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Controlled Anionic Polymerization of *tert*-Butyl Acrylate with the tBuOK/Triisobutylaluminum (iBu$_3$Al) Initiating System

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Introduction. The ability to control anionic polymerizations of alkyl acrylates has been one of the most challenging objectives in the field of polymer synthesis. Aggregation phenomena[1] and backbiting[2] have been shown to be the origins of difficulty in controlling the polymerization. Several methods have been developed for controlling the polymerization to obtain poly(alkyl acrylate)s with narrow molecular weight distributions (MWDs) in high yield. One main strategy for that purpose is stabilization of 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] ZnCl$_2$,[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.[10] In contrast to these examples where the presence of the highly nucleophilic reagent is essential for the initiation of controlled polymerization, our finding reported in this paper is that, without addition of carbanions or enolates, the combination of tBuOK and iBu$_3$Al (tBuOK/iBu$_3$Al initiating system) can be a very effective initiating system for the controlled polymerization of *tert*-butyl acrylate (tBA) in toluene at 0 °C, affording poly(tBuA)s with narrow molecular weight distributions in high yield.

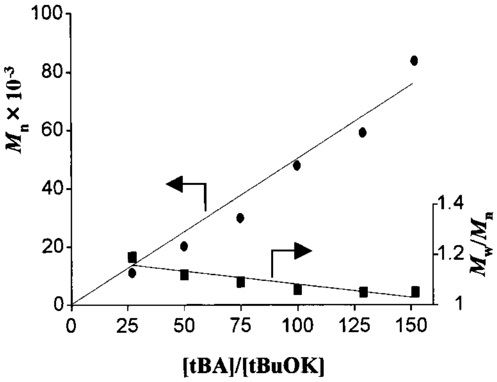

Figure 1. Relationship between M_n and M_w/M_n of poly(tBA) obtained with the tBuOK/iBu$_3$Al system and initial mole ratio of [tBA]/[tBuOK].

Results and Discussion. Polymerization of *tert*-butyl acrylate (tBA) initiated with the tBuOK/iBu$_3$Al system was carried out by the addition of tBA to a toluene solution of tBuOK and iBu$_3$Al at 0 °C in a nitrogen atmosphere. For example, when 3.1 mL of the monomer (21.2 mmol, 100 equiv to tBuOK) was added to a mixture of tBuOK (23.8 mg, 0.212 mmol) and iBu$_3$Al (0.97 M solution in hexane, 1.05 mL, 1.02 mmol)[11] in 15 mL of toluene, the polymerization proceeded smoothly, giving quantitative yield of poly(tBA) after 2 h of stirring at 0 °C (Table 1, run 4). GPC analysis of the resulting polymer indicated that the poly(tBA) had a very narrow molecular weight distribution (M_w/M_n = 1.06). When the feed ratio of tBA to tBuOK was varied from 25 to 152, the number-average molecular weights (M_ns) of the resulting poly(tBA) estimated from standard poly(methyl methacrylate)s by GPC[12] increased linearly from 10 500 up to 83 400, while MWDs remained narrow (M_w/M_n = 1.05−1.18) as shown in Table 1 (runs 1−6) and Figure 1. Although initiator efficiencies (IEs) calculated from the assumption that one polymer chain formed per tBuOK were rather low, M_ns of the poly(tBA) could be predictable up to nearly M_n = 85 000 from the feed ratio of tBA/tBuOK, since the IE values remain in a certain range (23−32%). When a higher feed ratio of tBA/tBuOK (205) was applied, although the initiator efficiency decreased further to 10%, poly(tBA) with a high molecular weight (M_n = 250 600) and a

