Controlled Anionic Polymerization of Methacrylonitrile with Diphenylmethylpotassium in the Presence of Triethylborane

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The controlled anionic polymerization of polar monomers in terms of molecular weights and chain structures is still an important target in the synthetic polymer chemistry. Recently, several new polymerization systems have been successfully developed to control the anionic polymerizations of alkyl (meth)acrylates for providing the polymers with well-defined chain structures without side reactions.[1]

However, the precise control in the anionic polymerization of methacrylonitrile (MAN) continues to be a long-standing problem,[2−7] since the side reactions such as nucleophilic attack of the anionic initiator or the propagating chain end toward the electrophilic cyano group inherently occurred. Such side reactions along with extremely high polymerization rate of MAN and low solubility of the produced poly(MAN) often resulted in heterogeneous polymerization systems, low initiator efficiencies, ill-controlled molecular weights, and broad molecular weight distributions (MWDs). Related with the anionic polymerization process, only one example succeeded in the synthesis of well-defined block copolymer containing poly(MAN) segment by using the bulky (enolato)aluminum porphyrin initiator in the presence of Lewis acids.[8] In this particular case, the living poly(methyl methacrylate) having the (enolato)aluminum porphyrin moiety at the growing terminal was employed as the macroinitiator of MAN to overcome the low solubility of the product. It was also reported that group transfer polymerization of MAN using 2-(trimethylsilyl)isobutyronitrile could not achieve any degree of molecular weight control.[9]

We have recently discovered that a new binary initiator system consisting of diphenylmethylpotassium (Ph_2CHK) and triethylborane (Et_3B) is very effective to polymerize *tert*-butyl acrylate (tBA)[10] and *N*,*N*-dialkylacrylamides[11] in THF at 0−30 °C in living fashions to form the polymers of predicted molecular weights with very narrow MWDs. The drastic decrease of k_p value was observed after the addition of Et_3B to the polymerization system even at 0−30 °C, although no apparent polymerization of tBA and *N*,*N*-dialkylacrylamides proceeded virtually with Ph_2CHK/Et_3B at −78 °C. It is now considered that the added Et_3B strongly coordinates with the initiator and the propagating carbanions as a Lewis acid, even in polar THF, to suppress the serious side reactions such as nucleophilic carbonyl attack and α-proton abstraction, which are often observed in the polymerizations of acrylates and acrylamides. A similar characteristic additive effect of Et_3B will be strongly expected in the anionic polymerizations of other polar monomers. In this communication, we report the controlled anionic homopolymerization of MAN via producing the well-defined polymer with predicted molecular weight and narrow MWD in the presence of Et_3B at 0 °C.

We first attempted the anionic polymerization of MAN with Ph_2CHK in THF at −78 °C in the absence of Et_3B.[12] When a THF solution of MAN was added to the initiator solution, the precipitation of polymer instantaneously appeared and the reaction system colored deep red. The rapid polymerization and the heterogeneous system are due to the high anionic polymerizability of MAN and the low solubility of the resulting poly(MAN) in THF. The polymerization of MAN certainly proceeded, and the polymer yields were 44% and 100% after 5 min and 20 h polymerizations, respectively. Under these polymerization conditions, the resulting poly(MAN)s possessed very broad MWDs ($M_w/M_n = 3$), and the observed molecular weight[13] was significantly higher than the calculated values based on the molar ratio of monomer to initiator. This indicates the occurrence of some side reactions during the course of polymerization of MAN even at low temperature of −78 °C, as previously suggested.[2−7]

We then added a ca. 3-fold amount of Et_3B to the THF solution of Ph_2CHK at −78 °C in order to prevent the side reactions.[12] The orange red color of Ph_2CHK immediately disappeared on mixing with Et_3B to give a colorless solution of **1**, presumably tetracoordinated diphenylmethyl triethylborate, and this initiator system was allowed to stand for 0.5 h at −78 °C. A THF solution of MAN was then added to the initiator system. No apparent polymerization of MAN however occurred with Ph_2CHK/Et_3B in THF at −78 °C even after 28 h reaction, and the starting monomer was recovered nearly quantitatively.

