Living Cationic Polymerization of Isobutyl Vinyl Ether by Benzoic Acid Derivatives/Zinc Chloride Initiating Systems: Slow Interconversion between Dormant and Activated Growing Species[1]

Masami Kamigaito, Katsushi Yamaoka, Mitsuo Sawamoto, and Toshinobu Higashimura*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606-01, Japan

Received March 23, 1992; Revised Manuscript Received July 17, 1992

ABSTRACT: A series of benzoic acid derivatives [2,4-di-NO_2, 3,4-di-NO_2, *p*-NO_2, *p*-CF_3, *p*-Cl, *p*-CH_3, and *p*-H (unsubstituted)], in conjunction with zinc chloride ($ZnCl_2$), led to living cationic polymerization of isobutyl vinyl ether (IBVE) in toluene at 0 °C. In the polymerization with the nitrobenzoic acids (2,4-di-NO_2, 3,4-di-NO_2, and *p*-NO_2), the number-average molecular weights ($\bar{M}_n$) of the polymers were directly proportional to monomer conversion and in good agreement with the calculated values assuming that one polymer chain forms per IBVE–benzoic acid adduct [$CH_3CH(OiBu)OCOR$ (**2**)]. With *p*-CF_3, *p*-Cl, *p*-H, and *p*-CH_3 benzoic acids, though the $\bar{M}_n$ values were larger than the calculated values at the early stages of the polymerizations, they agreed with the calculated values at higher conversions. The molecular weight distributions (MWDs) of the polymers became broader ($\bar{M}_w/\bar{M}_n$ = 1.1 → 2.4) as the acidity of benzoic acids decreased. The larger $\bar{M}_n$ values and the broadening of the MWD are due to the slow interconversion between dormant and activated species, which was shown by kinetics of the polymerizations and ^1H NMR analysis of model reactions.

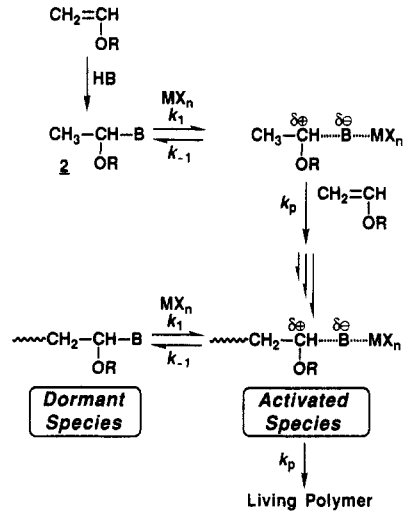
Introduction

Living cationic polymerization of vinyl monomers has been achieved by binary initiating systems which consist of a protonic acid (HB) and a weak Lewis acid (MX_n); typical examples of the HB/MX_n systems include HI/ZnI_2 and acetic acid/$ZnCl_2$.[2,3] As Scheme I shows, HB adds to the monomer prior to polymerization to give adduct **2** with an inert C–B bond, and then the C–B bond is subsequently "activated"[4] by MX_n to commence living propagation.[5-7] However, the growing polymer end is not always activated by MX_n, as implied by the molar ratio of MX_n to HB, where in most cases MX_n is equimolar to or less than HB. In the living polymerization of isobutyl vinyl ether (IBVE) with HB/MX_n, for example, kinetic studies of the polymerization and ^1H NMR analyses of model reactions[8] have suggested that the dormant (~~~C–B) and activated (~~~$C^{\delta+}$···$B^{\delta-}$···MX_n) species coexist in an equilibrium that is displaced to the dormant species' side ($K = k_1/k_{-1} \ll 1$; k_1 represents a rate constant of the process where the dormant species becomes capable of propagating by interaction with MX_n, and k_{-1} represents that of the backward process).

Such interconversion between dormant and activated species may considerably affect the molecular weight distribution (MWD) of the polymers formed by the HB/MX_n systems.[9-12] It is well-known that, in the living anionic polymerization of styrene mediated by free-ionic and ion pair growing species, the MWD is affected by the equilibrium between them, and the relationship equation has been derived.[13] By modifying it, an equation for the (cationic) living systems which involve an equilibrium between the dormant and the activated species has recently been obtained. The equation shows the $\bar{M}_w/\bar{M}_n$ ratios therein to be calculated from the ratio of k_p (rate constant of propagation) to k_{-1}.[11,12] Thus, one of the features of the polymerization with HB/MX_n is the existence of an equilibrium between dormant and activated species, and it now appears that the existence of the dormant species, which is more stable than the activated species, is crucial for attaining living cationic polymerization.

Along with the elucidation of the mechanism, we have developed a series of new initiating systems for living cationic polymerization, on the basis of the stabilization of the unstable carbocation with a nucleophilic counteranion.[3] By several independent research groups,[6-8,10,14-16] it has been found that a variety of nucleophilic anions B^- [I^-, Cl^-, $(PhO)_2PO_2^-$, $CF_3CO_2^-$, etc.], in conjunction with zinc halides (ZnX_2; X = I, Br, Cl), give well-defined living polymers of vinyl ethers with narrow MWD ($\bar{M}_w/\bar{M}_n$ < 1.1). In contrast, with a less nucleophilic anion such as $CF_3SO_3^-$, the polymerization cannot be well-controlled probably due to the absence of the stabilization of the carbocation.[17] With a more nucleophilic anion, $CH_3CO_2^-$, living polymerization indeed occurs in the presence of $ZnCl_2$, though the MWDs of the polymers are slightly broader ($\bar{M}_w/\bar{M}_n \approx 1.3$).[10] These observations suggest the nucleophilicity of the acid's anion B^- to be closely related to not only the living nature but also the MWD of the polymers. However, these relations still remain unknown, partly because the previous studies involve the counteranions B^- that differ not only in nucleophilicity but in basic structure and steric crowding.