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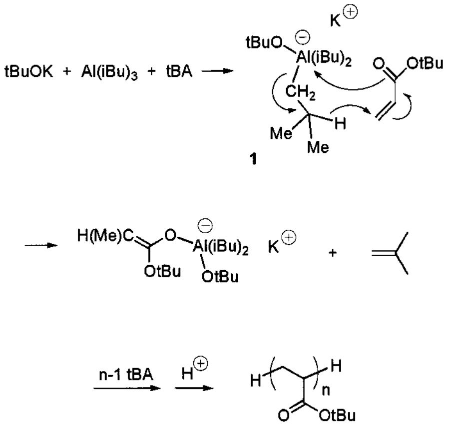
Table 1. Anionic Polymerization of tBA with tBuOK in the Presence of R_3Al in Toluene at 0 °C[a]

run	[tBA]/[tBuOK]	tBuOK, mmol	toluene, mL	R_3Al	time, h	$M_n \times 10^{-3}$ calcd[b]	$M_n \times 10^{-3}$ obsd[c]	M_w/M_n[c]	IE, %[d]
1	25	0.232	15	iBu_3Al	1	3.2	10.5	1.18	30
2	50	0.272	15	iBu_3Al	1	6.4	20.0	1.12	32
3	75	0.236	15	iBu_3Al	2	9.6	29.7	1.09	32
4	100	0.212	15	iBu_3Al	2	12.8	47.7	1.06	27
5	129	0.276	25	iBu_3Al	2	16.5	58.9	1.05	28
6	152	0.260	30	iBu_3Al	2	19.5	83.4	1.05	23
7	205	0.247	35	iBu_3Al	3	26.3	250.6	1.17	10
8	50	0.244	15	Et_3Al	1	6.4	170.9	1.06	4
9	101	0.256	15	Et_3Al	2	12.9	305.9	1.25	4
10	101	0.271	15	Me_3Al	2	12.9	437.9	1.61	3

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

Scheme 1



narrow MWD ($M_w/M_n = 1.17$) was obtained quantitatively (Table 1, run 7).

Triethylaluminum (Et_3Al) is also capable of giving narrow MWD poly(tBA)s in conjunction with tBuOK as shown in runs 8 and 9 in Table 1. Although the initiator efficiency calculated from the above-mentioned assumption is even lower (4%) than those of the tBuOK/iBu_3Al initiating system, this tBuOK/Et_3Al initiating system can also be an effective method for controlling the polymerization of tBA. On the other hand, the use of Me_3Al as R_3Al did not control the polymerization of tBA under similar reaction condition (Table 1, run 10).

MALDI-TOF-MS analysis of a low molecular weight poly(tBA) obtained by the tBuOK/iBu_3Al system (tBA:tBuOK:iBu_3Al = 13:1:5, in toluene at 0 °C for 1 h, yield = 100%, $M_n = 5300$, $M_w/M_n = 1.26$) clearly indicated that the polymer had hydrogens on both α and ω termini. Thus, the main set of peaks of the spectrum of the poly(tBA) obtained using 2,5-dihydroxybenzoic acid as a matrix are at an interval of 128.2 (MW of tBA), and the molecular weight of each peak agrees well with the chemical structure of poly(tBA) bearing two hydrogens at both polymer chain ends ($1(H) + 128.2n + 1(H) + 39(K)$).[13] In addition, the isotopic distributions of the peaks observed in reflector mode of the analysis completely matched the calculated ones. Therefore, the polymerization was initiated by the nucleophlic attack of H^-, which should be generated by the reaction of tBuOK with iBu_3Al. Recently, Müller and co-workers reported that the CsF/iBu_3Al 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), the initiation occurred by the nucleophilic attack of H^- to nBA. We are tentatively assuming that our tBuOK/iBu_3Al 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 $AliBu_2OtBu$ in an “ate” form with a potassium cation.[14] This mechanism also explains the poor efficiency of the tBuOK/Me_3Al system where the β-hydride transfer required for the initiation is not feasible.[15]