By sharp contrast to the result at −78 °C, the polymerization of MAN rapidly proceeded at 0 °C to produce the poly(MAN) in quantitative yield under similar conditions. At 0 °C, on the addition of a THF solution of MAN, the reaction mixture immediately changed from colorless to reddish brown. Whereas the reaction system became heterogeneous and the polymer precipitation appeared at 0 °C after 5 min, a soluble poly(MAN) was quantitatively obtained after termination.[14] The polymerization results on conversion, molecular weight, and MWD for different reaction conditions are summarized in Table 1. At 0 °C, the complete conversion of MAN was attained with Ph_2CHK/Et_3B within 1 min to produce the polymer quantitatively. Interestingly, the SEC curve of the poly(MAN) thus obtained showed a unimodal and very narrow MWD. The polydispersity indices were always around 1.1. Figure 1 shows the SEC curves of poly(MAN)s produced with Ph_2CHK in the absence or in the presence of Et_3B in THF. It is evident that the MWD of poly(MAN) was dramatically narrowed, when the polymerization of MAN was performed with Ph_2CHK in the presence of Et_3B at 0 °C. The M_n values of poly(MAN)s determined by ^1H NMR were in good agreement with the values calculated from the molar ratio between MAN and Ph_2CHK regardless of the amount of added Et_3B (2−20 equiv).[13] This indicates that the initiation reaction

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Table 1. Anionic Polymerization of MAN with Ph_2CHK in THF in the Absence and in the Presence of Et_3B

	amount of reagent, mmol							$M_n \times 10^{-3}$		
run	MAN	Ph_2CHK	Et_3B	B/I[a]	temp, °C	time, min	conversion,[b] %	calcd[c]	obsd[d]	M_w/M_n[e]
1	9.23	0.0810	0		−78	5	44	3.4	52[e]	3.52
2	8.97	0.0857	0		−78	20 h	100	7.2	82[e]	2.97
3	10.4	0.0907	0.190	2.1	−78	28 h	trace[f]			
4	9.34	0.0842	0.223	2.7	0	1	100	7.6	7.5	1.09
5	16.1	0.0625	0.270	4.3	0	30	100	17	18	1.06
6	19.7	0.0429	0.192	4.5	0	10	100	31	32	1.11
7	10.4	0.0936	1.84	20	0	10	100	7.6	8.5	1.11

[a] $[Et_3B]/[Ph_2CHK]$. [b] By GLC. [c] M_n(calcd) = (MW of MAN) × $[MAN]/[Ph_2CHK]$ × conversion/100 + MW of initiator. [d] M_n(obsd) was determined by end group analysis using ^1H NMR. [e] M_n(obsd) and M_w/M_n were obtained by SEC calibration using PMMA standards in DMF containing 0.01 M LiBr. [f] Lower than 4%.

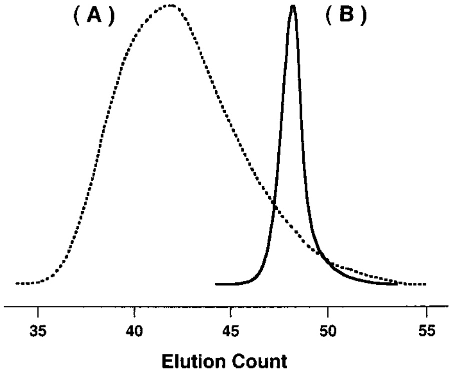
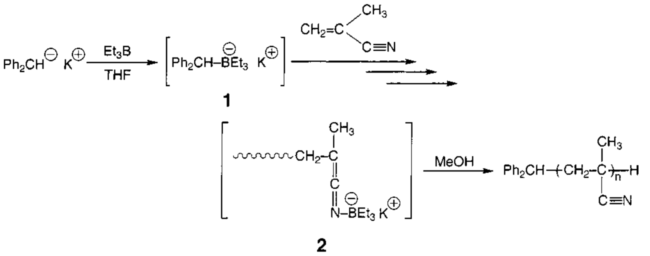


Figure 1. SEC curves of poly(MAN)s obtained with Ph_2CHK in THF at −78 °C for 20 h (A) and with Ph_2CHK and 3-fold excess of Et_3B at 0 °C for 1 min (B).

