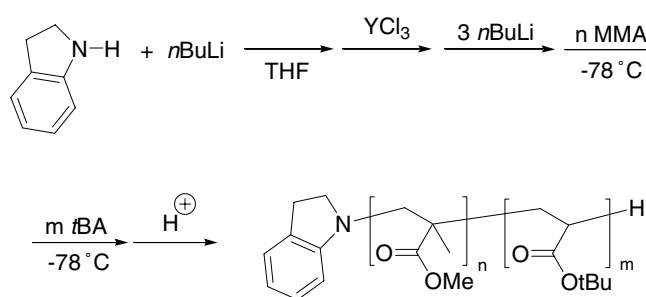Polymerization of MMA initiated with the YCl$_3$/lithium amide of secondary amine/nBuLi systems at 0 °C[a]

Run	Amine	Yield (%)	M_n 10^{3b}	M_w/M_n[b]
1	iPr$_2$NH	84	2.4	1.72
2	iPrPhNH	93	3.1	1.53
3	nBuPhNH	87	3.1	1.37
4	Indoline	87	3.0	1.49
5	N-Et-Toluidine	100	3.4	1.68
6	nBu$_2$NH	91	3.3	1.55
7	iBu$_2$NH	93	3.6	1.69

[a] Polymerization conditions: 0 °C for 3 h in 10 mL of THF.
[b] Estimated by GPC calibrated by PMMA standards.

THF at −78 °C, poly(tBA)s with very broad MWDs were obtained quantitatively. On the other hand, the Y-containing propagating chain end of MMA was found to be able to initiate the polymerization of tBA in a controlled manner. Although the systems with the [lithium amide of indoline]:[nBuLi] ratio of 4:0, 3:1, and 2:2 failed to give narrow MWD copolymers, the system with the ratio of 1:3 afforded copolymers with narrow MWDs. For example, after 20 equiv. of MMA with respect to the initiator was polymerized for 3 h at −78 °C in THF, 50 equiv. of tBA was added to the growing end and the mixture was stirred for 12 h at −78 °C (Scheme 5). The crude product obtained by extractive work-up with CHCl$_3$ and H$_2$O contained a small amount of a low molecular weight byproduct, which could possibly be a PMMA terminated after the first stage polymerization and was removed by preparative recycling GPC. The purified main product obtained in a 76% yield was a narrow MWD poly(MMA-b-tBA), whose composition determined by ^{1}H NMR corresponded to the feed ratio of the two monomers (run 2 in Table 5). As shown in Table 5, by changing the [MMA]:[tBA] ratio in the copolymerization, the composition of the two repeating units in the copolymer changed corresponding to the feed ratio. For this copolymerization, the stabilizing effect of the Y-containing growing end was remarkable, because the lithium amide/LiCl gave a broad MWD copolymer as shown in run 4.

Scheme 5.

Table 5
Block copolymerization of MMA and tBA initiated with the YCl$_3$/lithium amide of indoline/nBuLi system[a]

Run	YCl$_3$ (mmol)	First stage	Second stage	Yield (%)	M_n 10^{3b}	M_w/M_n[b]	[MMA]:[tBA]	
		[MMA]/[YCl$_3$]	[tBA]/[YCl$_3$]				Feed	Copolymer (^{1}H NMR)
1	0.174	20	20	85	10.5	1.09	1:1.0	1:1.30
2	0.164	20	50	76	39.8	1.06	1:2.5	1:3.57
3	0.171	20	100	84	43.9	1.11	1:5.0	1:7.63
4[c]	–	20 ([MMA]/[lithium amide])	50 ([tBA]/[lithium amide])	91	15.5	2.49	1:2.5	1:2.80

[a] Polymerization conditions: −78 °C for 3 h (first stage) and 12 h (second stage) in 30 mL of THF.
[b] Estimated by GPC calibrated by PMMA standards.
[c] Copolymerization initiated with the lithium amide of indoline/LiCl system ([LiCl]:[lithium amide] = 3:1).

3. Conclusions

We have demonstrated that the YCl$_3$/lithium amide of secondary amine/nBuLi systems are effective in preparing narrow MWD PMMAs and poly(MMA-b-tBA)s at −78 °C in THF. Compared to the analogous polymerization with the lithium amide/LiCl systems, the use of YCl$_3$ was proved to be more efficient at affording narrow MWD polymers. Although we do not have any direct evidence, we can reasonably assume that the reaction of YCl$_3$ with lithium amide and nBuLi generates Y-ate complexes whose amide group attacks MMA nucleophilically. The polymerization can be a very efficient method for preparing narrow MWD PMMAs and poly(MMA-b-tBA)s bearing various secondary amino groups at their α-chain ends.

4. Experimental

4.1. Materials

All operations were carried out under nitrogen using standard Schlenk techniques. Tetrahydrofuran was dried over sodium/potassium alloy and distilled before use. MMA (Nacalai, 99.0%) and tBA (TCI, 98%) were dried overnight over CaH$_2$ with stirring, distilled, and kept under nitrogen. n-Butyllithium (Kanto Chemical, 1.6 M solution in n-hexane), YCl$_3$ (Strem, 99.9%), and LiCl (Nacalai, 99%) were used as received. iPr$_2$NH (Nacalai, 99.0%), iPrPhNH (TCI, 98%), nBuPhNH (TCI, 98%), indoline (TCI, >98%), N-Et-o-toluidine (TCI, 98%), nBu$_2$NH (Nacalai, 99.0%), and iBu$_2$NH (Nacalai, 98%) were dried over CaH$_2$, and used as toluene solutions (0.45–0.65 M), whose concentrations were determined by titration with 0.1 N HCl aq. using bromophenol blue as an indicator.

