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tBuOK/iBu$_3$Al as New Initiating System for Controlled Anionic Polymerization of *tert*-Butyl Acrylate and Methyl Methacrylate

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ABSTRACT: The combination of potassium *tert*-butoxide (tBuOK) and triisobutylaluminum (iBu$_3$Al) (the tBuOK/iBu$_3$Al system) initiated the anionic polymerization of *tert*-butyl acrylate (tBA) and methyl methacrylate (MMA) and controlled the polymerization with respect to molecular weights and molecular weight distributions (MWDs). Poly(tBA)s (M_n = 20 000−80 000) with narrow MWDs (M_w/M_n = 1.05−1.12) were obtained quantitatively in toluene at 0 °C for 1−2 h. The controlled character of the polymerization remained intact even at high temperatures up to 50 °C. MALDI−TOF-MS analyses of a low molecular weight poly(tBA) prepared with the initiating system revealed that the polymer had hydrogens at both chain ends. Block copolymerizations of tBA and MMA were also successful in toluene at 0 °C by using the initiating system, giving poly(tBA-*b*-MMA)s with various compositions of the two monomer units and narrow MWDs in high yield. Although the tBuOK/iBu$_3$Al system failed to control the homopolymerization of MMA in toluene or THF, the use of diethyl ether (Et$_2$O) as a solvent for the polymerization coupled with cesium fluoride (CsF) resulted in the quantitative formation of high molecular weight poly(MMA)s with narrow MWDs.

Introduction

The ability to control anionic polymerizations of alkyl acrylates has been one of the most challenging objectives in the field of polymer synthesis, due to aggregation phenomena[1] and backbiting.[2] Much effort has been devoted to trying to control the polymerization of alkyl acrylates; generally, the most effective strategy is stabilization of the anionic growing species by conducting the polymerization in the presence of inorganic salts or Lewis acids such as LiCl,[3] LiClO$_4$,[4] tBuOLi,[5] lithium silanolate,[6] cesium fluoride/trialkylaluminum (CsF/R$_3$Al),[7] ZnEt$_2$,[8] and Et$_3$B,[9] where carbanions such as *sec*-BuLi, (1,1-diphenylhexyl)lithium, Ph$_2$CHK, or lithium enolate were employed as an initiator. In addition, metal-free carbanion initiators are also effective for controlling the anionic polymerization.[10]

In a previous communication,[11] we reported that the combination of tBuOK and iBu$_3$Al (the tBuOK/iBu$_3$Al system) can be a very effective initiating system for the controlled polymerization of *tert*-butyl acrylate (tBA) in toluene at 0 °C, affording poly(tBA)s with narrow molecular weight distributions in high yield. In contrast to the aforementioned initiating systems, the prominent feature of the tBuOK/iBu$_3$Al system is that it does not require the presence of highly nucleophilic reagents for the polymerization. We have also briefly reported that the anionic growing end of the tBA polymerization can initiate polymerization of methyl methacrylate (MMA) in a controlled manner, giving a poly(tBA-*b*-MMA) with a narrow MWD quantitatively.[11]

In the course of our study to explore the potential of this simple initiating system consisting of two common reagents, we have additionally found that it can afford well-defined poly(tBA)s even at higher temperatures up to 50 °C and the use of diethyl ether (Et$_2$O) as a solvent enables the homopolymerization of MMA to proceed in a controlled fashion in the presence of cesium fluoride (CsF). Thus, in this paper, we will describe the full details of our investigation into the initiating behavior of the tBuOK/iBu$_3$Al system for anionic polymerization of tBA and MMA.

Results and Discussion

Polymerization of tBA Initiated with the tBuOK/iBu$_3$Al System. As previously described,[11] the mixture of tBuOK and 5 equiv of iBu$_3$Al promotes the controlled polymerization of tBA in toluene at 0 °C. As shown in runs 1−3 in Table 1, the tBuOK/iBu$_3$Al initiating system polymerizes tBA quantitatively within 1−2 h, giving poly(tBA)s with very narrow MWDs. Although initiator efficiencies (IEs) calculated from the assumption that one polymer chain formed per tBuOK molecule were rather low, the number-average molecular weights (M_ns) of the resulting poly(tBA)s estimated from standard poly(methyl methacrylate)s by GPC[12] increased linearly with the feed ratio of tBA to tBuOK.

Surprisingly, the controlled character of the polymerization remained intact even at high temperatures up to 50 °C. For example, as listed in runs 4−7 in Table 1, the tBA polymerization with the tBuOK/iBu$_3$Al system at 40 °C proceeded in a controlled manner, giving poly(tBA)s with narrow MWDs. Moreover, the controlled polymerization was also possible even at 50 °C although M_w/M_n values increased slightly to 1.11−1.13 (runs 8−10 in Table 1). The controlled character of the polymerization at 50 °C is clearly seen from the linear relationship between the initial [tBA]/[tBuOK] ratios and M_ns illustrated in Figure 1. Even at 60 °C, poly(tBA)s with M_w/M_n = 1.2−1.4 were obtained quantitatively, and the M_ns increased linearly with the [tBA]/[tBuOK] ratio (runs 11−13). The controlled character observed with the tBuOK/iBu$_3$Al system at these high temperatures is quite remarkable, considering that the number of successful examples of the controlled tBA polymerization has been very limited even at 0 °C.[9]

