Macromolecules **1999,** *32,* 955−957 **955**

Controlled Anionic Polymerization of *tert*-Butyl Acrylate with Diphenylmethylpotassium in the Presence of Triethylborane

Takashi Ishizone, Ken Yoshimura,
Eriko Yanase, and Seiichi Nakahama*

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

Received August 14, 1998
Revised Manuscript Received November 25, 1998

Introduction. It is known that the anionic polymerization of acrylates is hardly controlled in terms of polymer yield, molecular weight, and its distribution due to inherent side reactions such as the nucleophilic attack of the initiator and/or the propagating enolate anion toward ester carbonyl group and the abstraction of acidic a-hydrogen from monomers and the resulting polymers.[1] Recently, several modified polymerization systems have been developed to prevent these serious side reactions and to afford poly(acrylate)s with well-defined chain structures.[2−6] The successful strategies for the polymerizations involved the addition of inorganic lithium salts[2,3] or lithium alkoxides[4,5] to the polymerization systems or the use of metal-free, large countercations such as tetraalkylammonium salts[6] to control the M_n values and the molecular weight distributions (MWDs) of the resulting poly(alkyl acrylate)s.

We have recently developed a new effective initiator system consisting of diphenylmethylpotassium (Ph_2CHK) and dialkylzinc in THF for the controlled polymerization of alkyl methacrylates[7] and *N*,*N*-dialkylacrylamides.[8] With this binary initiator system, *tert*-butyl acrylate (tBA) also underwent the anionic polymerization in a controlled fashion at −78 °C to give a polymer having a predetermined M_n value and a narrow MWD.[9] The drastic decrease of k_p values in the former cases[7,8] and the additive effect of dialkylzinc on the stereoregularity of the poly(*N*,*N*-dialkylacrylamide)s[8] were particularly observed besides the adequate control of M_ns and MWDs. It is considered that the added dialkylzinc coordinates with the initiator and the propagating chain end as a weak Lewis acid, even in polar THF during the course of polymerization, to suppress the above-mentioned side reactions in addition to affecting the polymerization rates and stereoregularities.

In this communication, we report the additive effect of triethylborane (Et_3B) which exhibits a similar Lewis acid character for the controlled anionic polymerization of tBA initiated with Ph_2CHK in THF even at 0 °C. Considering the stronger Lewis acidity of trialkylborane with respect to that of dialkylzinc,[10] a tighter coordination of the added Et_3B with the anionic species is expected in the present polymerization system.

Results and Discussions. We examined the anionic polymerization of tBA in the presence of Et_3B at −78 °C.[11,12] Upon the addition of a ca. 3-fold amount of Et_3B to the THF solution of Ph_2CHK at −78 °C, the orange red color of Ph_2CHK immediately disappeared to give a colorless solution. This suggests the strong coordination of Et_3B with Ph_2CHK or the formation of tetracoordinated diphenylmethyl triethylborate, **1**, in the mixture, under experimental conditions (Scheme 1). This initiator system was allowed to stand for 0.5 h at −78 °C, and tBA in THF was added to the mixture. No apparent polymerization of tBA virtually occurred with Ph_2CHK/Et_3B in THF at −78 °C, even after 24 h, and the starting monomer tBA was recovered nearly quantitatively, as shown in Table 1 (run 3).

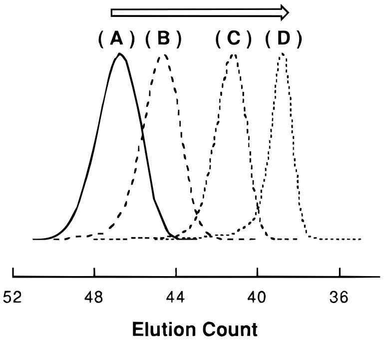

Figure 1. SEC curves of a series of poly(tBA)s obtained with Ph_2CHK and 19-fold excess of Et_3B in THF at 0 °C. Key: peak A, after 3 h, 25% conversion, $M_n = 1900$, $M_w/M_n = 1.05$; peak B, after 6 h, 34% conversion, $M_n = 2900$, $M_w/M_n = 1.05$; peak C, after 19 h, 65% conversion, $M_n = 6500$, $M_w/M_n = 1.03$; peak D, after 72 h, 96% conversion, $M_n = 11\,000$, $M_w/M_n = 1.04$.