Scheme I
Activated and Dormant Species in Living Cationic Polymerization with HB/MX_n Initiating Systems



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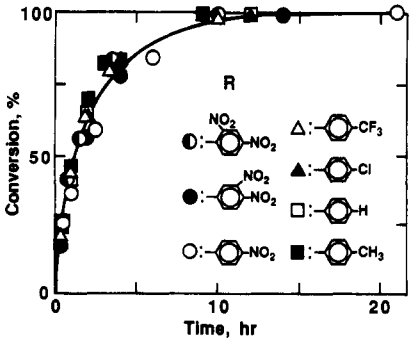
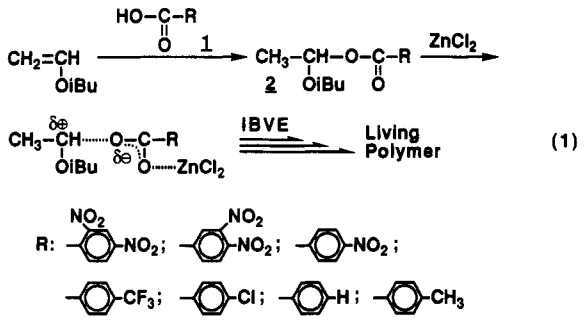


Figure 1. Time-conversion curves for the polymerization of IBVE by 2/$ZnCl_2$ in toluene at 0 °C: $[M]_0$ = 0.38 M; $[2]_0$ = 5.0 mM; $[ZnCl_2]_0$ = 2.0 mM. Substituent on the phenyl group of benzoic acid derivatives: 2,4-di-NO_2 (◐); 3,4-di-NO_2 (●); *p*-NO_2 (○); *p*-CF_3 (△); *p*-Cl (▲); unsubstituted (□); *p*-CH_3 (■).

We herein employed a series of mono- and disubstituted benzoic acid derivatives 1 [2,4-di-NO_2, 3,4-di-NO_2, *p*-NO_2, *p*-CF_3, *p*-Cl, *p*-CH_3, and *p*-H (unsubstituted)] in conjunction with $ZnCl_2$ for possible living cationic polymerization of IBVE (eq 1). Our primary objective was to obtain



(1)

further insight into the effects of the nucleophilicity of the acids' counteranions on living polymerization. As a protonic acid, benzoic acid (parent form) is as weak as acetic acid (pK_a = 4.2 vs 4.8; in H_2O);[18] thus, the nucleophilicity of the benzoate anion is probably comparable to that of the acetate. Furthermore, the nucleophilicity of the ring-substituted benzoate anions can be systematically varied with the electronic nature of the substituents but without altering the steric environment and other factors around the anionic site. The use of substituted benzoic acids will also permit us to study the resonance effects of the counteranions on the polymerization. In this study, we investigate the possibility of living cationic polymerization of IBVE by the benzoic acid derivative/$ZnCl_2$ systems and the effects of the nucleophilicity of benzoate anions on the MWD of the polymers.

Results and Discussion

1. Polymerization with Benzoic Acid Derivative–IBVE Adducts (2)/$ZnCl_2$. All of the benzoic acid derivatives 1 react with IBVE to form adducts 2 (see Experimental Section), which are so stable as to be distilled and accordingly cannot polymerize IBVE by themselves. However, IBVE could be polymerized with the isolated adducts 2 in conjunction with $ZnCl_2$ in toluene at 0 °C ($[M]_0/[2]_0/[ZnCl_2]_0$ = 380/5.0/2.0 mM). Irrespective of the substituents in 2, the polymerizations occurred smoothly, being first order with respect to monomer and completed in 10–20 h (Figure 1). The overall polymerization rate was nearly independent of the type of the substituents, which is in contrast to the fact that the rate increased with the acidity in the polymerization with acetic acid-based systems (RCOOH; R = CF_3, CCl_3, $CHCl_2$, CH_2Cl, CH_3).[10] Namely, with the benzoic acid- and acetic acid-based initiating systems, the polymerization rate appears to depend more on the inductive effects, rather than on the resonance effects, upon the nature of the acids' counteranions. Similar trends have been reported for the polymerization of isobutylene with the $RCOOC(CH_3)_2C(CH_3)_3/BCl_3$ system.[19] This point should be further investigated.

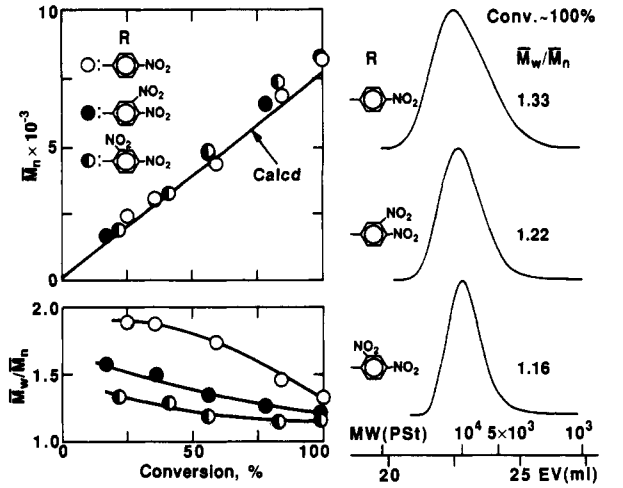


Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(IBVE) obtained with 2/$ZnCl_2$ in toluene at 0 °C: $[M]_0$ = 0.38 M; $[2]_0$ = 5.0 mM; $[ZnCl_2]_0$ = 2.0 mM. Substituent on the phenyl group of benzoic acid derivatives: 2,4-di-NO_2 (◐); 3,4-di-NO_2 (●); *p*-NO_2 (○). Solid line labeled Calcd indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per 2 molecule.

