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Quantitative Comparison of Theory and Experiment on Living Radical Polymerization Kinetics. 2. Atom Transfer Radical Polymerization

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ABSTRACT: The kinetic theories on the polymerization rate and polydispersity in atom transfer radical polymerization (ATRP) were, for the first time, quantitatively tested by experiments for the polymerization of styrene at 110 °C with a polystyryl bromide/Cu(I)Br/ligand initiating system in the presence or absence of the conventional radical initiator 2,2′-azobis(2,2,4-trimethylpentane) (VR110). The polymerization rate in the VR110-free system conformed to the theory on an absolute scale, showing a $^2/_3$-order time dependence of conversion index. The addition of VR110 increased the polymerization rate to reach a stationary state. Experimental results on polydispersity also quantitatively agreed with the theories in both the presence and absence of VR110, exhibiting the theoretically predicted time evolutions of polydispersity index characterized by the prefactors $^1/_2$ and $^3/_8$, respectively.

Introduction

In recent years, living radical polymerization (LRP) has attracted much attention as a facile and robust means to synthesize polymers with well-defined structures.[1] Mechanistically, LRP is based on the reversible activation (Scheme 1a), where the dormant species P−X is activated to the propagating radical $P^\bullet$, which, in the presence of monomer, propagates until it is deactivated back to P−X. Dissociation−combination (DC) and atom transfer (AT) processes (Scheme 1, b and c) are among the most important mechanisms of reversible activation. In LRP, termination unavoidably occurs and, in many cases, conventional initiation also exists. Because of the presence of these reactions, systems with a DC or a AT process are expected to show characteristic and interesting kinetic features, according to the theories with respect to polymerization rate and polydispersity.[2,3] Those theories have been experimentally confirmed on an absolute scale in some nitroxide-mediated (DC-type) systems.[3−6] However, no sufficient experimental verification has been achieved for AT radical polymerization (ATRP),[7,8] mainly due to the difficulty to meet the required experimental conditions. In this work, we have been able to overcome the difficulty and make a stringent test of the theories for a copper-mediate ATRP.[8] All the parameters necessary to compute theoretical rates and polydispersities were taken from independent reliable sources, which allowed us to make a quantitative comparison of the theories and experiments for the first time.

Theoretical Section

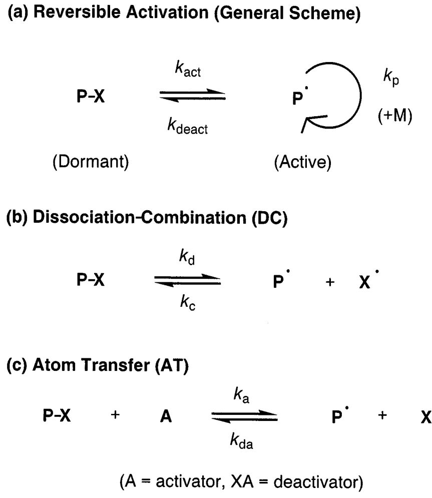
In this section, we only give a brief summary of the ATRP theories. For more details, the readers are referred to ref 3.

We will focus on the time range in which the quasi-equilibrium

$$k_a[A][P-X] = k_{da}[P^\bullet][XA] \qquad (1)$$

holds and in which the cumulative numbers of dead chains are sufficiently small compared to the number of dormant chains, i.e., $[P-X] \cong [P-X]_0$, where A is an activator, XA is a deactivator, and k_a and k_{da} are defined in Scheme 1c. The specific conditions that the rate constants should obey to meet these requirements are given elsewhere,[9,10] and it may be easily confirmed that the system to be experimentally studied in the next section meets them.