By contrast, the polymerization of tBA unequivocally proceeded at 0 °C to produce the polymer quantitatively under the similar conditions, although the rate of polymerization is significantly decreased upon increasing the amount of added Et_3B from 3-fold to 17−19-fold. The SEC curve of the resulting poly(tBA) showed a unimodal and very narrow MWD; the polydispersity indices were always within 1.1 (Table 1, run 4−9). Figure 1 clearly shows that the SEC curves of a series of poly(tBA)s produced with Ph_2CHK/Et_3B (19 equiv) are shifted from the lower molecular weight region to the higher one with increasing the conversion of tBA. This clearly demonstrates the absence of chain termination and transfer reactions and the remarkable stability of the propagating species derived from tBA in the presence of Et_3B in THF, even at 0 °C. Furthermore, the M_n values of the polymers obtained at 0 °C agreed well with the calculated ones, based on the molar ratios between tBA and Ph_2CHK regardless of the amount of added Et_3B, suggesting that initiation exclusively occurs by the nucleophilic attack of the diphenylmethyl group on the β-carbon of the vinyl group of tBA.[13]

To elucidate the polymerization mechanism clearly, the resulting poly(tBA)s were analyzed by the ^{1}H NMR and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI−TOF−MS).[14] These analyses of the poly(tBA)s revealed that one Ph_2CH group is incorporated in each polymer chain end as the initiator residue.[13] In the MALDI−TOF−MS, the major mass peaks corresponding to the expected value for the structure, [167 (Ph_2CH) + ($n \times 128.17$ (tBA)) + 1 (H) + 39 (K^+)], were observed, as expected. The polymerization of tBA was thus initiated with the diphenylmethyl anion and not with the ethylide derived from **1** even in the presence of excess Et_3B, as shown in Scheme 1. To the best of our knowledge, this is the first successful example for a precisely controlled anionic polymerization of tBA at relatively high temperatures (0 °C). On the other hand, the M_w/M_n value increased from 1.1 (at

10.1021/ma9812884 CCC: $18.00

Scheme 1

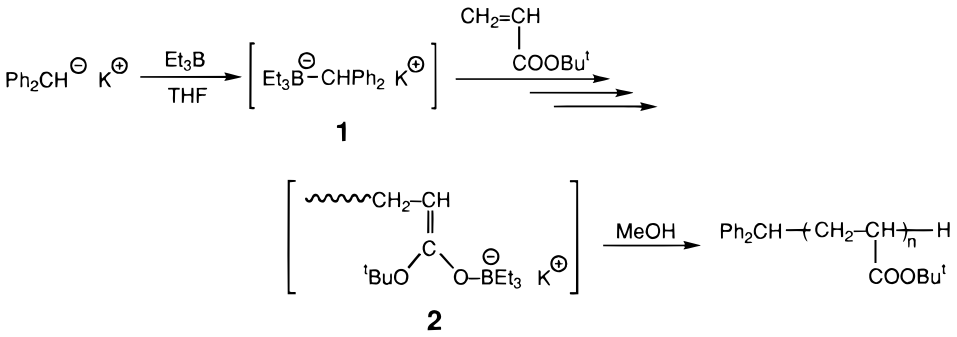

Table 1. Anionic Polymerization of tBA with Ph$_2$CHK in THF in the Absence and in the Presence of Et$_3$B

	amount of reagent, mmol						conversion,[a]	$M_n \times 10^{-3}$		
run	tBA	Ph$_2$CHK	Et$_3$B	B/I	temp, °C	time, h	%	calcd[b]	obsd[c]	M_w/M_n[c]
1	8.59	0.0656	0		−78	5 min	100	17	49	2.64
2	6.53	0.0968	0		0	5 min	83	7.3	7.7	2.67
3	7.33	0.0795	0.220	2.8	−78	24	trace[d]			
4	5.68	0.0776	0.184	2.4	0	1	57	5.4	4.1	1.05
5	5.86	0.0863	0.229	2.7	0	6	100	8.7	9.8	1.08
6	7.10	0.0814	0.229	2.8	0	24	100	13	13	1.08
7	8.80	0.0601	0.148	2.5	0	24	100	19	24	1.07
8	6.06	0.0790	1.38	17	0	6	32	3.1	2.7	1.06
9	1.07	0.0115	0.223	19	0	72	96	12	11	1.04
10	4.77	0.0496	0.127	2.6	30	1	100	13	13	1.27