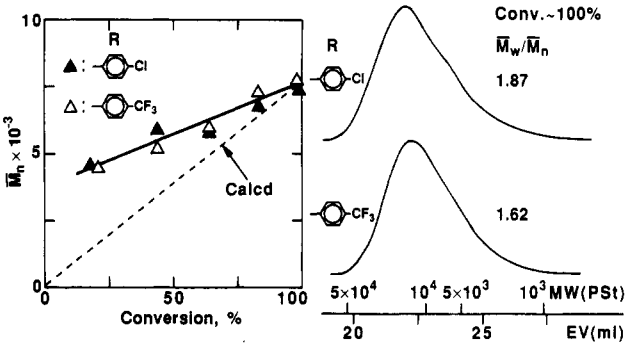


Figure 3. $\bar{M}_n$ and MWD curves of poly(IBVE) obtained with 2/$ZnCl_2$ in toluene at 0 °C: $[M]_0$ = 0.38 M; $[2]_0$ = 5.0 mM; $[ZnCl_2]_0$ = 2.0 mM. Substituent on the phenyl group of benzoic acid derivatives: *p*-CF_3 (△); *p*-Cl (▲). Broken line labeled Calcd indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per 2 molecule.

As shown in Figure 2, the number-average molecular weights ($\bar{M}_n$) of the polymers obtained with the three nitro-substituted benzoic acids were directly proportional to monomer conversion and in good agreement with the calculated values assuming that one polymer chain forms per adduct 2 molecule. As the polymerization proceeded, the MWDs became narrower. These results suggest that, in the presence of $ZnCl_2$, 2 with the strong electron-withdrawing nitro group(s) induces living cationic polymerization, where the $\bar{M}_n$ of the polymers increased in direct proportion to monomer conversion and the MWDs were narrow.

In the polymerization with *p*-CF_3 and *p*-Cl benzoic acids (Figure 3), both of which are weaker than *p*-NO_2 benzoic acid, the $\bar{M}_n$ values were obviously higher than the calculated values at the early stage but became close to them as the polymerization proceeded. The MWDs were broader than that with the *p*-NO_2 derivative.

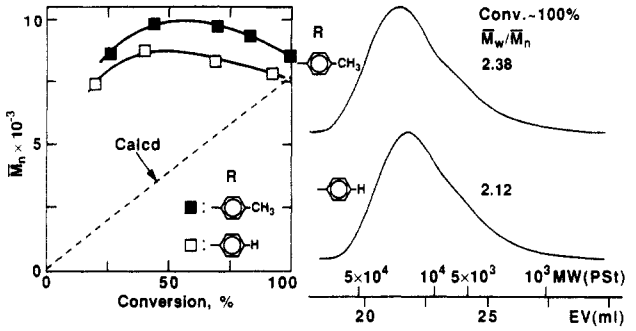


Figure 4. $\bar{M}_n$ and MWD curves of poly(IBVE) obtained with 2/$ZnCl_2$ in toluene at 0 °C: $[M]_0 = 0.38$ M; $[2]_0 = 5.0$ mM; $[ZnCl_2]_0 = 2.0$ mM. Substituent on the phenyl group of benzoic acid derivatives: unsubstituted (□); p-CH_3 (■). Broken line labeled Calcd indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per 2 molecule.

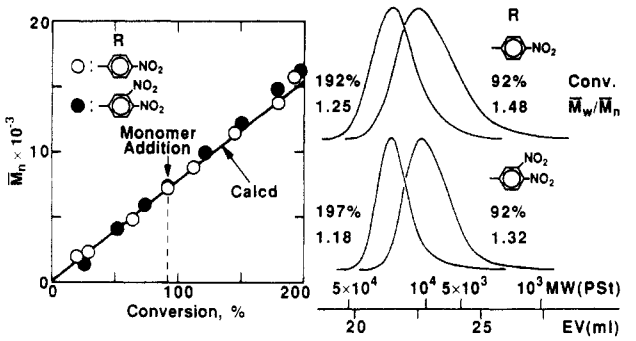


Figure 5. $\bar{M}_n$ and MWD curves of poly(IBVE) obtained in a monomer addition experiment in the polymerization with 2/$ZnCl_2$ in toluene at 0 °C: $[M]_0 = [M]_{add} = 0.38$ M; $[2]_0 = 5.0$ mM; $[ZnCl_2]_0 = 2.0$ mM. Substituent on the phenyl group of benzoic acid derivatives: 3,4-di-NO_2 (●); p-NO_2 (○). Solid line labeled Calcd indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per 2 molecule.

With much weaker benzoic acids, such as unsubstituted and p-CH_3 benzoic acids, the $\bar{M}_n$ values did not increase with conversion, and the MWDs were much broader ($\bar{M}_w/\bar{M}_n \approx 2$) (Figure 4); note, however, that the molecular weights for near 100% conversion were close to the calculated values. The living nature of the polymerizations is discussed in the next section. From Figures 2–4, it has become apparent that the $\bar{M}_w/\bar{M}_n$ ratios decrease and become close to unity in the order of the increasing acidity of benzoic acids.

Monomer Addition Experiments. To investigate the living nature of the IBVE polymerizations by 2/$ZnCl_2$, a fresh feed of IBVE was added to the reaction mixtures just before the initial charge of the monomer had completely been polymerized. In all cases, the added IBVE was smoothly polymerized at nearly the same rate as in the initial stage. As shown in Figure 5, the $\bar{M}_n$ of the polymers obtained with the two nitrobenzoic acids further increased in direct proportion to monomer conversion and agreed with the calculated values (one polymer chain per molecule of 2). The MWDs after the monomer addition were narrower than those before the addition. Thus, the living nature of the polymerization with nitrobenzoic acid/$ZnCl_2$ is further demonstrated.