Scheme 1. Reversible Activation Processes



(a) Reversible Activation (General Scheme)

(b) Dissociation-Combination (DC)

(c) Atom Transfer (AT)

(A = activator, XA = deactivator)

Rate Equations. When the mentioned conditions are met, and reactions other than activation, deactivation, propagation, termination, and conventional initiation are absent, the general equation for the concentration of the persistent species [XA] is given by[3,11]

$$\ln\{[(1+z)/(1-z)][(1-z_0)/(1+z_0)]\} - 2(z-z_0) = bt \qquad (2)$$

$$z = \{R_i/(k_t K^2[P-X]_0^{\,2})\}^{1/2}[XA] \qquad (3)$$

$$b = 2R_i^{\,3/2}/(k_t K^2[P-X]_0^{\,2})^{1/2} \qquad (4)$$

$$K = (k_a/k_{da})[A] = K_{AT}[A] \qquad (5)$$

where R_i is the conventional initiation rate, k_t is the termination rate constant, and K_{AT} is the equilibrium

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constant (= k_a/k_{da}). Here, it is assumed that R_i is constant and that all the rate constants are independent of chain length and other factors. Given [XA], the polymerization rate R_p is obtained from $R_p = k_p[P^\bullet][M]$ with $[P^\bullet]$ given by eq 1, where k_p is the propagation rate constant. Three special cases for R_p are particularly noteworthy in relation to the present work. The two cases are for $R_i = 0$: when $R_i = 0$, eq 2 reduces to eq 6,[12] and if, furthermore, $[XA]_0 = 0$, eq 6 gives the power-law eq 7[13,14] for of the conversion index $\ln([M]_0/[M])$, while in the other limit of $[XA]_0 \gg 0$, it yields the first-order law, eq 8.[12]

$$[XA]^3 = [XA]_0{}^3 + 3k_tK^2[P-X]_0{}^2t \quad (R_i = 0) \qquad (6)$$

$$\ln([M]_0/[M]) = (3/2)k_p(K[P-X]_0/3k_t)^{1/3}t^{2/3} \quad (R_i = [XA]_0 = 0) \qquad (7)$$

$$\ln([M]_0/[M]) = (k_pK[P-X]_0/[XA]_0)t \quad (R_i = 0,\ [XA]_0 \gg 0) \qquad (8)$$

The third case is the one with $R_i > 0$ and $bt \gg 1$. Equation 2 then reduces to $z = 1$ and yields eq 9,[15] as in the conventional free radical polymerization. In this limit, too, the conversion index is linear in t.

$$\ln([M]_0/[M]) = k_p(R_i/k_t)^{1/2}t \quad (R_i > 0,\ bt \gg 1) \qquad (9)$$

Polydispersity Equations. We define the polydispersity factor Y by $Y = (x_w/x_n) - 1$, where x_w and x_n are the weight- and number-average degrees of polymerization, respectively, and write the Y of the "grown portion" of the chain Y_B. The factors Y_B of the system corresponding to the power-law equation (eq 7)[16] and that of the stationary-law eqs 8 and 9[5,17] are given by eqs 10 and 11, respectively:

$$[Y_B - (1/x_{n,B})]^{-1} = (3/8)k_a[A]t \quad (R_i = [XA]_0 = 0) \qquad (10)$$

$$[Y_B - (1/x_{n,B})]^{-1} = (1/2)k_a[A]t \quad (R_i = 0,\ [XA]_0 \gg 0) \text{ or } (R_i > 0,\ bt \gg 1) \qquad (11)$$

Here the conversion is assumed to be small enough, and $x_{n,B}$ is the x_n of the grown portion of the chain. Equations 10 and 11 predict that at the same t the polydispersity factor, or more precisely, $Y_B - (1/x_{n,B})$ is smaller in the stationary-law system than in the power-law system. This originates in the difference in the time dependence of [XA] between the two systems. Since this discussion neglects the contribution of terminated and (conventionally) initiated chains, it is strictly valid only for small t or small c. In other words, experiments to verify these theoretical predictions must be designed so strictly. All eqs 1−11 can be applied to DC systems by the reinterpretation of $XA = X^\bullet$, $k_a[A] = k_d$, and $k_{da} = k_c$ ($K = k_d/k_c$), where the rate constants are defined in Scheme 1b.[3]

