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Controlled Anionic Polymerization of *tert*-Butyl Acrylate with Diphenylmethyl Anions in the Presence of Dialkylzinc

Takashi Ishizone, Ken Yoshimura, Akira Hirao, and Seiichi Nakahama*

Department of Polymer Chemistry, Faculty of Engineering, Tokyo Institute of Technology, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152-8552, Japan

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ABSTRACT: The anionic polymerization of *tert*-butyl acrylate (tBA) was carried out with a binary initiator system prepared from diphenylmethyllithium, -potassium, or -cesium (Ph_2CHM) and dimethylzinc or diethylzinc in THF at −78 °C. In the absence of dialkylzinc (R_2Zn), the poly(tBA)s produced with Ph_2CHM possessed ill-controlled molecular weights and broad molecular weight distributions (MWDs). On the other hand, poly(tBA)s having predicted molecular weights based on the molar ratio of monomer to initiators and narrow MWDs ($M_w/M_n < 1.15$) were obtained in quantitative yields by the initiation with Ph_2CHK or Ph_2CHCs in the presence of 10−20-fold excess R_2Zn, although the polymers obtained with Ph_2CHLi/R_2Zn still possessed broad MWDs ($M_w/M_n = 2$). The growing chain end of poly(tBA) associated with cesium counterion is completely stable to reinitiate the further polymerization of tBA in the presence of R_2Zn at −78 °C for 1 h, but 56% deactivation occurred after 24 h. It is thus demonstrated that Ph_2CHK or Ph_2CHCs in conjunction with R_2Zn induces the controlled anionic polymerization of tBA in THF at −78 °C. By contrast, addition of R_2Zn to the polymerization systems of methyl, ethyl, and isopropyl acrylates showed little effects on the improvement of polymer yields and the molecular weight controls. Well-defined block copolymers, poly(styrene-*b*-tBA), poly(methyl methacrylate-*b*-tBA), and poly(tBA-*b*-*N*,*N*-diethylacrylamide), were also anionically prepared by the sequential addition of styrene, methyl methacrylate, or *N*,*N*-diethylacrylamide with tBA in the presence of R_2Zn.

Introduction

It has been known that the anionic polymerization of alkyl acrylates is hardly controlled and usually disturbed by inherent side reactions of the ester carbonyl group and the labile α-hydrogen with the anionic initiators and the active chain ends.[1,2] The occurrence of such undesirable side reactions often results in low polymer yields, uncontrolled molecular weights, and broad molecular weight distributions (MWD)s. To overcome these serious problems, several new polymerization systems have been recently developed to achieve the controlled anionic polymerization of alkyl acrylates.[3−10]

The first successful development was the report by Teyssié and co-workers that in the presence of LiCl *tert*-butyl acrylate (tBA) was quantitatively polymerized with oligo(α-methylstyryl)lithium in THF at −78 °C to provide the polymers having predetermined molecular weights and relatively narrow MWDs; M_w/M_n values were around 1.2.[3] Such addition of LiCl to the polymerization system also enabled to provide well-defined block copolymers of styrene[4] or MMA[5] with tBA in quantitative block efficiencies. Similar improvement by the addition of lithium perchlorate as an additive was recently attained by Sivaram for the anionic polymerization of tBA.[6] In this case, it was reported that the propagating enolate anion of the polyacrylate was much more stable than the enolate anion in the presence of LiCl.

A similar favorable effect was observed in the polymerization of acrylate monomers by the addition of lithium *tert*-butoxide by Vlcek and Lochmann.[7] In the polymerizations of 2-ethylhexyl acrylate and butyl acrylate at −60 °C, the molecular weights of the polymers produced were found to depend on the molar ratios between monomers to initiators. All the polymers possessed fairly narrow MWDs ($M_w/M_n = 1.04−1.15$). Very recently, Teyssié et al. have shown that a multidentate alkoxide ligand, lithium 2-(2-methoxyethoxy)ethoxide, induced the controlled anionic polymerizations of primary alkyl acrylates such as butyl and nonyl acrylates in conjunction with the organolithium initiator.[8] This system also produced poly(methyl acrylate)s and poly(ethyl acrylate)s having unimodal MWDs in quantitative yields, although the MWDs were rather broad ($M_w/M_n = 1.3−1.8$).

Reetz and co-workers reported that the resonance-stabilized, metal-free ammonium methanides were efficient anionic initiators for the controlled polymerization of butyl acrylates even at room temperature.[9] For example, using the tetrabutylammonium dimethyl malonate as an initiator, a poly(butyl acrylate) with a M_n of 20 000 and a M_w/M_n value of 1.30 was successfully prepared. This metal-free carbanion system was also effective for the partial control of polymerization of methyl acrylate.[10] Poly(methyl acrylate)s ($M_n = 1260−9500$ and $M_w/M_n = 1.4−1.5$) were obtained by initiation with tetrabutylammonium di-*tert*-butyl malonate.