For the adducts 2 of the three weaker acids (p-Cl, p-H, and p-CH_3) (Figure 6), the polymers' $\bar{M}_n$ also increased nearly in direct proportion to conversion specifically after the monomer addition, in sharp contrast to the clear deviations from such linear dependence during the first-stage polymerizations (Figures 3 and 4). The $\bar{M}_n$'s for the p-Cl derivative (triangles), in particular, are very close to the calculated values, whereas those for the p-H and p-CH_3 analogues (open and filled squares) are slightly higher (Figure 6).[20] The monomer additions also rendered MWDs invariably narrower. These results indicate that the systems with the weaker acids indeed induce living polymerizations where, however, consumption of the initiators 2 might be slower than propagation (see below).

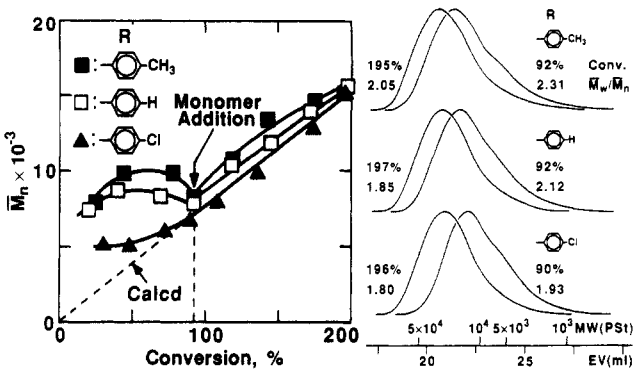


Figure 6. $\bar{M}_n$ and MWD curves of poly(IBVE) obtained in a monomer addition experiment in the polymerization with 2/$ZnCl_2$ in toluene at 0 °C: $[M]_0 = [M]_{add} = 0.38$ M; $[2]_0 = 5.0$ mM; $[ZnCl_2]_0 = 2.0$ mM. Substituent on the phenyl group of benzoic acid derivatives: p-Cl (▲); unsubstituted (□); p-CH_3 (■). Line labeled Calcd indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per 2 molecule.

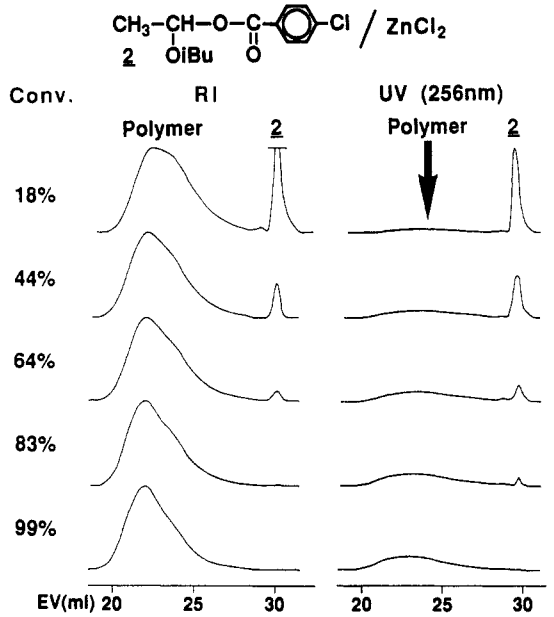


Figure 7. GPC profiles of the products obtained with 2(p-Cl)/$ZnCl_2$ at varying monomer conversions in toluene at 0 °C: $[M]_0 = 0.38$ M; $[2]_0 = 5.0$ mM; $[ZnCl_2]_0 = 2.0$ mM.

2. Initiator Consumption. Figure 7 illustrates the gel permeation chromatography (GPC) profiles of the products obtained with 2(p-Cl)/$ZnCl_2$ at varying monomer conversions, which permitted us to follow the consumption of the initiator as a function of conversion (see Experimental Section). Similar series of GPC eluograms were obtained with all the other 2/$ZnCl_2$ systems employed. As seen in both refractive index and UV traces, the initiator 2 (elution volume ~30 mL) still remains even at medium conversions of monomer, which shows that the consumption of the initiator is slower than the monomer consumption (polymerization).

The extent of initiator consumption [α_I (%)], thus obtained from the UV traces, was plotted against monomer conversion (Figure 8). The weaker the benzoic acid derivatives, the slower the consumption. In the polymerizations with the dinitrobenzoic acids, where the $\bar{M}_n$

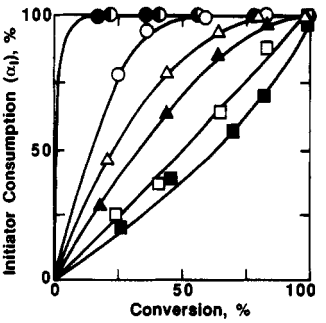


Figure 8. Initiator consumption (α_I) in the polymerization with 2/$ZnCl_2$ in toluene at 0 °C: $[M]_0$ = 0.38 M; $[2]_0$ = 5.0 mM; $[ZnCl_2]_0$ = 2.0 mM. Substituent on the phenyl group of benzoic acid derivatives: 2,4-di-NO_2 (◐); 3,4-di-NO_2 (●); *p*-NO_2 (○); *p*-CF_3 (△); *p*-Cl (▲); unsubstituted (□); *p*-CH_3 (■).