Scheme 1



of MAN exclusively occurs with the diphenylmethyl anion and not with the ethylide derived from Et_3B or **1**, even in the presence of excess Et_3B, as shown in Scheme 1.

In our previous reports, the drastic decrease of polymerization rates of tBA[10] and *N*,*N*-dialkylacrylamides[11] has been observed after the addition of Et_3B to the reaction system. Although several hours or days is needed to complete the polymerizations of tBA and *N*,*N*-dialkylacrylamides at 0−30 °C, MAN undergoes the quantitative polymerization rather rapidly within 1 min on the addition of Et_3B under the identical reaction conditions. It is now considered that serious side reactions are effectively diminished by the coordination of Lewis acidic Et_3B to the initiator and/or the propagating enolate anion to stabilize the anionic species including **1**- and **2**-ate complexes[15] of the initiator and the propagating anion, respectively (Scheme 1). In the present study, another possible contribution of Et_3B in accelerating the polymerization of MAN cannot be ruled out by forming the activated monomer complex of Et_3B with a cyano group of MAN, which is not true in the polymerizations of tBA[10] and *N*,*N*-dialkylacrylamides.[11] Further kinetic study on the polymerization of MAN is necessary to discuss the role of the added Et_3B and the polymerization mechanism in detail.

In conclusion, we thus demonstrate the new strategy of control in the anionic polymerization of typical polar monomer, MAN, under the mild conditions by means of the simple addition of Lewis acidic Et_3B[16] to tune the reactivity of the propagating species not by the additive effect of common salts of initiators.[1c,f,i,j] To the best of our knowledge, this is the first successful synthesis of homopoly(MAN)s having precisely controlled M_n values and narrow MWDs. The detailed polymerization results and additive effects of various organoboranes will be discussed in a forthcoming publication.

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(12) MAN was distilled from CaH_2 on a vacuum line into an all-glass apparatus with break-seals and was diluted with dry THF. 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 conditions and diluted with dry THF. The polymerization of MAN was carried out in THF under high-vacuum conditions in a sealed all-glass reactor with breakseals. Et_3B in THF was added to a THF solution of Ph_2CHK at −78 °C and allowed to stand for 0.5 h. Then, a THF solution of MAN was added into the initiator system at 0 °C with vigorous stirring. After standing the reaction mixture for an appropriate time at 0 °C, the polymerization was terminated with methanol containing a small amount of 2 N HCl, and the conversion was analyzed by GLC. The off-white powder of poly(MAN) was obtained by precipitating into MeOH. The polymer was purified by the reprecipitations into MeOH from the DMF solution.

(13) The M_n value of poly(MAN) was determined by the ^1H NMR analysis by assuming that two phenyl groups derived from the initiator residue (Ph_2CH) are present in each polymer chain. M_w/M_n and M_n (SEC) were estimated by the SEC analysis using poly(methyl methacrylate) standards in DMF containing 0.01 M LiBr at 40 °C. The M_n (SEC)s were always 2.7 times higher than the M_n values obtained by ^1H NMR. This indicates that the M_n (SEC)s of poly(MAN) are overestimated compared with those of poly(methyl methacrylate)s due to the difference in hydrodynamic volume in DMF solution.

(14) No apparent additive effect of Et_3B on the stereoregularity was observed in the ^1H and ^{13}C NMR spectra of poly(MAN)s obtained in the absence and in the presence of Et_3B.

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(16) We have already succeeded in the controlled anionic polymerizations of alkyl (meth)acrylates and *N*,*N*-dialkylacrylamides via the similar strategy of addition of Lewis acidic dialkylzinc. See refs 1g, 1k, and 17.

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