Experimental Section

Materials. Styrene (99%, Nacalai Tesque, Japan) and *tert*-butylbenzene (*t*BB) (99%, Nacalai) were purified by fractional distillation. 4,4′-Di-*n*-heptyl-2,2′-bipyridine (dHbipy) was prepared according to Matyjaszewski et al.[18] A polystyrene (PS)−Br adduct (M_n = 1200 and M_w/M_n = 1.08) was obtained as described previously,[19] which was used as an initiating adduct P_0−X in the following experiments. A chain extension test[19,20] showed that this polymer contains 4% of potentially inactive species (without a Br moiety at the chain end). The experimental data presented below have been corrected for this impurity. Cu(I)Br (99.9%, Wako Pure Chemical, Japan), Cu(II)Br_2 (99%, Nacalai), 2,2′-azobis(2,4,4-trimethylpentane) (VR110) (99.9%, Wako), and galvinoxyl (98%, Acros) were used as received.

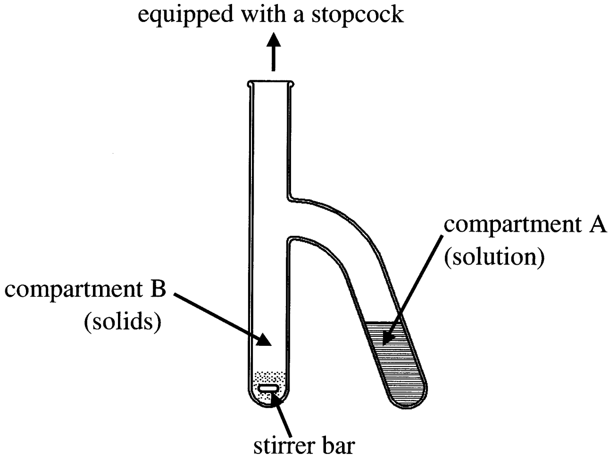

Figure 1. Reaction vessel for ATRP used in the present work.

Determination of Initiation Rate Constant $k_{i,VR110}$ with VR110. A styrene/*t*BB (50/50 v/v) solution of galvinoxyl (3.8 mM) and VR110 (0 or 40 mM) in a quartz tube was degassed by three freeze−pump−thaw cycles, sealed off under vacuum, and analyzed by electron spin resonance (ESR) at 110 °C.

Kinetic Analysis of Polymerization. A forked glass tube (Figure 1) was charged with a styrene/*t*BB (50/50 v/v) solution (5 mL) of P_0−X (13 mM) and VR110 (0 or 40 mM) in one side (compartment A) and with Cu(I)Br (10 mM), Cu(II)Br_2 (0 or 2.8 mM), and dHbipy (30 or 38.4 mM) in the other side (compartment B). The glass tube was then equipped with a stopcock, attached to a vacuum line, and subjected to three cycles of freeze−pump−(argon introduction)−thaw. The reactants were then mixed by pouring the solution in compartment A to the copper species in compartment B and immediately immersed in an oil bath at 110 °C with magnetic stirring (t = 0). After a prescribed time t, an aliquot (0.1 mL) of the solution was taken out with a syringe, quenched in the air at room temperature, and then diluted with tetrahydrofuran (THF) to a known concentration to be analyzed by gel permeation chromatography (GPC).

Measurements. The ESR spectra were recorded at 110 °C on a Bruker EMX spectrometer (Karlsruhe, Germany) equipped with a cavity of the type ER4119ST and a variable temperature accessory of the type ER4131VT. The measurement was performed with 100 kHz magnetic field modulation at microwave output of 0.5 mW. The GPC analysis was made on a Tosoh HLC-802 UR high-speed liquid chromatograph equipped with Tosoh gel columns G2500H, G3000H, and G4000H (Tokyo, Japan). THF was used as eluent (40 °C). The column system was calibrated with Tosoh standard PSs. A known amount of sample solution (of a known concentration) was injected in the column system, and the elution profile was analyzed with a Tosoh differential refractometer RI-8020 calibrated with known concentrations of PSs in THF.