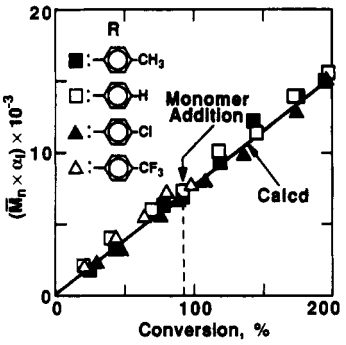


Figure 9. Conversion vs $\bar{M}_n\alpha_I$ plot for the polymerization with 2/$ZnCl_2$ in toluene at 0 °C (α_I, extent of initiator consumption): $[M]_0$ = $[M]_{add}$ = 0.38 M; $[2]_0$ = 5.0 mM; $[ZnCl_2]_0$ = 2.0 mM. Substituent on the phenyl group of benzoic acid derivatives: *p*-CF_3 (△); *p*-Cl (▲); unsubstituted (□); *p*-CH_3 (■).

values were consistently in good agreement with the calculated values (see Figures 2 and 5), the initiators were completely consumed at the early stages.

If a polymerization is living but with a slow initiator consumption ($\alpha_I < 1$), the $\bar{M}_n$ of the polymers should be $\bar{M}_n = [M]_0(\%\ \text{conv}/100)/([I]_0\alpha_I)$, where $[I]_0\alpha_I$ indicates the number of initiator molecules that have been consumed until a particular conversion and equal to the number of the (living) growing species thus far generated. Thus, under these conditions, a modified molecular weight $\bar{M}_n\alpha_I$ ($=[M]_0(\%\ \text{conv}/100)/[I]_0$) should be independent of the initiator structure and be equal to the calculated value with the assumption that initiation is rapid and quantitative ($\alpha_I = 1$). The values of $\bar{M}_n\alpha_I$ were then plotted against monomer conversion for the systems with *p*-CF_3, *p*-Cl, *p*-H, and *p*-CH_3 benzoic acids (Figure 9). In all cases, the $\bar{M}_n\alpha_I$ values increased in direct proportion to monomer conversion and agreed with the calculated values before and after the monomer addition. These results indicate that living cationic polymerization is indeed feasible with the weaker benzoic acids and that the larger $\bar{M}_n$ values at the early stages of the polymerizations (Figures 3 and 4) are due to the slow consumption of the initiator 2.

A slow initiation in living cationic polymerization has already been studied well.[21-25] However, the slow initiator consumption found in this polymerization is thought to be different from the so-called slow initiation for the following reasons. Despite the large difference in initiator consumption rate among the seven adducts 2 (Figure 8), the polymerizations were invariably of first order with respect to monomer and not accelerated with the consumption of the initiator; i.e., an increase in the concentration of the "active" species was not observed. As described above, the polymerizations with 2/$ZnCl_2$ should involve an equilibrium between dormant and activated species, and the concentration of the activated species is much lower than that of the dormant species. Thus, the activated polymer end should revert to the dormant polymer end, which has the same terminal structure as that of the initiator 2. Assuming that the initiator 2, which is regarded as a unimer of the dormant polymer end, has almost the same reactivity with the dormant polymer end, the slow initiator consumption without an increase in the concentration of the active species is explained by the slow interconversion between the dormant and the activated species (see below).

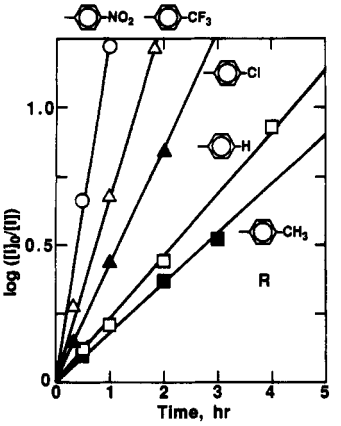


Figure 10. First-order plots for the initiator consumption in the polymerization with 2/$ZnCl_2$ in toluene at 0 °C: $[M]_0$ = 0.38 M; $[2]_0$ = 5.0 mM; $[ZnCl_2]_0$ = 2.0 mM. Substituent on the phenyl group of benzoic acid derivatives: *p*-NO_2 (○); *p*-CF_3 (△); *p*-Cl (▲); unsubstituted (□); *p*-CH_3 (■).

3. Kinetics. As has been suggested,[9-12] the MWDs of the polymers obtained in a polymerization involving an equilibrium between dormant and activated species are greatly dependent on the rate constants of k_p, k_1, and k_{-1} (Scheme I). To investigate the relationship between the MWDs and the rate constants, the polymerizations with the 2/$ZnCl_2$ initiating systems are then analyzed kinetically. Figure 10 shows the logarithmic initiator consumption data, log ($[I]_0/[I]$), plotted against t. The initiator consumption proved to be of first order with respect to initiator. As described above, the polymerization was of first order with respect to monomer; thus

$$-d[I]/dt = k_i[I] \quad (2)$$

$$-d[M]/dt = k[M] \quad (3)$$

where I and M denote the initiator and monomer, respectively. Thus, k_i and k values are obtained from Figure 10 and the first-order plots for Figure 1, respectively.