Although the controlled anionic polymerization of alkyl acrylates can be thus achieved to some extent, this still has been an unsolved and important subject in the polymer synthesis at the present time.[1,2] We have recently developed a new anionic initiator system prepared from diphenylmethylpotassium (Ph_2CHK) and diethylzinc (Et_2Zn) for the controlled polymerization of alkyl methacrylates.[11] With this binary initiator system, methyl methacrylate (MMA) was quantitatively polymerized to provide a PMMA with a quite narrow MWD ($M_w/M_n = 1.05$), whereas the polydispersity index was around 2.0 under similar conditions in the absence of Et_2Zn. More recently, *N*,*N*-dialkylacrylamides[12] and alkynyl methacrylates[13] also underwent the anionic polymerizations in a controlled fashion with the use of

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Table 1. Anionic Polymerization of tBA with Diphenylmethyl Anion in THF at −78 °C for 5 min in the Absence or in the Presence of Dialkylzinc[a]

run	tBA (mmol)	initiator (mmol)	R_2Zn (mmol)	Zn/I	$10^{-3}M_n$ calcd[b]	$10^{-3}M_n$ obsd[c]	M_w/M_n[c]
1	4.63	Ph_2CHLi/0.0690		0	8.7	9.9	2.60
2	6.42	Ph_2CHNa/0.0770		0	11	18	2.15
3	5.66	Ph_2CHK/0.0918		0	7.8	29	2.89
4	8.59	Ph_2CHK/0.0656		0	17	49	2.64
5	5.26	Ph_2CHCs/0.116		0	5.9	7.4	3.19
6	4.42	Ph_2CHLi/0.0680	Me_2Zn/1.22	18	8.5	5.9	7.93
7	7.47	*sec*-BuLi/0.0792[d]	Et_2Zn/1.22	15	12	13	3.32
8	6.51	Ph_2CHNa/0.0792	Me_2Zn/1.34	17	11	11	1.27
9	5.43	Ph_2CHNa//0.0700	Et_2Zn/1.34	19	10	8.7	1.10

[a] Yields of poly(tBA)s were quantitative in all cases. [b] M_n(calcd) = (MW of monomer) × [monomer]/[initiator] + MW of initiator. [c] M_n(obsd) and M_w/M_n were obtained by SEC calibration using standard PMMA in THF solution. [d] The polymerization was carried out after the addition of 1.5 equiv of 1,1-diphenylethylene to prepare 1,1-diphenyl-3-methylpentyllithium.

Ph_2CHK/Et_2Zn. It was observed from these studies that the added Et_2Zn certainly reduced the polymerization rates of methacrylates[11] and acrylamides and in particular affected the stereoregularity of the resulting poly(*N*,*N*-dialkylacrylamide)s.[12] Considering from these polymerization results, important factors are the Lewis acid character of dialkylzinc (R_2Zn) and probable coordination of R_2Zn with the growing chain ends to prevent the secondary side reactions by stabilizing the enolate-type anions.

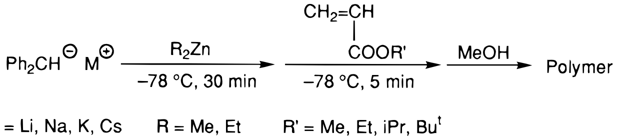
We herein report the results of anionic polymerization of acrylic esters with the above-described binary initiator system (Ph_2CHM and R_2Zn) to control the primary chain structures of the resulting polymers. The effects of counterions of the initiator on the M_n and MWD controls and the stability of the propagating carbanion are also discussed.

Results and Discussion

Effect of R_2Zn on Anionic Polymerization of *tert*-Butyl Acrylate with Diphenylmethyl Anions. In this report, we employed four alkyl acrylates as monomers to investigate the steric effect of alkyl substituents. The monomers involved methyl-, ethyl-, isopropyl-, and *tert*-butyl acrylates (MA, EA, IPA, and tBA, respectively). Among these monomers, the bulky *tert*-butyl ester is expected to be most resistant toward the side reaction such as nucleophilic carbonyl attack during the course of anionic polymerization.[1,2,5]

First of all, the anionic polymerization of tBA was carried out directly with diphenylmethyl anions in THF at −78 °C for 5 min, as shown in Table 1. The initiators included 1,1-diphenyl-3-methylpentyllithium and diphenylmethyllithium (Ph_2CHLi), -sodium (Ph_2CHNa), -potassium (Ph_2CHK), and -cesium (Ph_2CHCs). The orange-red color of initiators immediately disappeared on the addition of tBA to the initiator solutions at −78 °C. The polymerization of tBA was always completed within 5 min, and the poly(tBA) was obtained in quantitative yield. The resulting poly(tBA)s possessed fairly broad MWDs (M_w/M_n = 2.2−3.2) regardless of the counterions of the initiators. The observed molecular weights[14] of the polymers were usually much higher than the predicted values based on the molar ratios of tBA to initiators. This is consistent with the previous observation reported by Teyssié et al.,[3] where a poly(tBA) having a very broad MWD (M_w/M_n = 3.61) is obtained with oligo(α-methylstyryl)lithium in THF at −78 °C. It is thus obvious that the polymerization of tBA in the absence of R_2Zn is far from the controlled polymerization.

Scheme 1



Then, tBA polymerization was attempted with our developed binary initiator system, diphenylmethylides (Ph_2CHM) and R_2Zn,[11−13] under similar conditions, as shown in Scheme 1. In this report, Me_2Zn was also employed as an additive as well as Et_2Zn. To prepare the initiator system, R_2Zn was added to the diphenylmethyl anions in THF at −78 °C. The characteristic orange-red color of Ph_2CHM changed immediately to a pale yellow color, and it was allowed to stand for 0.5 h at −78 °C before the polymerization of tBA. In the presence of 15−25-fold of R_2Zn based on the initiator, the polymerization of tBA was similarly very rapid and proceeded quantitatively within 1 min at −78 °C.[15] The polymerizations were usually carried out for 5 min by the way of precaution to achieve the quantitative conversion.