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Table 1. Anionic Polymerization of tBA with tBuOK/R3Al Systems in Toluene[a]

run	[tBA]/[tBuOK]	tBuOK, mmol	toluene, mL	R_3Al	time, h	temp, °C	$M_n \times 10^{-3}$ calcd[b]	$M_n \times 10^{-3}$ obsd[c]	M_w/M_n[c]	IE, %[d]
1	50	0.272	15	iBu_3Al	1	0	6.4	20.0	1.12	32
2	100	0.212	15	iBu_3Al	2	0	12.8	47.7	1.06	27
3	152	0.260	30	iBu_3Al	2	0	19.5	83.4	1.05	23
4	26	0.225	15	iBu_3Al	0.5	40	3.3	9.5	1.20	35
5	51	0.162	15	iBu_3Al	0.5	40	6.5	25.9	1.09	25
6	74	0.153	15	iBu_3Al	0.5	40	9.5	46.5	1.07	20
7	108	0.127	15	iBu_3Al	1	40	13.8	68.5	1.06	20
8	50	0.170	15	iBu_3Al	0.5	50	6.4	25.5	1.13	25
9	99	0.165	15	iBu_3Al	0.5	50	12.7	42.4	1.11	30
10	152	0.162	15	iBu_3Al	1	50	19.5	63.8	1.13	30
11	25	0.188	15	iBu_3Al	0.5	60	3.2	11.2	1.33	29
12	50	0.170	15	iBu_3Al	0.5	60	6.4	21.4	1.41	30
13	103	0.153	15	iBu_3Al	0.5	60	13.2	52.4	1.23	25
14	101	0.169	20	iBu_3Al	3.0	−78	12.9	31.7	1.14	41
15	51	0.133	15	Et_3Al	1	0	6.5	67.3	1.06	10
16	102	0.110	15	Et_3Al	2	0	13.1	147.4	1.12	9
17	101	0.271	15	Me_3Al	2	0	12.9	437.9	1.61	3

[a] $[R_3Al]/[tBuOK] = 5$. Yields of poly(tBA)s were quantitative in all runs. [b] $M_n(\text{calcd}) = (\text{MW of tBA}) \times [\text{tBA}]/[\text{tBuOK}] + 2\ (\text{H} \times 2)$. [c] M_n(obsd) and M_w/M_n were obtained by GPC calibration using standard PMMAs in THF. [d] Initiator efficiencies (IEs) = $M_n(\text{calcd})/M_n(\text{obsd})$.

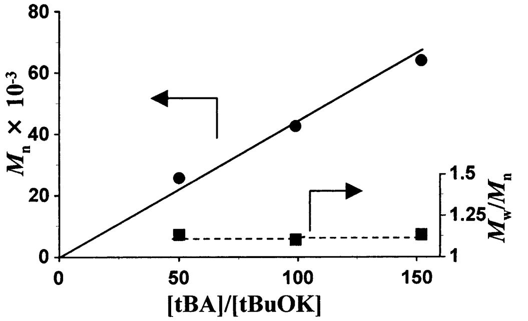


Figure 1. Relationship between M_n and M_w/M_n of poly(tBA) obtained with the tBuOK/iBu3Al system at 50 °C and initial mole ratio of [tBA]/[tBuOK] (runs 8−10 in Table 1). See Table 1 for details of the polymerization conditions.

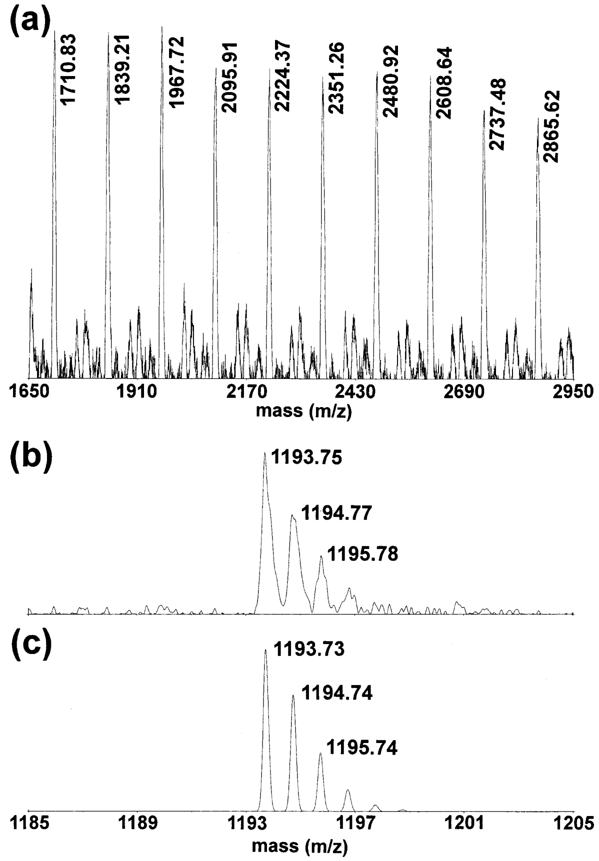
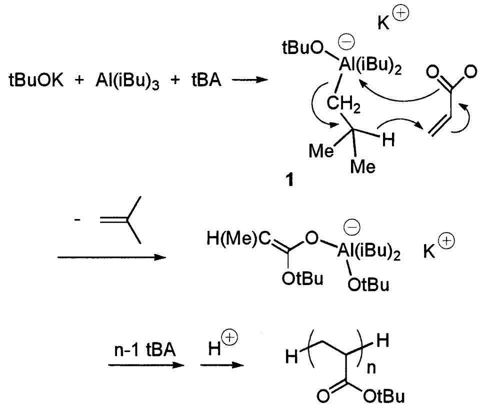