[a] By GLC. [b] M_n (calcd) = (MW of tBA) × [tBA]/[Ph$_2$CHK] × yield/100 + MW of initiator. [c] M_n (obsd) and M_w/M_n were obtained by SEC calibration using standard PMMA in THF solution. [d] Lower than 4%.

0 °C) to 1.27 (at 30 °C), although all of the tBA was consumed within 1 h at 30 °C, and the SEC curve of poly(tBA) obtained still maintained its unimodal shape.

It should be emphasized that the drastic decrease of k_p value in the polymerization of tBA was observed to depend on the amount of added Et$_3$B (Table 1, runs 5, 8, and 9). While the k_p value for the polymerization of tBA with Ph$_2$CHK in THF at 0 °C was roughly estimated to be over 10 L mol^{-1} s^{-1} without Et$_3$B, those in the presence of 2.2 and 19 equivalents of Et$_3$B were determined to be 3.05×10^{-2} and 3.65×10^{-3} L mol^{-1} s^{-1}, respectively. This retardation effect due to the added Et$_3$B is more drastic than our previous finding using dialkylzinc as an additive to control the anionic polymerizations of alkyl meth(acrylate)s[7] and *N,N*-dialkylacrylamide.[8] Although the detailed polymerization mechanism is not clear yet, we now consider that the added Et$_3$B (showing Lewis acidity) coordinates with the propagating enolate anion to form a possible ate complex,[15] **2**, to retard the propagation to a considerable extent during the polymerization, even in a polar basic THF. Another potential activation of the carbon−carbon double bond of tBA molecule by forming a carbonyl-coordinating complex with Et$_3$B may have a minor contribution, if any, to accelerate the polymerization.

Although the above finding indicates the formation of a strongly coordinated propagating species over the course of polymerization, no effect of the added Et$_3$B on the stereoregularity was observed in the ^{13}C NMR spectra of poly(tBA)s obtained in the absence or in the presence of Et$_3$B. The triad tacticity in the ester carbonyl region was split into three peaks and those were estimated to be rr = 39%, mr = 38%, and mm = 23% for the poly(tBA) obtained with Ph$_2$CHK and to be rr = 40%, mr = 42%, and mm = 18% for the polymer produced with the binary initiator of Ph$_2$CHK/Et$_3$B (19 equiv).[16] This is consistent with our previous observation for the polymerizations of alkyl methacrylates[7] and tBA initiated with Ph$_2$CHK/Et$_2$Zn,[9] but it is sharp contrast to that of *N,N*-diethylacrylamide[8] using the Ph$_2$CHLi/Et$_2$Zn system, where the stereoregularity of the resulting polymers strongly depends on the stoichiometry of the added Et$_2$Zn. In the present study, the additive effects of Et$_3$B on the control of M_n and MWD and on the polymerization rate are apparent in the anionic polymerization of tBA initiated with the Ph$_2$CHK/Et$_3$B system, but the stereoregularity is not affected.

In conclusion, we have substantiated that the new binary initiator system consisting of Ph$_2$CHK and Et$_3$B induces the controlled anionic polymerization of tBA even at 0 °C to afford polymers having extremely narrow MWDs and predicted M_n values. The detailed polymerization results including the role of the added Et$_3$B and the structure of the propagating species will be discussed in the forthcoming publication.

Acknowledgment. The authors thank Mr. Takashi Nirasawa (Bruker) for his measurement of MALDI−TOF−MS. This study was supported by Grant-in Aid for Scientific Research on Priority Areas (No. 277/08246102) from the Ministry of Education, Science, Sports, and Culture, Japan.