In the polymerizations using organolithium/R_2Zn systems, the resulting poly(tBA)s still had broad MWDs, while the observed M_n values were fairly close to the theoretical ones. No effect of the added R_2Zn on the MWD controls was observed, when the polymerization of tBA was initiated with organolithiums. A similar polymerization was then performed with organosodium initiator after the addition of R_2Zn. Interestingly, addition of Me_2Zn (17 equiv) or Et_2Zn (19 equiv) to Ph_2CHNa initiator remarkably decreased the polydispersity index, from around 2.2 to 1.27 or 1.10, respectively. Thus, the additive effect of R_2Zn on the anionic polymerization of tBA is indicated to some extent.

More striking results concerning the MWD control were attained by the initiation of Ph_2CHK/R_2Zn or Ph_2CHCs/R_2Zn, as shown in Table 2. The MWDs of poly(tBA)s thus produced were unimodal and quite narrow, and the polydispersity indices were dramatically reduced to around 1.1. Furthermore, the M_n values of these poly(tBA)s were in accordance with the calculated values,[14] meaning that we could control the molecular weights by changing the molar ratio of monomer to initiator. To examine the effect of R_2Zn further, two binary initiator systems of Ph_2CHK/Et_2Zn and Ph_2CHCs/Me_2Zn were investigated in detail by changing the molar ratios of R_2Zn and counterion from 0 to 27. It should be pointed out again that the polymers produced directly with either Ph_2CHK or Ph_2CHCs had ill-

Table 2. Anionic Polymerization of tBA with Ph_2CHM in THF at − 78 °C for 5 min in the Presence of Dialkylzinc[a]

					$M_n \times 10^{-3}$		
run	tBa (mmol)	initiator (mmol)	R_2Zn (mmol)	Zn/I	calcd	obsd	M_w/M_n
10	5.27	Ph_2CHK/0.0630	Me_2Zn/1.42	23	11	10	1.11
11	8.45	Ph_2CHK/0.0808	Et_2Zn/0.183	2.3	14	11	2.93
12	6.20	Ph_2CHK/0.0654	Et_2Zn/0.486	7.4	12	11	1.29
13	9.13	Ph_2CHK/0.105	Et_2Zn/1.11	11	11	15	1.08
14	5.36	Ph_2CHK/0.0655	Et_2Zn/1.01	15	11	11	1.09
15	6.53	Ph_2CHK/0.0759	Et_2Zn/1.49	20	11	13	1.07
16	8.97	Ph_2CHK/0.0820	Et_2Zn/2.17	27	14	18	1.04
17[b]	9.15	Ph_2CHK/0.104	Et_2Zn/1.67	11	8.7	9.4	1.50
18	6.98	Ph_2CHK/0.0333	Et_2Zn/0.458	14	27	35	1.06
19	15.9	Ph_2CHK/0.0377	Et_2Zn/0.672	18	54	55	1.09
20	5.31	Ph_2CHCs/0.0668	Me_2Zn/0.116	1.7	10	9.3	1.40
21	6.54	Ph_2CHCs/0.112	Me_2Zn/0.639	5.7	7.6	7.2	1.19
22	5.42	Ph_2CHCs/0.106	Me_2Zn/1.69	16	6.7	6.0	1.10
23	7.44	Ph_2CHCs/0.0770	Me_2Zn/1.37	18	12	12	1.12
24	8.23	Ph_2CHCs/0.0606	Me_2Zn/1.43	24	27	27	1.10
25[c]	5.12	Ph_2CHCs/0.0617	Me_2Zn/1.32	21	11	12	1.15
26[d]	3.25	Ph_2CHCs/0.0422	Me_2Zn/1.30	32	9.9	10	1.51[e]
27	6.07	Ph_2CHCs/0.0799	Et_2Zn/1.48	19	9.7	7.8	1.13

[a] Yields of poly(tBA)s were quantitative in all cases. [b] At −30 °C. [c] At −40 °C. [d] At 0 °C. [e] Significant tailing in the SEC curve.

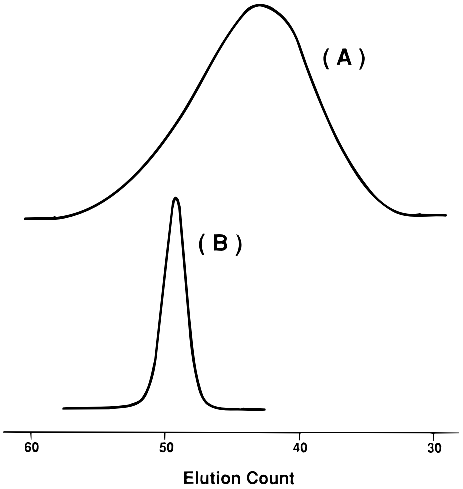


Figure 1. SEC curves of poly(tBA)s obtained with Ph_2CHK in the absence (A) and in the presence of Et_2Zn (15 equiv) (B): peak A, M_n = 29 000, M_w/M_n = 2.89; peak B, M_n = 11 000, M_w/M_n = 1.08.