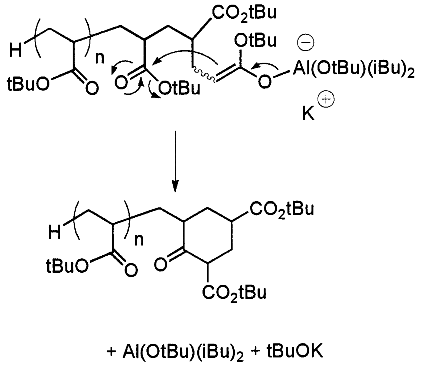
Figure 2. MALDI−TOF−MS spectra of poly(tBA) with the tBuOK/iBu3Al system (tBA:tBuOK:iBu3Al = 14:1:5, in toluene at 0 °C for 1 h, yield = 100%, $M_n = 5300$, $M_w/M_n = 1.26$) in linear mode (a), one of the peak clusters in the spectrum in reflector mode (b), and theoretical isotopic distribution of K-adduct 9-mer of tBA bearing hydrogens at both chain ends (c).

To characterize the precise chain-end structure of the poly(tBA)s and estimate the mechanism of initiation and termination of this polymerization, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI−TOF-MS) was carried out for a low molecular weight poly(tBA) obtained by the tBuOK/iBu3Al system. In the MS spectrum measured in linear mode (Figure 2a), we observe one main set of peaks with an interval of $m/z = 128.2$ (MW of tBA), which indicates that one series of initiation, propagation, and termination dominated in the course of the polymerization. Figure 2b shows the appearance of one of the main peaks around $m/z = 1194$ in reflector mode, which agrees well with the theoretical isotopic distribution of K-adduct of 9-mer of tBA bearing hydrogens at both polymer chain ends. Therefore, the real initiating species of the tBuOK/iBu3Al system is hydride (H^-) generated from the reaction of tBuOK with iBu3Al, and most of the propagating species are stable enough to give H-terminated *ω*-chain end without backbiting. Recently, Müller and co-workers reported that the CsF/iBu3Al system can initiate polymerization of *n*-butyl acrylate (nBA) without carbanionic reagents, where the resulting poly(nBA)s had broad MWDs.[7] On the basis of the MALDI−TOF−MS analysis of the poly(nBA), they proposed that the initiation occurred by the nucleophilic attack of H^- to nBA. From the results of the MALDI−TOF−MS analyses described above, we assume that our tBuOK/iBu3Al system initiates the polymerization by the same mechanism as that proposed by Müller and co-workers.[7] Thus, as shown in Scheme 1, the initially formed potassium aluminate **1** would release both nucleophilic hydride and isobutene at the same time by contact with tBA, and the growing species of the polymerization would be the enolate bonded to $Al(iBu)_2(OtBu)$ in an “ate” form with potassium cation. In contrast to the highly electron-withdrawing F in the Müller’s system,

Scheme 1. Initiation Mechanism for tBA Polymerization with the tBuOK/iBu$_3$Al System



Scheme 2. Backbiting Mechanism for tBA Polymerization with the tBuOK/iBu$_3$Al System



the electron-donating tBuO group attaching to Al may facilitate the transfer of β-hydride, which should be the reason for the more efficient initiation of this system.

In Figure 2a, in addition to the main set of peaks, two minor sets of peaks both with an interval of MW of tBA are observed. The molecular weights of one of the minor sets of peaks with lower molecular weights are m/z = 74 lower than those of the main peaks, which suggests that these minor peaks derive from the backbiting at the growing end resulting in the formation of six-membered cyclic structure, as shown in Scheme 2, because the side reaction should remove a tBuOH moiety (m/z = 74) from the parent poly(tBA) molecule. The origin of another minor set of peaks with higher molecular weights could be ascribed to the elimination of isobutene (MW = 56) from the poly(tBA), judging from their difference in the mass number from the main peaks. The observation of the latter minor signals in a MALDI−TOF−MS spectrum of a poly(tBA) was recently reported in the literature.[13]

The effect of the [iBu$_3$Al]/[tBuOK] ratio for the system on the tBA polymerization is summarized in Table 2. Although the mechanism proposed above for the initiation requires only 1 equiv of iBu$_3$Al, the polymerization with the [iBu$_3$Al]/[tBuOK] ratio of 1 and 3 (runs 1 and 2) did not proceed in a controlled manner: poly(tBA)s with broad MWDs were obtained in low yield (run 1) or quantitatively (run 2), both with very low IEs. On the other hand, the use of 5−9 equiv of iBu$_3$Al with respect to tBuOK resulted in the formation of poly(tBA)s with narrow MWDs (runs 3−5). These results suggest that excess iBu$_3$Al is essential for the efficient generation of H$^-$ and/or the activation of tBA by the highly electrophilic iBu$_3$Al in order to control the polymerization. Although the IEs became higher with increasing [iBu$_3$Al]/[tBuOK] ratio, poly(tBA) with the narrowest MWDs was obtained with the ratio of 5, which we employed as the standard condition throughout this study.