4.2. Polymer characterization and purification

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer using tetramethylsilane (TMS) as an internal standard in chloroform-d (CDCl$_3$) at 50 °C. Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were measured by means of gel permeation chromatography (GPC) on a Jasco-Bowin system (ver. 1.50) equipped with a differential refractometer detector using tetrahydrofuran as eluent at a flow rate of 1.0 mL/min and 40 °C, calibrated with poly(MMA) standards (Shodex M-75, M_n = 2190–653,000, M_w/M_n = 1.03–1.08). The columns used for the GPC analyses were a combination of G6000HHR (TOSOH; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 4000 K for polystyrene), G4000HHR (TOSOH; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 400 K for polystyrene), and G3000HHR (TOSOH; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 60 K for polystyrene).

MALDI-TOF-MS analyses were performed on a PerSeptive Biosystems Voyager RP equipped with 1.3 m linear flight tubes and a 337 nm nitrogen laser (pulse width, 3 ns). All experiments were carried out at an accelerating potential of 20 kV in linear mode under the pressure of ca. (2–3) × 10^{-7} mm Hg. In general, mass spectra from 100 laser shots were accumulated to produce a final spectrum. Angiotensin I (human; MW = 1296.5) (Sigma, 97%), and insulin (bovine pancreas, MW = 5733.50) (Nacalai, 28.0 U/mg) were used as internal standards to calibrate the mass scale. A 1.5 μL portion of the mixture consisting of a polymer solution (100 μL, 10 mg/mL in THF), a matrix, 1,8-dihydroxy-9(10H)-anthracenone (Nacalai, 95%), solution (300 μL, 30 mg/mL in THF), and a cationizing agent, sodium trifluoracetate (TCI, >98%), solution (100 μL, 10 mg/mL in THF) was deposited onto a sample target plate and allowed to dry in air at room temperature.

Purification by preparative recycling GPC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-4H (600 mm × 20 mm i.d., exclusion molecular weight of 500 K for polystyrene) and a JAIGEL-3H (600 mm × 20 mm i.d., exclusion molecular weight of 70 K for polystyrene) using CHCl$_3$ as eluent at a flow rate of 3.8 mL/min at 25 °C. The sample solution (3 mL containing ca. 0.3 g of the crude product) was injected and recycled before fractionation.

4.3. Polymerization of MMA with the YCl$_3$/lithium amide of secondary amine/nBuLi systems

As a typical procedure for the polymerization of MMA with the YCl$_3$/lithium amide of secondary amine/nBuLi systems, the procedure for run 5 in Table 1 is described as follows.

Under a nitrogen atmosphere, nBuLi (0.11 mL of 1.54 M solution in n-hexane, 0.17 mmol) was added to a THF solution (30 mL) of indoline (0.022 g, 0.19 mmol) placed in a Schlenk tube at 0 °C, and the mixture was stirred at 0 °C for 30 min. The lithium amide solution was added to a suspension of YCl$_3$ (0.326 g, 0.167 mmol) in THF (5 mL), and it was stirred at 0 °C–room temperature for 2 h. After the mixture was cooled to 0 °C, additional nBuLi (0.32 mL of 1.54 M solution in n-hexane, 0.49 mmol) was added, and it was stirred at 0 °C for 0.5 h. After the mixture was cooled to −78 °C, MMA (1.80 mL, 16.8 mmol) was added to the initiating mixture, and the polymerization was carried out at −78 °C for 14 h. The polymerization was quenched by addition of MeOH (5 mL) at −78 °C. After the mixture was warmed to room temperature, volatiles were removed under reduced pressure and the residual solid was washed with 10 mL of MeOH. Reprecipitation was carried out for the remaining solid using CHCl$_3$ (20 mL) and MeOH (300 mL). The resulting crude product was dried under reduced pressure to afford 1.55 g of PMMA in a 92% yield.

Other homopolymerizations of MMA were basically carried out in similar procedures. For the polymerization

with the lithium amide/LiCl systems, the initiating system was prepared by adding a THF solution of lithium amide to LiCl in a Schlenk tube at 0 °C. For the polymerizations with [MMA]/[YCl$_3$] ratio of 20, the products were isolated by extractive work-up using CHCl$_3$ and H$_2$O.

4.4. Block copolymerization of MMA and tBA with a mixture of lithium amide, nBuLi, and YCl$_3$

As a typical procedure for the block copolymerization of MMA and tBA with the YCl$_3$/lithium amide of indoline/nBuLi system, the procedure for run 2 in Table 5 is described as follows.

The initiating mixture in THF (30 mL) was prepared in the aforementioned procedure using nBuLi (0.10 mL [0.16 mmol] + 0.31 mL [0.49 mmol] of 1.58 M solution in n-hexane), indoline (0.197 g, 0.165 mmol), and YCl$_3$ (0.320 g, 0.164 mmol). After it was cooled to −78 °C, MMA (0.35 mL, 3.3 mmol) was added, and the polymerization was carried out at −78 °C for 3 h. Then, tBA (1.20 mL, 8.24 mmol) was added at −78 °C, and the mixture was stirred at −78 °C for 12 h. The polymerization was quenched by addition of MeOH (5 mL) at −78 °C. After the mixture was warmed to room temperature, volatiles were removed under reduced pressure and the residual solid was subjected to extractive work-up with CHCl$_3$ and H$_2$O. The resulting crude product was purified using preparative recycling GPC, affording 1.05 g of poly(MMA-b-tBA) in a 76% yield.

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