controlled M_ns and very broad MWDs. On the other hand, on the addition of only 2.3 equiv of Et_2Zn to Ph_2CHK in THF, the M_n value of the polymer became close to the predicted one, whereas the MWD was still broad (Table 2, run 11). In the case of Ph_2CHCs, the M_w/M_n value of the poly(tBA) was reduced from 3.19 to 1.40 only by the addition of 1.7-fold of Me_2Zn in addition to the fine M_n control. It is apparent from the results shown in Table 2 (runs 11−16 and 20−24) that the MWDs became narrower as the number of equivalents of R_2Zn increased. The polydispersity indices became almost constant and satisfactory values (M_w/M_n = ca. 1.1) from the synthetic viewpoints, when 10-fold of R_2Zn was added to the initiator system. Typical SEC curves of the resulting poly(tBA)s are illustrated in Figure 1. The narrowing of the MWD is evidently achieved during the course of the addition of R_2Zn. Thus, we have certainly realized the MWD and M_n controls in the anionic polymerization of tBA initiated with the binary systems of Ph_2CHK/R_2Zn and Ph_2CHCs/R_2Zn.

The effect of polymerization temperature is also critical. Raising the temperature from −78 to −30 °C in the polymerization using Ph_2CHK/Et_2Zn (Table 2, run 17), a polymer having a broad MWD was obtained after 5 min. In the case of the Ph_2CHCs/Me_2Zn system, the polymerization system seemed to be more stable than that of Ph_2CHK/Et_2Zn. At −40 °C, the resulting poly(tBA) still maintained its unimodal and narrow MWD (M_w/M_n = 1.15), but the significant tailing toward the lower molecular weight region was observed in the SEC curve of the polymer produced at 0 °C. This observed broadening of the MWD might be derived from the α-proton abstraction adjacent to the ester carbonyl group or the intramolecular backbiting between the propagating chain end and the carbonyl group of the pendant *tert*-butyl ester during the course of polymerization, as discussed later. At −78 °C, these side reactions are negligible, but they are significant at the elevated temperatures ranging −30 to 0 °C.

Another important aspect in this polymerization system is that the observed molecular weights by SEC are in agreement with those predicted from molar ratios of monomer to initiator within an experimental error, as shown in Table 2. The molecular weights of the poly(tBA)s could be satisfactorily controlled in the range 6000−55 000 by changing the [M]/[I] ratios. Narrow MWDs were maintained in each polymer sample, and their M_w/M_n values were less than 1.1.

Stability of Active Chain Ends of Poly(tBA). To evaluate the living character of the polymerization system of tBA with Ph_2CHK/Et_2Zn or Ph_2CHCs/Me_2Zn, the stability of the active growing chain end was examined by means of a second monomer addition (two-stage polymerization). As mentioned before, the polymerization of tBA was extremely rapid and found to be complete within 1 min under the conditions employed here. tBA was first polymerized with Ph_2CHK/Et_2Zn in THF at −78 °C for 1 min, and a second feed of tBA in THF was added to the mixture. After further addition of tBA, the SEC trace of the postpolymer shifted from the elution count of homopolymer toward the higher molecular weight side (Figure 2). It maintained a sharp unimodal peak with a predicted molecular weight. This suggests that the propagating species of poly(tBA) are sufficiently stable at −78 °C for 1 min in the presence of Et_2Zn to propagate the second stage of the polymerization. On the other hand, a bimodal SEC curve was observed in the polymer obtained by addition of more monomer after 5 min. The SEC peak

Table 3. Two-Stage Polymerization of tBA with Ph_2CHM/R_2Zn in THF at −78 °C[a]

run	countercation	R_2Zn[b]	time[c] (min)	$10^{-3}M_n$[d] calcd	$10^{-3}M_n$[d] obsd	M_w/M_n[d]	deactivated propagating carbanion (%)[e]
28	K^+	Et_2Zn	1	13	14	1.08	nd[f]
29	K^+	Et_2Zn	5	16	20	1.33[g]	61
30	K^+	Me_2Zn	5	19	19	1.36[g]	34
31	Cs^+	Et_2Zn	5	10	12	1.16	nd
32	Cs^+	Et_2Zn	60	13	11	1.17	nd
33	Cs^+	Me_2Zn	5	27	27	1.10	nd
34	Cs^+	Me_2Zn	30	16	15	1.15	nd
35	Cs^+	Me_2Zn	1440	12	12	1.77[g]	56
36[h]	Cs^+	Me_2Zn	5	13	13	1.19[i]	13

[a] Yields of postpolymers were quantitative in all cases. Second-stage polymerizations were carried out for 5 min. [b] R_2Zn/initiator = 13−24. [c] Polymerization time of first-stage polymerization. After standing for the present time, a second feed of tBA was added to the polymerization system. [d] M_n and M_w/M_n for the postpolymer. [e] The percentage of the deactivated propagating carbanion of poly(tBA) obtained in the first-stage polymerization. This was estimated from the SEC curve of the postpolymer. [f] Not detected within the experimental error (3%). [g] Bimodal MWD. [h] At −40°C. [i] The SEC curve of postpolymer possessed a significant tailing probably due to the partial deactivation of propagating species.