Table 2. Anionic Polymerization of tBA with the tBuOK/iBu$_3$Al System; Effect of [iBu$_3$Al]/[tBuOK] on the Polymerization Behavior[a]

run	[iBu$_3$Al]/[tBuOK]	yield, %	$M_n \times 10^{-3}$ [b]	M_w/M_n [b]	IE, % [c]
1	1	14	175.0	1.62	1
2	3	100	197.5	1.40	6
3	5	100	47.7	1.06	27
4	7	100	31.2	1.10	41
5	9	100	23.9	1.13	54

[a] In toluene (15 mL) at 0 °C for 2 h; [tBA]/[tBuOK] = 100; tBuOK = 0.177−0.380 mmol. [b] M_n(obsd) and M_w/M_n were obtained by GPC calibration using standard PMMAs in THF solution. [c] Initiator efficiencies (IEs) = M_n(calcd)/M_n(obsd). M_n (calcd) = (MW of tBA) × [tBA]/[tBuOK] × yield (%)/100 + 2 (H × 2); 1800 for run 1, 12 800 for runs 2−5.

Table 3. Anionic Polymerization of Various Monomers with the tBuOK/iBu$_3$Al System[a]

run	monomer[d]	[monomer]/[tBuOK]	yield, %	$M_n \times 10^{-3}$ [b]	M_w/M_n [b]
1[c]	tBA	100	100	47.7	1.06
2	nBA	100	100	46.1	2.30
3	MMA	105	31	123.0	2.32
4	tBMA	116	100	63.0	1.95
5	nBMA	97	92	22.3	8.30
6	ϵ-CL	101	89	*e*	*e*
7	styrene	106	0		

[a] In toluene (15 mL) at 0 °C to RT overnight; tBuOK = 0.152−0.299 mmol. [b] M_n(obsd) and M_w/M_n were obtained by GPC calibration using standard PMMAs in THF solution. [c] At 0 °C for 2 h (run 2 in Table 1). [d] tBA = *tert*-butyl acrylate, nBA = *n*-butyl acrylate, MMA = methyl methacrylate, tBMA = *tert*-butyl methacrylate, nBMA = *n*-butyl methacrylate, ϵ-CL = ϵ-caprolactone. [e] Multimodal.

Triethylaluminum (Et$_3$Al) is also capable of giving narrow MWD poly(tBA)s in conjunction with tBuOK as shown in runs 15 and 16 in Table 1. Although the initiator efficiency calculated from the above-mentioned assumption is even lower (9−10%) than those of the tBuOK/iBu$_3$Al initiating system, the tBuOK/Et$_3$Al system can also be an effective method for controlling the polymerization of tBA. On the other hand, the use of Me$_3$Al as R$_3$Al did not control the polymerization of tBA under similar conditions (Table 1, run 17). These results are consistent with the aforementioned proposed initiation mechanism: whereas Et$_3$Al with β-hydrogens transferable as H$^-$ can be used for initiating the controlled polymerization, such a reaction is not possible for the tBuOK/Me$_3$Al system, and tBuOK itself would initiate the uncontrolled polymerization of tBA.

The polymerization can be conducted at −78 °C in a controlled manner, affording a narrow MWD poly(tBA) quantitatively with a higher IE than those of the polymerizations at 0 °C (run 14 in Table 1). The tacticity of the polymer (*mm*:*mr*:*rr* = 46:38:16) determined by ^{13}C NMR[8] is almost the same as that of the poly(tBA) obtained at 0 °C (*mm*:*mr*:*rr* = 47:38:15, run 2 in Table 1).

Polymerization of Various Monomers Initiated with the tBuOK/iBu$_3$Al System. Table 3 summarizes the polymerization results of various monomers with the tBuOK/iBu$_3$Al system in toluene at 0 °C to room temperature. Although *n*-butyl acrylate (nBA), *tert*-butyl methacrylate (tBMA), *n*-butyl methacrylate (nBMA),