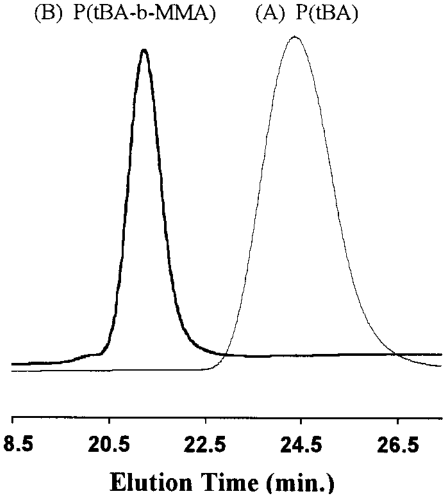


Figure 2. GPC traces of block copolymerization of tBA and MMA initiated with the tBuOK/iBu_3Al system. (A) Poly(tBA) obtained by the first stage polymerization; $M_n = 18\,700$, $M_w/M_n = 1.15$. (B) Poly(tBA-*b*-MMA) obtained by the second stage polymerization; $M_n = 108\,400$, $M_w/M_n = 1.05$.

Under the same conditions applied for tBA polymerization, *n*-butyl acrylate (nBA) and methyl methacrylate (MMA) cannot be polymerized in a controlled manner [poly(nBA); nBA:tBuOK:iBu_3Al = 100:1:5, in toluene at 0 °C for 1 h and at room temperature for 17 h, yield = 100%, $M_n = 46\,100$, $M_w/M_n = 2.30$, poly(MMA); MMA:tBuOK:iBu_3Al = 105:1:5, in toluene at 0 °C for 1 h and at room temperature for 17 h, yield = 31%, $M_n = 123\,000$, $M_w/M_n = 2.32$]. However, the growing end of tBA polymerization of this system could effectively initiate polymerization of MMA. For example, after tBA was polymerized using the tBuOK/iBu_3Al system (tBA:tBuOK:iBu_3Al = 51:1:5) in toluene at 0 °C for 20 min ($M_n = 18\,700$, $M_w/M_n = 1.15$), MMA (302 equiv with respect to tBuOK) was added at 0 °C, and the mixture was stirred for 1 h at 0 °C and 17 h at room temperature. As a result, the tBA−MMA block copolymer with a narrow MWD (M_n = 108 400, M_w/M_n = 1.05) was obtained in 96% yield. GPC charts of the polymers obtained in both stages (Figure 2) and a good agreement between the [tBA]:[MMA] in the initial feed ratio (14:86) and the copolymer composition determined from ^{1}H NMR (tBA unit: MMA unit = 13:87)[16] demonstrate that the block copolymerization indeed proceeded in a highly efficient manner, giving the narrow MWD copolymer. This result clearly indicates that the growing species of tBA polymerization in this system can initiate the polymerization of MMA.

In conclusion, we have demonstrated that the tBuOK/$i\mathrm{Bu}_3\mathrm{Al}$ system can initiate controlled polymerization of tBA and block copolymerization of tBA and MMA at 0 °C in toluene, giving narrow MWD (co)polymers. This initiating system will provide a new method to control anionic polymerization of various acrylate monomers.

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(11) An excess (ca. 5 equiv with respect to tBuOK) of $i\mathrm{Bu}_3\mathrm{Al}$ was employed since the use of 1 and 3 equiv of $i\mathrm{Bu}_3\mathrm{Al}$ resulted in the formation of poly(tBA)s with broad MWDs.
(12) Estimation of M_n of poly(tBA) by GPC using PMMA standards has been established to be reliable in the literature.[9]
(13) MALDI-TOF-MS analyses were performed on a PerSeptive Biosystems Voyager RP. Samples were prepared according to the method described in the literature. Nonaka, H.; Ouchi, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 2083.
(14) In contrast to highly electron withdrawing F, the electron donating nature of the tBuO group attaching to Al may facilitate the transfer of β-hydride, which should be the reason for the highly efficient initiation of this system.
(15) In the tBuOK/$\mathrm{Me}_3\mathrm{Al}$ system, the polymerization would be initiated with tBuO anion.
(16) Tacticity of the poly(MMA) unit of the copolymer determined by ^{1}H NMR is mm:mr:rr = 1:25:74.

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