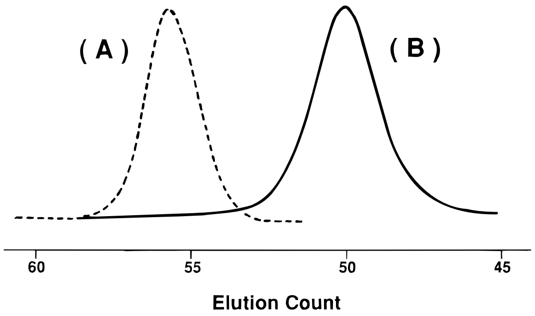


Figure 2. SEC curves of poly(tBA)s obtained with Ph_2CHK/Et_2Zn at the first-stage polymerization for 1 min (A, M_w/M_n = 1.08) and at the second-stage polymerization after 1 min (B, M_w/M_n = 1.08).

eluted at lower molecular weight side was identical to that obtained by the first polymerization. This indicates that the active growing chain ends are deactivated considerably after 5 min of the first polymerization, although no apparent deactivation is observed within 1 min. The degree of deactivation was estimated to be 61% at −78 °C after 5 min by comparing the SEC peak areas. In the case of the Ph_2CHK/Me_2Zn system, 34% of propagating species was deactivated after 5 min under similar conditions, as shown in Table 3.

The propagating chain ends associated with the cesium counterion were remarkably more stable than those of the potassium counterpart. No apparent deactivation was observed even after 1 h at −78 °C (Table 3, run 32), and the postpolymer maintained its unimodal and relatively narrow MWD (M_w/M_n = 1.17). Even after 24 h at −78 °C, the percentage of the dead prepolymer was around 56%, and 44% of the terminal carbanion kept its reactivity to reinitiate further polymerization. The poly(tBA) produced with Ph_2CHCs/Me_2Zn at −40 °C still maintained its unimodal MWD and well-defined M_n value, but 13% of the growing chain end lost its activity after 5 min. It seems that the propagating enolate anion is still considerably unstable even in the presence of R_2Zn at −40 °C.

To elucidate the termination mechanism of the polymerization, polymerizations carried out with Ph_2CHCs/Me_2Zn under identical conditions were terminated with methanol after 1 min and 1 h, respectively. Both resulting polymers were analyzed by SEC. It was observed that their molecular weights were predicted values, and the MWDs were maintained to be unimodal and narrow in both polymers. No peaks at higher molecular weight side were observed. Thus, intermolecular termination reactions between polymer chains leading to the broadening of MWD are ruled out. One of the most probable terminations is an intramolecular backbiting reaction toward the antepenultimate ester group with the terminal enolate anion. This side reaction often occurs in the anionic polymerization of alkyl methacrylates[1,2,5] as well as in the so-called group transfer polymerization.[16] Another possible candidate for the termination reaction is a proton abstraction of a labile acidic α-hydrogen of the polymer main chain.[1−3] This backbiting reaction and the proton abstraction inherent in the anionic polymerization of acrylate monomers are most likely for the termination reactions in our polymerization system examined above, although the former is relatively slow in THF at −78 °C in the anionic polymerization of alkyl methacrylates.

From the synthetic viewpoint, it should be noted that larger amounts of R_2Zn (ca. 15-fold) were required to control the polymerization of tBA, compared with the polymerization systems of alkyl methacrylates,[11] where the polymers having M_w/M_n values of 1.05 were obtained even when the Ph_2CHK/Et_2Zn was only ca. 3. A real structure of the combined initiator prepared from Ph_2CHM and Et_2Zn is not clear yet at the present time. From the ^1H NMR analysis of the resulting polymer, it is however certain that the polymerization of tBA is initiated with diphenylmethyl anion even in the presence of excess R_2Zn.[14] The instantaneous color change of Ph_2CHM on the addition of R_2Zn suggests that the ionic dissociation of diphenylmethyl anions is strongly influenced by the added R_2Zn.

On the other hand, the added R_2Zn has no significant effect on the stereoregularity of the resulting poly(tBA) in THF at −78 °C, as can be seen in Table 4. Tacticities of the resulting poly(tBA)s were estimated by triad sequence of the ester carbonyl carbons in ^{13}C NMR spectroscopy (see Experimental Section). Regardless of the counterion of the initiators, the resulting poly(tBA) possessed atactic triad tacticity either in the absence or in the presence of R_2Zn. This is sharp contrast to our recent observation for the anionic polymerization of *N,N*-dialkylacrylamides[12] but quite similar to those of alkyl methacrylates.[11] In the former case, the stereoregularity of the resulting poly(*N,N*-dialkylacrylamide)s is strongly influenced by the stoichiometry of the added R_2Zn, polymerization temperature, and counterion of the initiators. By contrast, in the latter case of poly(alkyl methacrylate)s, the stereoregularity is only dependent on the counterion but not on the presence of R_2Zn. The strong coordination of the added R_2Zn with

Table 4. Stereoregularity of Poly(tBA) Produced with Ph_2CHK in THF at −78 °C in the Absence or in the Presence of Dialkylzinc[a]

run	initiator system	Zn/I	M_w/M_n	tacticity (%)[a]		
				rr	*mr*	*mm*
1	Ph_2CHLi	0	2.60	42	38	20
2	Ph_2CHNa	0	2.15	30	42	28
3	Ph_2CHK	0	2.89	39	38	23
5	Ph_2CHCs	0	3.19	35	45	20
6	Ph_2CHLi/Me_2Zn	18	7.93	44	37	19
7	*sec*-BuLi/Et_2Zn	15	3.32	44	37	19
8	Ph_2CHNa/Me_2Zn	17	1.27	41	29	28
9	Ph_2CHNa/Et_2Zn	19	1.10	41	30	28
10	Ph_2CHK/Me_2Zn	23	1.11	40	39	21
14	Ph_2CHK/Et_2Zn	15	1.09	35	45	20
23	Ph_2CHCs/Me_2Zn	18	1.12	38	41	21
27	Ph_2CHCs/Et_2Zn	19	1.13	42	40	18