Table 4. Block Copolymerization of tBA and MMA with the tBuOK/iBu$_3$Al System in Toluene[a]

run	[tBA]/[tBuOK]	first stage time	M_n[c] ($\times 10^{-3}$)	M_w/M_n[c]	[MMA]/[tBuOK]	M_n[c] ($\times 10^{-3}$)	second stage[b] M_w/M_n[c]	yield[d] (%)	[tBA]:[MMA] feed	[tBA]:[MMA] ^{1}H NMR (copolymer)
1	51	16 min	20.6	1.15	100	62.2	1.07	81	1:1.96	1:3.23
2	49	19 min	20.3	1.14	295	109.9	1.06	99	1:6.02	1:7.32
3	50	17 min	21.1	1.13	499	211.2	1.17	75	1:9.98	1:13.0
4	106	16 min	44.9	1.07	11	51.5	1.06	99	9.64:1	9.38:1
5	100	19 min	65.9	1.06	50	85.6	1.09	99	2.00:1	2.22:1
6[e]	10	15 min	nd[f]	nd[f]	101	28.4	1.09	93	1:10.1	1:9.68
7	10	17 min	nd[f]	nd[f]	208	50.0	1.06	100	1:20.8	1:17.7
8	12	16 min	nd[f]	nd[f]	302	73.3	1.06	98	1:25.2	1:23.1
9	11	18 min	nd[f]	nd[f]	508	143.4	1.09	100	1:46.8	nd[f]
10[g]	12	18 min	nd[f]	nd[f]	99	27.7	1.11	67	1:8.25	1:15.0
11	10	3 h	nd[f]	nd[f]	101	30.2	1.12	93	1:10.1	1:12.5
12	10	5 h	nd[f]	nd[f]	101	33.3	1.11	95	1.10.1	1:13.0
13	10	15.5 h	nd[f]	nd[f]	101	59.6	1.12	96	1:10.1	1:20.0

[a] Toluene = 20−43 mL; [iBu$_3$Al]/[tBuOK] = 5. tBuOK = 0.107−0.240 mmol. [b] The second stage polymerizations were carried out at 0 °C for 1 h followed by 15−17 h at room temperature except for run 4 (0 °C for 1 h) and run 10 (−78 °C for 2 h). [c] M_n(obsd) and M_w/M_n were obtained by GPC calibration using standard PMMAs in THF solution. [d] Total yield for the two stage polymerizations. [e] Tacticity for the PMMA block is *mm:mr:rr* = 2:28:70. [f] Not determined. [g] Polymerization at −78 °C; tacticity for the PMMA block is *mm:mr:rr* = 1:19:80.

and ϵ-caprolactone (ϵ-CL) were converted to polymers in high yield, their MWDs were broad. Polymerization of methyl methacrylate (MMA) gave a polymer in low yield, and styrene did not react with this initiating system at all. These results indicate that the ability for controlling anionic polymerization of the tBuOK/iBu$_3$Al system is very specific for tBA. In addition, because the propagating chain end of tBA derived from the initiating system can initiate controlled polymerization of MMA and nBMA (vide infra), the reactivity for the initiation toward tBA and alkyl methacrylates should be quite different. We assume that the nucleophilicity of the initiating ate complex $[Al(iBu)_3(OtBu)]^-K^+$ (**1**) is just high enough for the rapid initiation of tBA but not for those of alkyl methacrylates.

Copolymerization of tBA with Alkyl Methacrylates. Although the homopolymerization of MMA with the tBuOK/iBu$_3$Al system described in the previous section failed to produce polymers with a well-defined structure, the growing end of the tBA can initiate the polymerization of MMA to give poly(tBA-*b*-MMA) with narrow MWDs, as shown in Table 4. For example, after 50 equiv of tBA was polymerized at 0 °C for 15−20 min and a small portion of the mixture was removed by a syringe for analyzing the product of the first stage polymerization, 100−500 equiv of MMA was added to the growing end and the mixture was stirred at 0 °C to room temperature overnight (runs 1−3). The following observation indicates the occurrence of efficient block copolymerizations: (1) the resulting copolymers obtained in high yield possessed narrow MWDs, (2) their GPC traces are free from the peaks of poly(tBA) obtained in the first stage, (3) the M_ns of the block copolymers increased corresponding to the amount of MMA added in the second feed, and (4) the composition of tBA/MMA in the copolymers determined by ^{1}H NMR spectra corresponds to the feed ratio of the monomers. Similarly, it is also possible to prepare tBA-rich block copolymers with narrow MWDs in high yield (runs 4 and 5).

With this high efficiency for the block copolymerization, we attempted to synthesize poly(MMA)s bearing a short poly(tBA) segment at the α-chain end by using a very small amount of tBA as the first block monomer. Table 4 (runs 6−9) summarizes the results of such copolymerizations where various amounts of MMA were added to the growing end of 10 equiv of tBA with the tBuOK/iBu$_3$Al system. As expected, copolymers with high MMA contents were obtained in a controlled manner, where M_ns of the polymers increased linearly with increasing amounts of MMA as illustrated in Figure 3. This result is in sharp contrast to the homopolymerization of MMA with this initiating system. The tacticity of the poly(MMA)[14] segment of the copolymers is syndiotacitic (*mm*:*mr*:*rr* = 2:28:70, run 6). The syndiotactic selectivity slightly increased to *mm*:*mr*:*rr* = 1:19:80 for the polymer obtained by the polymerization at −78 °C in a controlled manner (run 10).