References and Notes

(1) (a) Davis, T.; Haddleton, D.; Richards, S. *J. Macromol. Sci.—Rev. Macromol. Chem. Phys.* **1994**, *C34*, 243. (b) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization*; Marcel Dekker: New York, 1996; p 641.
(2) (a) Fayt, R.; Forte, R.; Jacobs, C.; Jérôme, R.; Ouhadi, T.; Teyssié, Ph.; Varshney, S. K. *Macromolecules* **1987**, *20*, 1442. (b) Klein, J. W.; Gnanou, Y.; Rempp, P. *Polym. Bull.* **1990**, *24*, 39.
(3) Baskaran, D.; Sivaram, S. *Macromolecules* **1997**, *30*, 1550.
(4) (a) Vlcek, P.; Lochmann, L.; Otoupalová, J. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 163. (b) Vlcek, P.; Lochmann, L. *Makromol. Symp.* **1993**, *67*, 111. (c) Dvoránek, L.; Vlcek, P. *Macromolecules* **1994**, *27*, 4881. (d) Vlcek, P.;

Dvoránek, L.; Otoupalová, J.; Lochmann, L. *Polym. Bull.* **1995**, *34*, 1.

(5) Nugay, N.; Nugay, T.; Jerôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Chem.* **1997**, *35*, 361.

(6) (a) Reetz, M. T.; Knauf, T.; Minet, U.; Bingel, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1373. (b) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 994.

(7) (a) Ozaki, H.; Hirao, A.; Nakahama, S.; *Macromol. Chem. Phys.* **1995**, *196*, 2099. (b) Ishizone, T.; Uehara, G.; Hirao, A.; Nakahama, S.; Tsuda, K. *Macromol. Chem. Phys.* **1998**, *199*, 1827.

(8) Nakahama, S.; Kobayashi, M.; Ishizone, T.; Hirao, A.; Kobayashi, M. *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 1845.

(9) Ishizone, T.; Yoshimura, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1998**, *31*, 8706.

(10) Negishi, E. *Organometallics in Organic Synthesis*, Wiley: New York, 1980; p 23.

(11) tBA was distilled from CaH_2 and then from trioctylaluminum (ca. 2 mol %) on a vacuum line into the all-glass apparatus with breakseals and was diluted with dry THF, as previously reported.[9] Ph_2CHK was prepared by the reaction of diphenylmethane and potassium naphthalenide in THF at room temperature for 2 days. Et_3B (Aldrich) was distilled from CaH_2 and then from trioctylaluminum (ca. 2 mol %) under high vacuum condition and diluted with dry THF. The polymerization of tBA was carried out in THF under high vacuum condition in a sealed all-glass reactor with breakseals. A THF solution of Et_3B was added to Ph_2CHK in THF at −78 °C and allowed to react for 0.5 h at −78 °C. The orange red color of initiator disappeared instantaneously on mixing with Et_3B. tBA solution in THF was rapidly added into the initiator system prepared at 0 °C with vigorous stirring. After the reaction was allowed to stand for an appropriate time at 0 °C, the polymerization was terminated with degassed methanol and the conversion of tBA was analyzed by GLC. The poly(tBA) was obtained after precipitation in 0.05 M HCl aqueous solution and purified by freeze-drying from the benzene solution.

(12) In the absence of Et_3B, the polymerization of tBA rapidly proceeded directly with Ph_2CHK in THF at either −78 or 0 °C to produce the polymer, as shown in Table 1 (run 1, 2). However, the poly(tBA)s thus obtained possessed ill-controlled molecular weights much higher than the calculated values and/or very broad MWDs ($M_w/M_n = 2-3$), indicating the occurrence of the serious side reactions which were described in the previous literature.[1−5]

(13) The M_n and M_w/M_n values of poly(tBA)s were estimated by the SEC analysis using poly(methyl methacrylate) standards in THF. The M_ns were also obtained by the ^{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 anion quantitatively is used for the initiation of tBA.

(14) MALDI−TOF−MS data were obtained with a Bruker REFREX II MALDI−TOF−MS mass spectrometer using *trans*-3-indoleacrylic acid as a matrix.

(15) Reference 10, p 191.

(16) Stereoregularity of poly(tBA) was determined by the ^{13}C NMR integral ratio of three split ester carbonyl signals measured by a Bruker DPX300S (75 MHz, ^{13}C) spectrometer in $CDCl_3$. 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, respectively.

MA9812884