[a] Tacticity of the resulting polymers was determined by the ^{13}C NMR spectrum of the carbonyl region.

the propagating species is suggested from the observed tacticity of polymers only in the former case but not in the latter case, although the drastic decrease of k_p values was actually confirmed after the addition of Et_2Zn to each polymerization system.[11,15] On the basis of these polymerization results and the weak Lewis acid character of R_2Zn, we consider that some R_2Zn molecules may weakly coordinate with diphenylmethyl anions as well as the propagating enolate anion of poly(tBA) during the course of polymerization, but zinc enolate is not likely formed by the transmetalation. Even in a polar solvent such as THF, such coordination of R_2Zn might be possible to prevent the propagating carbanion from the side reaction but not to affect the stereoregularity.

Block Copolymerization of tBA with Styrene, MMA, and *N,N*-Diethylacrylamide. One of the most important features of living polymerization is the synthetic potential of preparation of well-defined block copolymers by the sequential copolymerization. To evaluate the capability of the present polymerization system, the sequential anionic block copolymerization of styrene and tBA was carried out in THF at −78 °C, as shown in Table 5. Styrene was polymerized first with cumylpotassium in THF at −78 °C for 20 min followed by the addition of 17 equiv of Et_2Zn, and the mixture was allowed to stand for 30 min. tBA was then added to this polymerization system at −78 °C. The SEC traces of the resulting polymer showed bimodal peaks corresponding to a homopolymer of styrene and a block copolymer, although tBA was consumed quantitatively. This suggests that the significant termination reaction takes place at the initiation stage of the polymerization of tBA even in the presence of an excess amount of Et_2Zn. Since diphenylmethyl anions were effective initiators in the presence of R_2Zn for the polymerization of tBA, polystyryl anion was end-capped with 1,1-diphenylethylene to convert into a bulky and less-nucleophilic carbanion which resembles the diphenylmethyl anion. The end-capped polystyryl anion was hence allowed to react with Et_2Zn (12 equiv excess to the anion) for 30 min in THF at −78 °C, and then tBA was added to the mixture. By this modified pathway, a well-defined diblock copolymer of styrene and tBA was successfully prepared (Table 5, run 37). A similar result was obtained by the use of Me_2Zn to afford a poly(styrene-*b*-tBA) having a narrow MWD. Thus, the termination observed as above could be completely eliminated by the end-capping of polystyryl anion with 1,1-diphenylethylene. This strongly indicates that the choice of anionic initiator in our system using Et_2Zn is very important for success of the controlled polymerization of tBA to suppress some side reactions. A living polymer of MMA, which was prepared with Ph_2CHK/Et_2Zn in THF at −78 °C, could also initiate the polymerization of tBA to give a block copolymer of MMA and tBA, although a very small portion (~3%) of homopoly(MMA) was observed in the copolymerization product. This is accordance with the previous report of Teyssié and co-workers for the anionic copolymerization of MMA and tBA, where a similar partial termination has been observed.[5]

Next, a sequential block copolymerization of tBA and MMA was similarly attempted by changing the additional order of comonomers. tBA was first polymerized with Ph_2CHCs/Me_2Zn at −78 °C, and MMA was then added to the polymerization system. MMA was completely consumed under the employed conditions, as expected from our previous report.[11] However, a copolymerization product included a significant amount of homopolymer of tBA in addition to a block copolymer with a M_n value higher than the expected one, although a reason was not clear yet. On the other hand, when *N,N*-diethylacrylamide (DEAA)[12] was added as a second monomer to the polymerization system of tBA under similar conditions, a new tailored block copolymer, poly(tBA-*b*-DEAA), was successfully obtained. The resulting block copolymer is found to be free of homopoly(tBA) and possess a predicted M_n value with a relatively narrow distribution ($M_w/M_n = 1.17$), as can be seen in Table 5. It is demonstrated that the living poly(tBA) prepared with Ph_2CHM/R_2Zn is a versatile macroinitiator for the sequential copolymerization to prepare block copolymers of well-defined chain structures.

Anionic Polymerizations of MA, EA, and IPA with Ph_2CHM/R_2Zn. In the preceding sections, we have succeeded in the controlled anionic polymerization of tBA with the Ph_2CHM ($M^+ = K^+$ or Cs^+)/R_2Zn system in THF at −78 °C. The polymerizations of MA, EA, and IPA were similarly attempted in the absence or in the presence of the reagent prepared from Ph_2CHM and ca. 10-fold of R_2Zn. The results are summarized in Table 6.