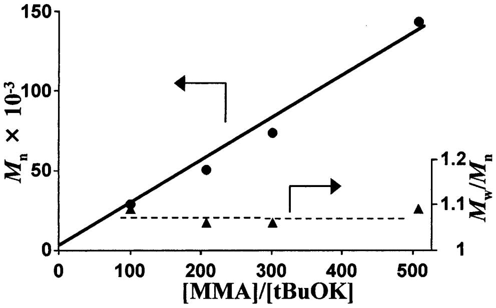


Figure 3. Relationship between M_n and M_w/M_n of poly(tBA-*b*-MMA) obtained with the tBuOK/iBu$_3$Al system and initial mole ratio of [MMA]/[tBuOK] (runs 6−9 in Table 4). The intercept of the *y*-axis (M_n = ca. 5000) should be derived from the presence of the poly(tBA) block at the initiating chain end. See Table 4 for details of the polymerization conditions.

To examine the stability of the propagating chain end of tBA, a series of copolymerizations of tBA with MMA ([tBuOK]:[tBA]:[MMA] = 1:10:101)were carried out, where MMA was added after first stage polymerization of tBA for 15 min, 3 h, 5 h, and 15.5 h (runs 6 and 11−13 in Table 4). Irrespective of the period for the first stage polymerization, block copolymers with narrow MWDs were obtained in high yield, although the M_n increased gradually with the increase of the period. IEs calculated on the aforementioned assumption are 37% for both runs 6 and 11, 32% for run 12, and 18% for run 13, which indicates that, at 0 °C in toluene, the propagating chain end of tBA of the tBuOK/iBu$_3$Al system remains intact at least for 3 h, and the half-life of the chain end is about 15 h.

Similarly, synthesis of poly(*n*-butyl methacrylate) (poly(nBMA)) with a short poly(tBA) segment is possible. As shown in Table 5, addition of nBMA to the growing end of tBA (10 equiv) with the initiator resulted

Table 5. Block Copolymerization of tBA and nBMA with the tBuOK/iBu$_3$Al System in Toluene[a]

	first stage[b]	second stage[c]			
run	[tBA]/ [tBuOK]	[nBMA]/ [tBuOK]	yield, %[d]	$M_n \times 10^{-3}$ [e]	M_w/M_n[e]
1	11	55	81	23.3	1.08
2	12	102	99	45.9	1.05
3	10	201	100	77.8	1.09

[a] Toluene = 15−20 mL; [iBu$_3$Al]/[tBuOK] = 5. tBuOK = 0.114−0.181 mmol. The composition of the poly(tBA-*b*-nBMA)s cannot be determined because of the overlapping of signals in their ^{1}H NMR spectra. [b] At 0 °C for 15 min. [c] At 0 °C for 1 h (run 1), at 0 °C for 1 h and at room temperature for 1 h (run 2), and at 0 °C for 1 h and at room temperature for 17 h (run 3). [d] Total yield for the two-stage polymerizations. [e] M_n(obsd) and M_w/M_n were obtained by GPC calibration using standard PMMAs in THF solution.

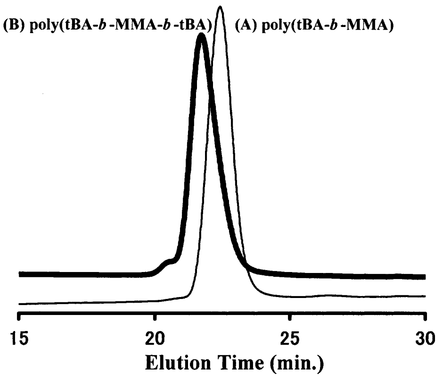


Figure 4. GPC traces of triblock copolymerization of tBA and MMA initiated with the tBuOK/iBu$_3$Al system. Conditions: first stage; 11 equiv of tBA, 0 °C, 14 min, second stage; 201 equiv of MMA, 0 °C, 21 min, and third stage; 50 equiv of tBA, 0 °C for 1 h and room temperature for 16 h. (A) Poly(tBA-*b*-MMA) obtained by the second stage polymerization; M_n = 56 900, M_w/M_n = 1.06. (B) Poly(tBA-*b*-MMA-*b*-tBA) obtained by the third stage polymerization; M_n = 76 000, M_w/M_n = 1.11.

in the formation of block copolymers with narrow MWDs. As in the case of MMA, the M_ns of the copolymers increased linearly with the initial feed ratio of [nBMA]/[tBuOK]. On the other hand, a similar attempt using *tert*-butyl methacrylate (tBMA) as a second monomer failed to give well-defined block copolymers.

Next, synthesis of an A−B−A type triblock copolymer, poly(tBA-*b*-MMA-*b*-tBA), was attempted with the initiating system by a three-step sequential addition of these monomers. As a successful example of such a three-stage block copolymerization, the GPC traces of the products after the second and third stages are shown in Figure 4. The efficient progress of the block copolymerization was confirmed by the smooth shift of the GPC traces to a higher molecular weight region from second to third stage, maintaining the narrow MWDs and quantitative yield of the final product. In addition, a good agreement was observed among the feed ratio of the monomers, the M_ns (GPC) of the copolymers from the second and third stages, and the tBA/MMA ratio in composition determined by ^{1}H NMR (tBA:MMA = 26:74). Therefore, the propagating end of the MMA polymerization with this system is stable enough under the condition to initiate the anionic polymerization of tBA.