If the polymerizations with this system proceed as shown in Scheme I, the equation concerning the monomer consumption is derived as follows, where P_i and A mean the i-mer of the polymer (or initiator 2 for i = 1) and Lewis acid activator, respectively:

$$\begin{aligned} -d[M]/dt &= k_p(\textstyle\sum[P_i^*])[M] \\ &= k_p(k_1/k_{-1})(\textstyle\sum[P_i])[A][M] \\ &= k_p(k_1/k_{-1})([I]_0 - \textstyle\sum[P_i^*]) \times \\ &\qquad ([A]_0 - \textstyle\sum[P_i^*])[M] \end{aligned}$$

By ^1H NMR analysis, it has been shown that the equilibrium between the dormant and activated species is shifted to the dormant side (for example, see Figure 11).[8] Thus, $[P_i^*] \ll [P_i]$, $\sum[P_i^*] \ll [I]_0$ or $[A]_0$, and

$$-d[M]/dt = k_p(k_1/k_{-1})[I]_0[A]_0[M] \quad (4)$$

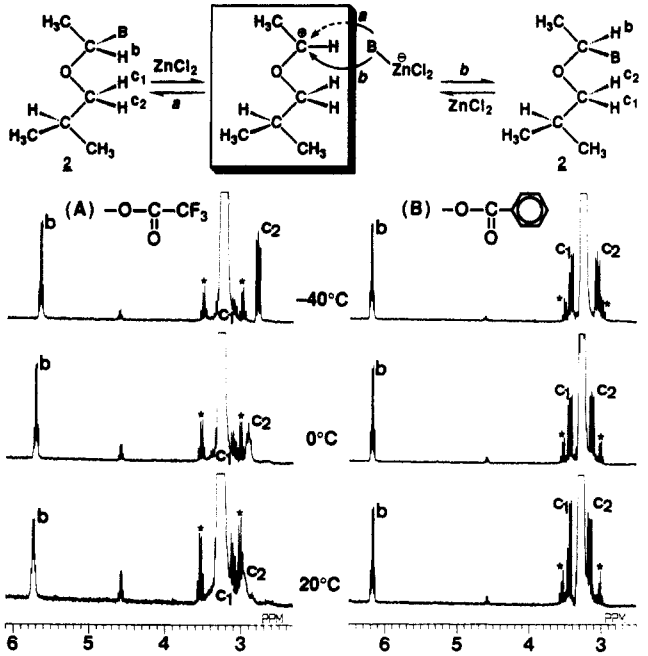


Figure 11. ^{1}H NMR spectra of the mixture of $[2]_0$ = 100 mM and $[ZnCl_2]_0$ = 20 mM in toluene-d_8/*n*-hexane/Et_2O (8/1/1) at −40, 0, and 20 °C. B: $OCOCF_3$ (A); OCOPh (B). The signals marked by an asterisk are the spinning side bands of diethyl ether (solvent for $ZnCl_2$).

It has already been revealed that this relation indeed holds in the polymerization of IBVE by the HI/ZnX_2 initiating system ($-d[M]/dt \propto [HI]_0[ZnX_2]_0[M]$).[7]

For the consumption of the initiator, the following equations hold:

$$-d[I]/dt = k_1[A][I] - k_{-1}[I^*] \quad (5)$$

$$-d[I^*]/dt = -k_1[A][I] + k_{-1}[I^*] + k_p[I^*][M] \quad (6)$$

If it is safe to assume that $[I^*]$ is very low and almost constant during the consumption of the initiator

$$-d[I^*]/dt = 0 \quad (7)$$

From eqs 5–7

$$-d[I]/dt = k_1[A][I]\{k_{-1}/(k_p[M]) + 1\}^{-1} \quad (8)$$

For the system with slow initiator consumption, $k_p[M]$ is much larger than k_{-1}, i.e., $k_{-1}/(k_p[M]) \ll 1$; thus

$$-d[I]/dt = k_1[A][I] = k_1[A]_0[I] \quad (9)$$

From eqs 2–4 and 9

$$k_i = k_1[A]_0 \quad (10)$$

$$k = k_p(k_1/k_{-1})[I]_0[A]_0 \quad (11)$$

Thus, the k_1 and k_p/k_{-1} values are obtained. These values are summarized in Table I along with other relevant data.

As seen from Table I, the weaker the benzoic acids, the smaller the k_1 values and the larger the k_p/k_{-1} ratios. The ^{13}C NMR data also show that the methine carbon b of the initiator **2** is less electron deficient as the parent acid of the ester becomes weaker; the ester bond of a weaker acid is less polarized. This suggests that the ester bond of a weaker acid is hard to dissociate by $ZnCl_2$ to give cationic activated species. In fact, the k_1 values for the weaker acids are smaller. The $\bar{M}_w/\bar{M}_n$ ratios (observed) become larger as the k_p/k_{-1} values become larger. This means that all the polymer ends cannot propagate uniformly if the activated species grows many times in succession until it reverts to the dormant species. It cannot be decided whether the increase of the k_p/k_{-1} ratios is mainly due to the increase of k_p values or the decrease of k_{-1} values. However, the former case may be excluded, because it is rather unacceptable that the cationic activated species derived from a weaker acid's ester has higher reactivity. It is concluded that, with the decrease of acidity, both of the k_1 and k_{-1} values become smaller; i.e., the interconversion between the dormant and the activated species becomes slower.

Table I
Acidity of Benzoic Acid Derivatives, Kinetic Data for Polymerizations, and MWD of Polymers[a]

substituent	pK_a[b]	$\delta(C^b)$,[c] ppm	$k_1 \times 10^2$, $M^{-1}\,s^{-1}$	k_p/k_{-1}, M^{-1}	$\bar{M}_w/\bar{M}_n$ calcd[d]	$\bar{M}_w/\bar{M}_n$ obsd[e]
2,4-di-NO_2	1.43	100.6				1.16
3,4-di-NO_2	2.82	99.7				1.22
p-NO_2	3.44	98.5	39.7	22.2	1.12	1.33
p-CF_3		98.0	21.6	65.4	1.34	1.62
p-Cl	3.99	97.5	13.7	94.2	1.48	1.87
p-H	4.21	97.1	7.25	178	1.90	2.12
p-CH_3		96.9	5.75	280	2.41	2.38

[a] In toluene at 0 °C; $[M]_0/[2]_0/[ZnCl_2]_0$ = 380/5.0/2.0 mM. [b] In H_2O at 25 °C (ref 18). [c] ^{13}C NMR chemical shifts of the methine carbon b of adducts **2** (400 mM) in a mixture of solvents ($CDCl_3/CCl_4$ = 1/4) at 25 °C. [d] Calculated from eq 12 (ref 12). [e] Polymers obtained at a monomer conversion of ~100%.