Table 5. Block Copolymerization of tBA with Styrene, MMA, and *N,N*-Diethylacrylamide in THF at −78 °C[a]

run	1st monomer (mmol)	2nd monomer (mmol)	initiator (mmol)	R_2Zn (mmol)	$10^{-3}M_n$		M_w/M_n[b]
					calcd	obsd[d]	
37[c]	styrene, 6.61	tBA, 6.78	Cumyl-K,[d] 0.0872	Et_2Zn, 1.29	17	16	1.13
38[c]	styrene, 3.66	tBA, 5.40	Cumyl-K, 0.0850	Me_2Zn, 1.42	13	12	1.11
39	MMA, 6.54	tBA, 5.39	Ph_2CHK, 0.0666	Et_2Zn, 1.15	23	20	1.08[e]
40	tBA, 6.54	DEAA, 5.88	Ph_2CHCs, 0.0712	Me_2Zn, 1.92	14	14	1.17

[a] Yields were quantitative in all cases. [b] M_n and M_w/M_n for the block copolymer. M_n(obsd) was determined by using the molecular weight of homopolymer and the molar ratio of the monomer units in the block copolymer analyzed by ^1H NMR. [c] After first-stage polymerization of styrene, the propagating carbanion of polystyrene was end-capped with 1,1-diphenylethylene to reduce the basicity and nucleophilicity. [d] Cumylpotassium. [e] A very small portion (~3%) of homopoly(MMA) was included in the copolymerization product.

Table 6. Anionic Polymerization of MA, EA, and IPA with Ph_2CHM in THF at −78 °C

run	monomer (mmol)	initiator (mmol)	R_2Zn (mmol)	Zn/I	time (min)	yield[a] (%)	$10^{-3}M_n$		M_w/M_n
							calcd[c]	obsd	
41	MA/9.80	Ph_2CHK/0.0864		0	5	31	3.1	*b*	1.59
42	EA/8.67	Ph_2CHK/0.0890		0	5	44	3.8	*b*	1.40
43	IPA/6.80	Ph_2CHK/0.0640		0	5	67	8.1	4.3	2.49
44	MA/10.7	Ph_2CHK/0.102	Et_2Zn/1.16	11	5	25	2.5	0.58	1.51
45	MA/8.62	Ph_2CHK/0.126	Et_2Zn/1.25	10	240	30	1.8	0.61	1.62
46	MA/8.01	Ph_2CHCs/0.114	Me_2Zn/2.41	21	5	15	1.4	0.98	1.62
47	EA/9.73	Ph_2CHK/0.105	Et_2Zn/0.953	11	5	44	4.2	0.82	2.05
48	EA/7.57	Ph_2CHK/0.0785	Et_2Zn/0.804	10	240	56	5.5	0.76	1.95
49	EA/8.78	Ph_2CHCs/0.111	Me_2Zn/2.01	18	5	17	1.7	1.9	1.42
50	IPA/8.46	Ph_2CHK/0.111	Et_2Zn/1.05	10	5	55	4.8	5.9	1.47
51	IPA/6.89	Ph_2CHK/0.0698	Et_2Zn/1.05	21	240	78	8.9	2.4	1.57
52	IPA/7.70	Ph_2CHCs/0.0713	Me_2Zn/1.30	19	5	85	11	11	1.54

[a] Polymer yield of water insoluble part. [b] Oligomers having M_ns lower than 2000 were obtained. [c] M_n (calcd) (MW of monomer) × yield × [monomer]/[initiator]/100 + MW of initiator.

In the absence of R_2Zn, all these acrylate monomers underwent the anionic polymerization with Ph_2CHK in THF at −78 °C, but the yields of polymers were considerably low after 5 min, i.e., 31, 44, and 67% yields for MA, EA, and IPA, respectively. The molecular weights of the polymeric products derived from MA and EA were quite low and the MWDs were broad (M_w/M_n = 1.5). The polymerization of IPA also gave the polymer having an uncontrolled M_n value and a very broad MWD.

Then, MA, EA, and IPA were polymerized with the binary initiator system consisting of Ph_2CHK and Et_2Zn under identical conditions. However, the polymerization results of MA and EA in the presence of Et_2Zn were unexpectedly disappointing and similar to those obtained directly with Ph_2CHK. The yields of polymers were quite low, and the M_ns and MWDs were ill-controlled. Yields of polymers did not significantly increase even when the polymerizations were carried out for a longer time of 4 h at −78 °C. The use of another initiator system of Ph_2CHCs/Me_2Zn also provided the poly(MA) and the poly(EA) having ill-controlled chain structures in very low yields, 15 and 17%, respectively. A rather better result was obtained in the polymerization of IPA in the presence of R_2Zn. IPA was polymerized with Ph_2CHK/Et_2Zn in 55% yield after 5 min to provide a polymer with a M_w/M_n of 1.5 ($M_n^{obsd} = 5900$ vs $M_n^{calcd} = 4800$). However, a longer polymerization time of 4 h or use of cesium counterion (Cs^+) did not effectively improve the polymer yield of IPA. Thus, the initiator system consisted of Ph_2CHM and R_2Zn could not induce the anionic polymerizations of MA, EA, and IPA in a controlled fashion, although they were particularly effective to promote the controlled anionic polymerization of tBA as discussed above. This limitation on the monomer structure is sharp contrast to our previous finding for alkyl methacrylates.[11,13] Methyl,[11] isopropyl,[11] *tert*-butyl,[11] and even functional alkynyl esters,[13] containing C≡C linkages, underwent controlled anionic polymerizations with Ph_2CHM/R_2Zn systems to afford the polymers of well-defined chain structures.