Table 6. Anionic Polymerization of MMA with the tBuOK/iBu$_3$Al System in Various Solvents[a]

run	[MMA]/ [tBuOK]	solvent	[CsF]/ [tBuOK]	yield, %	$M_n \times 10^{-3}$ [b]	M_w/M_n[b]
1	105	toluene		31	123.0	2.32
2	101	ether		100	513.9	1.65
3	52	ether	2.7	100	93.0	1.14
4	76	ether	2.8	100	180.1	1.10
5	101	ether	2.8	100	240.2	1.11
6	102	THF	3.5	5		

[a] Solvent = 10−15 mL; [iBu$_3$Al]/[tBuOK] = 5, tBuOK = 0.139−0.284 mmol, at 0 °C for 1 h and at room temperature for 15−17 h. [b] M_n and M_w/M_n were obtained by GPC calibration using standard PMMAs in THF solution.

Homopolymerization of MMA Initiated with the tBuOK/iBu$_3$Al System. Whereas the homopolymerization of MMA with the tBuOK/iBu$_3$Al system in toluene produced poly(MMA) with a broad MWD in low yield, the yield of the polymer increased drastically by conducting the polymerization in diethyl ether (Et$_2$O) as shown in runs 1 and 2 in Table 6. In addition, we have found that poly(MMA)s with a narrow MWD can be obtained quantitatively by the polymerization in Et$_2$O at 0 °C in the presence of cesium fluoride (CsF) (runs 3−5). Although IEs were low (4−6%), M_ns of PMMAs increased linearly with the [MMA]:[tBuOK] ratio up to M_n = 240 000, while MWDs remain narrow ($M_w/M_n < 1.14$). Because of the low solubility of PMMA into Et$_2$O, the reaction became heterogeneous as the polymerization proceeded. The tacticity of the PMMA obtained in run 5 was *mm*:*mr*:*rr* = 2:32:66. These results indicate that the MMA polymerization with tBuOK/iBu$_3$Al system in Et$_2$O at 0 °C can be a convenient method to prepare narrow MWD PMMAs with high molecular weight.[15] On the other hand, the use of tetrahydrofuran as a polar solvent was not effective for the controlled polymerization, giving a PMMA in very low yield (run 6).

Conclusions

We have demonstrated that the tBuOK/iBu$_3$Al system can initiate controlled polymerization of tBA and block copolymerization of tBA and MMA at 0 °C in toluene, giving narrow MWD (co)polymers. Narrow MWD poly(tBA)s can be obtained in a controlled manner at high temperatures up to 50 °C, owing to the high stability of the propagating chain end consisting anionic aluminum moiety in a form of ate complex. Homopolymerization of MMA was also possible with the initiating system by the use of Et$_2$O as a solvent in the presence of CsF. We believe that the tBuOK/iBu$_3$Al system can be one of the most useful methods for the controlled polymerization of tBA.

Experimental Section

Materials. Toluene, THF, and Et$_2$O were dried over sodium, Na/K alloy, and calcium hydride (CaH$_2$), respectively, and distilled before use. tBA (TCI, >98%), MMA (Nacalai, 99%), nBMA (TCI, >99.0%), tBMA (TCI, >98.0%), nBA (TCI, >99.0%), ϵ-CL (Nacalai, 99%), and styrene (Nacalai, 99%) were dried overnight over CaH$_2$ with stirring, distilled, and kept under nitrogen. tBuOK (Kanto Chemical, >97.0%), iBu$_3$Al (Kanto Chemical, 0.97 M solution in *n*-hexane), Et$_3$Al (Kanto Chemical, 0.99 M solution in toluene), Me$_3$Al (Kanto Chemical, 1.00 M solution in *n*-hexane), and CsF (Aldrich, 99%) were used as received.

Measurements. ^{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 25 °C. The tacticity of PMMA was determined from the integral ratio of C−CH_3 signals, which separated into three peaks with respect to the *mm* (1.21 ppm), *mr* (1.02 ppm), and *rr* (0.83 ppm) triads.[14] The tacticity of poly(tBA) was determined by ^{13}C NMR following the method reported in the literature.[8] The composition of the monomer units in poly(tBA-*b*-MMA) was determined from the integral ratio of the O−C(CH_3)$_3$ signal at 1.43 ppm (tBA) and the O−CH_3 signal at 3.60 ppm (MMA). 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 G6000H_{HR} (TOSOH; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 4000K for polystyrene), G4000H_{HR} (TOSOH; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 400K for polystyrene), and G3000H_{HR} (TOSOH; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 60K for polystyrene).

MALDI−TOF−MS analyses were performed on a PerSeptive Biosystems Voyager RP equipped with 1.3 m linear and 2 m reflector 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 both linear and reflector modes under the pressure of ca. $(2-3) \times 10^{-7}$ mmHg. 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 solid) 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, 2,5-dihydroxybenzoic acid (Kanto Chemical, >98%), solution (300 μL, 10 mg/mL in THF), and a cationizing agent, potassium trifluoroacetate (Acros, 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. The theoretical isotopic distribution of the 9-mer of tBA in Figure 2c was obtained using Isotope Calculator program on Data Explorer Software (version 4.0, Applied Biosystems).