It has been shown that, if the polymerization proceeds as shown in Scheme I, the $\bar{M}_w/\bar{M}_n$ ratios are determined by the k_p/k_{-1} ratios and calculated from the following equation:[11,12]

$$\bar{M}_w/\bar{M}_n = 1 + \bar{l}_0\overline{DP}_n \quad (12)$$

where $\bar{l}_0 = 1 + (k_p/k_{-1})[M]_0$. The calculated $\bar{M}_w/\bar{M}_n$ values are also summarized in Table I, which are in rough agreement with the observed values. This suggests that the assumptions on deriving eqs 4 and 9 are reasonable.

4. ^{1}H NMR Analysis of the Model Reaction for the Polymerization. The slow interconversion between the dormant and the activated species is also demonstrated by the ^{1}H NMR analysis of the model reaction for the polymerization with **2**/$ZnCl_2$. Parts A and B of Figure 11 show the spectra of **2** (B = $OCOCF_3$)/$ZnCl_2$ and **2** (B = OCOPh)/$ZnCl_2$ mixtures, respectively. As reported,[8,26] the adduct **2** has two inequivalent methylene protons c_1 and c_2, and these protons are interchangeable in the presence of $ZnCl_2$. The interchange occurs via the interconversion between the dormant and the activated species. The rate of interchange ($c_1 \rightleftharpoons c_2$) is estimated from the broadening of the methylene signals, from which the rate of the interconversion (activated $\rightleftharpoons$ dormant) is estimated.

As shown in Figure 11A, one of the methylene protons c_2 obviously broadened at 0 and 20 °C, which indicates that the interconversion between the two species occurs frequently in the $CF_3CO_2H/ZnCl_2$ system[8] [a similar broadening should occur in signal c_1 but was undetectable due to the overlapping peak of diethyl ether (solvent for $ZnCl_2$)]. Consistent with the rapid interconversion, this system indeed gave living poly(IBVE) with narrow MWDs ($\bar{M}_w/\bar{M}_n < 1.1$).[8,10] In contrast, for the $PhCO_2H/ZnCl_2$ system, which induced the polymerization nearly at the same rate as for $CF_3CO_2H/ZnCl_2$[8] but gave broad MWDs ($\bar{M}_w/\bar{M}_n \approx 2$) (Figure 4), the methylene signals c_1 and c_2 did not broaden even at 20 °C. These results clearly show that the "activated $\rightleftharpoons$ dormant" interconversion with benzoic acid is very slow.

Figure 11A also indicates that there were no signals of the HCl–IBVE adduct (B = Cl) which might be formed by the exchange reaction between the benzoate group of

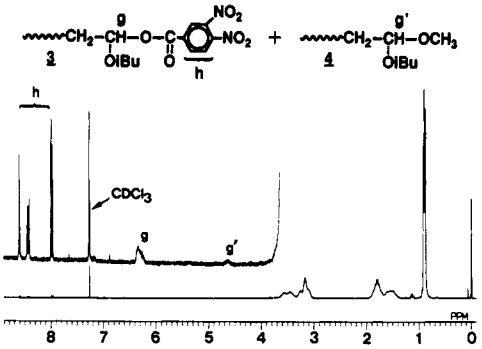


Figure 12. ^{1}H NMR spectrum in $CDCl_3$. Poly(IBVE) obtained with 2(3,4-di-NO_2)/$ZnCl_2$ in toluene at 0 °C after quenching with methanol. Monomer conversion 52%; $\bar{M}_n$ = 4800; $\bar{M}_w/\bar{M}_n$ = 1.35. $[M]_0$ = 0.38 M; $[2]_0$ = 5.0 mM; $[ZnCl_2]_0$ = 2.0 mM.

C–OCOPh and the chloride in $ZnCl_2$.[8] This shows that the dormant species in the polymerization is a benzoate ester.

5. Terminated Polymer End Structure. Figure 12 shows the ^{1}H NMR spectrum of the IBVE polymer obtained with 2(3,4-di-NO_2)/$ZnCl_2$ after quenching the polymerization with methanol at a monomer conversion of 52% ($\bar{M}_n$ = 4800, $\bar{M}_w/\bar{M}_n$ = 1.35). In addition to the signals at 0.8–3.7 ppm due to the IBVE repeat unit, a small broad peak g′ appeared at 4.6 ppm, which is assignable to the methine proton of the terminal acetal 4 that arises on quenching the polymerization with methanol. It is worth noting that the downfield signals h, characteristic of the aromatic protons of the 3,4-dinitrobenzoate group, appeared along with the absorption g at 6.3 ppm, which is ascribed to the methine proton of the terminal ester 3 of the benzoic acid. The peak intensity ratio of h to g is 2.9, which is in good agreement with the calculated value, 3, assuming the structure of macromolecular ester 3. These results show that there were two kinds of terminated polymer structures, 4 (acetal) and 3 (ester). On the basis of the peak intensity ratio g to (g + g′), the ester terminal amounted to 83%. In the other systems with benzoic acid derivatives, the relative amount of the ester ranged 70–80%, irrespective of the substituents (HB, mol % of 3): 3,4-di-NO_2, 83%; p-NO_2, 84%; p-CF_3, 85%; p-Cl, 84%; p-H, 73%; p-CH_3, 77%. These results indicate that most of the ester terminals remain intact on quenching with methanol. In contrast, all the polymers obtained with CF_3CO_2H/$ZnCl_2$ after quenching with methanol have the acetal terminals 4. The difference is explained by the difference in the strength of the ester bonds, which also suggests that the ester bond of benzoic acid derivatives is hard to activate with $ZnCl_2$.