Conclusion

We have realized the effectiveness of Ph_2CHM (M = K^+ or Cs^+)/R_2Zn (R = Me or Et) as the anionic initiator for the controlled polymerization of tBA in THF at −78 °C. These binary initiator systems provide well-defined poly(tBA)s having predicted molecular weights based on the feed molar ratios and fairly narrow MWDs in quantitative yields. The growing chain end of the resulting poly(tBA) by the initiation with Ph_2CHCs/Me_2Zn is found to be stable at −78 °C within 1 h to reinitiate the further propagation, but its deactivation is observed in 56% after 24 h. Although these features of the polymerizations indicate a certain association of added R_2Zn toward the propagating carbanion as the weak Lewis acid, no effect on the stereoregularity of the resulting poly(tBA) was observed.

Experimental Section

Materials. Alkyl acrylates and MMA were distilled over CaH_2 in vacuo and sealed off in the presence of CaH_2 in an ampule equipped with a break-seal under high-vacuum conditions. The monomers were stirred overnight at room temperature and then distilled over CaH_2 on a vacuum line into the all-glass apparatus with break-seals. For further purification, trioctylaluminum or triethylaluminum (ca. 3 mol %) was added to the monomers and stirred for 0.5 h at room temperature.[17] The acrylates and MMA were finally purified by distillation over trialkylaluminum, and the purified monomers were diluted with dry THF. Styrene, 1,1-diphenylethylene, diphenylmethane, and *N*,*N*-diethylacrylamide were distilled from CaH_2 and diluted with dry THF. The resulting monomer solutions (ca. 0.6−0.8 M) in THF were stored at −30 °C just prior to the polymerization. Me_2Zn and Et_2Zn (TOSOH Akuzo Co.) were distilled from phenylmagnesium chloride (ca. 5 mol %) under high-vacuum conditions and diluted with dry THF.

Initiators. Ph_2CHLi, Ph_2CHNa, and Ph_2CHK were prepared by the reactions of diphenylmethane and the corresponding metal naphthalenides in THF at room temperature for 2 days. Ph_2CHCs was synthesized by the reaction of diphenylmethane and cesium metal in the presence of a catalytic amount of naphthalene in THF at ambient temperature for 1 day. The concentration of initiator was determined by colorimetric titration in a sealed reactor under vacuum, as previously reported.[18]

Anionic Polymerization. All the polymerizations were carried out in THF under high-vacuum conditions in a sealed all-glass reactor with break-seals.[18] A THF solution of R_2Zn was added to diphenylmethylides in THF at −78 °C and allowed to react for 0.5 h at −78 °C. The orange-red color of initiator was instantaneously changed to pale yellow on mixing with R_2Zn. Acrylate solutions in THF cooled to −78 °C were rapidly added into the initiator system prepared at −78 °C with vigorous stirring. The polymerization of tBA was very rapid and completed within 1 min under the conditions employed here, whereas the conversions of other acrylates were usually far from quantitative. The polymerization was terminated with degassed methanol. After concentration of the polymerization mixture by evaporation, the residue was dissolved in a small volume of THF and poured into 0.05 M HCl aqueous solution to precipitate a polymer. The precipitated polymer was collected by filtration to measure the M_n

and MWD and further purified by the reprecipitations from THF to water and by freeze-drying from the benzene solution.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX300S (300 MHz ^{1}H and 75 MHz ^{13}C) or a JEOL GSX-500 (500 MHz ^{1}H and 125 MHz ^{13}C) spectrometer in $CDCl_3$. Stereoregularity of poly(tBA) was determined by the ^{13}C NMR integral ratio of three splitted ester carbonyl signals appearing at 173.70−174.25 ppm. Three signals were assigned as *rr* (173.70−173.85 ppm), *mr* (173.85−174.03 ppm), and *mm* (174.03−174.25 ppm) triads. Size exclusion chromatography (SEC) was obtained at 40 °C with a TOSOH HLC 8020 instrument equipped with a series of three polystyrene gel columns (TOSOH TSKgel G4000H_{XL}, G3000H_{XL}, and G2000H_{XL}) and with refractive index or UV (254 nm) detection. THF was a carrier solvent at a flow rate of 1.0 mL min^{-1}. An SEC calibration curve was made to determine M_n and M_w/M_n values by using standard PMMA samples.[14]

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(14) The M_n value of poly(tBA) was estimated by the SEC analysis using poly(methyl methacrylate) standards. The M_ns were also obtained by ^{1}H NMR analysis by assuming that two phenyl groups derived from the initiator residue (Ph_2CH) are present in each polymer chain. Since both values are found to be nearly equal to each other, the M_n and M_w/M_n values estimated from the SEC measurement are considered to be reliable. This also indicates that all the diphenylmethyl anions quantitatively initiate the tBA.
(15) In our previous report on the polymerization of alkyl methacrylates with Ph_2CHK in THF,[11] the drastic decrease of polymerization rate was observed after the addition of 65-fold of Et_2Zn. The apparent k_p value was actually reduced from 142 to 3.5 L mol^{-1} s^{-1} for the polymerization of MMA. However, it seems very difficult to determine the rate constant of the polymerization of tBA initiated with Ph_2CHM/R_2Zn due to its rapidness in our system. A detailed experiment using flow-tube reactor might be needed for the information on the rate constant.
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