Polymerization of tBA Initiated with the tBuOK/iBu$_3$Al System. As a typical procedure for the polymerization of tBA, the procedure for run 2 in Table 1 is described as follows. Under a nitrogen atmosphere, tBuOK (23.8 mg, 0.212 mmol) and toluene (15 mL) were placed in a Schlenk tube to form a suspension. iBu$_3$Al (1.05 mL of 0.97 M solution in *n*-hexane, 1.02 mmol) was added to the suspension cooled at 0 °C dropwise with stirring, and then the suspension became a clear solution during 0.5 h of stirring, indicating the formation of the initiating aluminum ate complex $[(\mathrm{tBuO})(\mathrm{iBu})_3\mathrm{Al}]^-\mathrm{K}^+$ (**1**). tBA (3.1 mL, 21.2 mmol) was added to the solution containing the initiator dropwise at 0 °C with stirring, and the mixture was stirred at 0 °C for 2 h. After the polymerization was quenched by the addition of MeOH (5 mL) at 0 °C, volatiles were removed under reduced pressure. An extractive workup was carried out for the residue using 40 mL of $CHCl_3$ and 150 mL of 1 N HCl(aq) to remove side products derived from tBuOK and iBu$_3$Al. Then, the $CHCl_3$ solution was washed with water (400 mL). After $CHCl_3$ was removed under reduced pressure, the resulting solid was dried in vacuo at 40 °C for 12 h to yield poly(tBA) in quantitative yield.

For the polymerization at higher temperatures, after the initiator was generated at 0 °C in the same procedure described above, the solution was warmed to the polymerization temperature using oil bath, and the polymerization was initiated by injecting tBA at that temperature.

tBA polymerization with the tBuOK/Et$_3$Al and tBuOK/Me$_3$Al systems and homopolymerization of other monomers in Table 3 were carried out in similar procedures.

Block Copolymerization of tBA and MMA Initiated with tBuOK/iBu$_3$Al System. As a typical procedure for the block copolymerization of tBA and MMA, the procedure for run 2 in Table 4 is described as follows. Under a nitrogen atmosphere, the solution of the initiating system was prepared from tBuOK (22.8 mg, 0.203 mmol), toluene (25 mL), and iBu$_3$Al (1.05 mL of 0.97 M solution in *n*-hexane, 1.02 mmol) in the same procedure described for the tBA polymerization. After the first stage polymerization of tBA (1.45 mL, 9.90 mmol) was carried out at 0 °C for 15 min, a small portion of the polymerization mixture was removed with a syringe and subjected to extractive workup with $CHCl_3$ and 1 N HCl(aq) to isolate the poly(tBA), whose M_n and M_w/M_n were analyzed with GPC. Just after the small portion was removed, MMA (6.40 mL, 59.8 mmol) was added at 0 °C to perform the second stage polymerization, and the mixture was stirred at 0 °C for 1 h and at room temperature for 17 h. After the polymerization was quenched by the addition of MeOH (5 mL) at room temperature, volatiles were removed under reduced pressure. After the resulting solid was washed once with 1 N HCl/MeOH (10 mL) and twice with MeOH (20 mL), it was dissolved into $CHCl_3$ (15 mL) and reprecipitated into 400 mL of 0.025 N HCl/MeOH. The resulting solid was collected by filtration and dried under reduced pressure at 40 °C for 12 h to give poly(tBA-*b*-MMA) in 99% yield.

The block copolymerizations in runs 1 and 3−5 in Table 4 were carried out in a similar procedure except that the isolation of the products were carried out by the extractive workup for runs 4 and 5. The block copolymerizations of tBA and MMA in runs 6−10 in Table 4 were carried out in a similar procedure without the process of sampling after the first stage polymerization. The synthesis of poly(tBA-*b*-MMA-*b*-tBA) and the block copolymerizations of tBA and nBMA were carried out in similar procedures.

Polymerization of MMA Initiated with the tBuOK/iBu$_3$Al/CsF System in Et$_2$O. As a typical procedure for the polymerization of MMA in Et$_2$O, the procedure for run 3 in Table 6 is described as follows. Under a nitrogen atmosphere, the solution of the tBuOK/iBu$_3$Al system was prepared from tBuOK (18.1 mg, 0.161 mmol), Et$_2$O (10 mL), and iBu$_3$Al (0.86 mL of 0.97 M solution in *n*-hexane, 0.83 mmol) in a similar procedure described for the tBA polymerization. The addition of CsF (66.6 mg, 0.438 mmol) to the solution and the stirring at 0 °C for 60 min resulted in the formation of a suspension because of the low solubility of an excess of CsF and/or KF to Et$_2$O. The polymerization was started by injection of MMA (0.90 mL, 8.4 mmol) to the suspension and carried out at 0 °C for 1 h and at room temperature for 15 h. After the polymerization was quenched by the addition of MeOH (5 mL), volatiles were removed under reduced pressure. The residue was dissolved into 15 mL of $CHCl_3$ and reprecipitated into 0.3 N HCl/MeOH (400 mL). The resulting solid was collected with filtration, washed with 200 mL of MeOH, and dried under reduced pressure at 40 °C for 12 h to give PMMA quantitatively.

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