6. Conclusions. In conclusion, living cationic polymerization of IBVE is feasible with the nitrobenzoic acid/$ZnCl_2$ systems, where the $\bar{M}_n$ of the polymer increased in direct proportion to monomer conversion being in good agreement with the calculated value and MWD is narrow. With weaker benzoic acids (p-CF_3, p-Cl, p-H, and p-CH_3), the polymerizations were living but gave $\bar{M}_n$ values larger than the calculated values as well as broader MWDs. The consumption of the initiator was accelerated by introducing an electron-withdrawing group into benzoic acids. These results show that the less polarized ester bond derived from a weaker benzoic acid is more reluctant to dissociate, which results in slower interconversion between dormant and activated species to give polymers with broader MWDs. An anion B^- derived from a weak acid indeed stabilizes carbocation; however, its nucleofugality may become low,[27] which is not suited for giving narrow MWDs. Thus, for attaining living cationic polymerization where the MWDs of polymers are narrow, the selection of an anion with moderate nucleophilicity and nucleofugality is critical.

Table II
Synthesis of Benzoic Acid–IBVE Adducts (2)

substituent	synthesis[a] temp, °C	time, h	^{1}H NMR, δ,[b] ppm CH_3	–CHO–	CH_2	purification
2,4-di-NO_2	55	1	0.93	6.17	3.38, 3.56	recrystn
3,4-di-NO_2	70	3	0.93	6.20	3.34, 3.50	recrystn
p-NO_2	70	10	0.92	6.17	3.33, 3.50	recrystn
p-CF_3	85	1	0.92	6.17	3.33, 3.49	distiln
p-Cl	85	6	0.91	6.14	3.31, 3.48	distiln
p-H	60	6	0.92	6.16	3.32, 3.50	distiln
p-CH_3	80	4	0.91	6.14	3.30, 3.48	distiln

[a] The reactions were all quantitative (by ^{1}H NMR). [b] In a mixture of solvents ($CDCl_3/CCl_4$ = 3/1) at 25 °C ([2] = 125 mM).

Experimental Section

Materials. $ZnCl_2$ (Aldrich, 1.0 M solution in diethyl ether) was commercially supplied as a solution, which was diluted with Et_2O. IBVE (Tokyo Kasei) was washed with 10% aqueous sodium hydroxide solution and then water, dried overnight over potassium hydroxide, and distilled twice over calcium hydride before use. Toluene (solvent) and carbon tetrachloride (internal standard for gas chromatography) were purified by the usual methods and distilled twice over calcium hydride before use.[5] Diethyl ether (Dojin, purity >99%, anhydrous) was distilled in the presence of $LiAlH_4$ before use.

Synthesis of Benzoic Acid–IBVE Adducts (2). As summarized in Table II, adducts 2 were synthesized by magnetically stirring a mixture of benzoic acid derivatives [1; purity >98%; as received from Tokyo Kasei (2,4-di-NO_2, 3,4-di-NO_2, p-NO_2, p-Cl, and p-CH_3), Wako Chemicals (unsubstituted), and Aldrich (p-CF_3)] and IBVE (molar ratio 1/IBVE = 1/2) at 55–85 °C for 1–10 h. The unreacted IBVE in excess was evaporated off, and the remaining liquid or solid was distilled under reduced pressure or recrystallized from toluene, respectively, and then the adducts 2 were isolated. The formation of 2 was confirmed by ^{1}H and ^{13}C NMR spectroscopy. The adducts 2, especially the dinitro-substituted derivatives, were moisture sensitive; thus, they were all sealed in brown ampules in a dry nitrogen atmosphere and stored in a refrigerator.

Polymerization Procedures. Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. The reaction was initiated by adding, via dry syringes, a solution of $ZnCl_2$ (in Et_2O; 0.50 mL) into a monomer solution (in toluene; 4.5 mL) containing 2. The polymerization was terminated with prechilled methanol (2.0 mL).

Monomer conversion was determined from its residual concentration measured by gas chromatography with CCl_4 as an internal standard. The polymer yield by gravimetry was in good agreement with the gas chromatographic conversion of the monomer.

The quenched reaction mixture was washed with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum dried to give the product polymers.

Measurements. The MWD of polymers was measured by size exclusion chromatography in chloroform at room temperature on a Jasco Trirotar-V chromatograph equipped with three polystyrene gel columns (Shodex K-802, K-803, and K-804). The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of the polymers were calculated from size exclusion eluograms on the basis of a polystyrene calibration, excluding the remaining adduct 2. Initiator consumption was determined from the ratio of the integrated intensity of 2 to that of polymers in GPC curves by a UV detector (256 nm), because the UV absorption of both 2 and the polymers is due to the benzoate group at the terminal; poly(IBVE) has no UV absorption at 256 nm. ^{1}H and ^{13}C NMR spectra (270 and 67.5 MHz, respectively) were recorded on a JEOL JNM-GSX270 spectrometer. Polymer samples for ^{1}H NMR spectroscopy were separated from the products (mixtures of the polymers and the

unreacted initiator) by preparative size exclusion chromatography (column, Shodex K-2002).

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research (No. 02453107) from the Ministry of Education, Science and Culture, Japan.

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(27) Approximately, an anion B^- derived from a weak acid may have low nucleofugality and high nucleophilicity. However, strictly speaking, their relationship is not so simple. We herein discuss from the former viewpoint for simplicity.