Results and Discussion

Theoretical relations to be studied here are the rate eqs 7−9 and the polydispersity formulas 10 and 11. The power-law eq 7 has been tested in some ATRP systems. However, most experimental results disagreed with eq 7 for several reasons.[21−23] ESR studies have shown that there is a finite concentration of Cu(II) at time zero in many cases,[24−26] which conflicts with the basic assumption for eq 7. An important origin of Cu(II) may be the oxidation of Cu(I) in the air,[27,28] particularly when Cu(I) is mixed with other reagents under insufficient

Table 1. Kinetic Parameters Used in This Work (110 °C)

parameter	value	ref
$k_{i,th}$ ($M^{-2}\,s^{-1}$)	9.6×10^{-11}	32
$k_{i,VR110}$ (s^{-1})	3.0×10^{-5}	this work
k_p ($M^{-1}\,s^{-1}$)	1560	35
k_t ($M^{-1}\,s^{-1}$)	3.6×10^{8} [a]	this work
k_a ($M^{-1}\,s^{-1}$)	0.45	19
$K_{AT} = k_a/k_{da}$	2.4×10^{-8}	this work

[a] Applicable for an early-stage polymerization with PS−Br (M_n = 1200, M_w/M_n = 1.08).

deoxygenation. To avoid this, we in this work used a forked Schlenk flask to avoid the contact of Cu(I) with the other reagents, until deoxygenation is completed and they are mixed at time zero. The second factor that causes deviations from eq 7 is the chain length dependence of k_t.[21] The third factor may be a subtle change of the reaction medium caused by polymerization, which can alter, e.g., the solubility and activity of the catalyst.[22] To minimize these effects, we used a polymeric compound (polystyryl bromide) as an initiating adduct and focused our attention on an early stage of polymerization so that changes in the relative chain length and the polymer mass fraction in the medium are relatively small. Some research groups have recently settled these problems by different approaches and observed the power-law behavior in ATRP.[28−30] We in this work assessed the validity of eq 7 in a more rigorous fashion. The stationary-law behavior indicated by eq 8 has been observed in some systems, and the relation was used to determine K_{AT}.[18,29,31] The rate eq 9 and the polydispersity eqs 10 and 11 have never been experimentally tested before in ATRP. In the following, we comprehensively examine these equations for the solution ATRP of styrene with *t*BB (50/50 v/v).

Rate Constants. The parameters used in this work are listed in Table 1. In the table, $k_{i,th}$[32] and $k_{i,VR110}$ are the rate constant of thermal initiation and that of the initiation due to the VR110 decomposition (with the initiation efficiency included). The initiation rate R_i, which is assumed here to be constant, is given by

$$R_i = k_{i,th}[M]_0^{\,3} + k_{i,VR110}[VR110]_0 \qquad (12)$$

with $[M]_0 = 3.9$ M and $[VR110]_0 = 0$ or 40 mM in this study. We determined $k_{i,VR110}$ by the inhibitor method. Namely, the styrene/*t*BB (50/50 v/v) solution of VR110 (40 mM) was heated in the presence of galvinoxyl (3.8 mM) as an inhibitor at 110 °C, and the decay of the galvinoxyl concentration [Gal] was chased by ESR. Figure 2 (filled square) shows the plot of [Gal] vs *t* for this system. The figure shows that even in the absence of VR110, galvinoxyl spontaneously disappeared at the present experimental temperature of 110 °C (filled triangle).[33,34] Thus, the decay of [Gal] in the presence of VR110 (filled square) has to be split into a spontaneous decay (filled triangle) and the decay due to the VR110 decomposition (open circle). The plot for the latter (open circle) represents a linear line at small *t* (<20 min), giving $k_{i,VR110} = 3.0 \times 10^{-5}\ s^{-1}$, according to

$$\begin{aligned} -d[Gal]/dt &= k_{i,VR110}[VR110] + k_{deg}[Gal] \\ &\cong k_{i,VR110}[VR110]_0 + k_{deg}[Gal]_0 \\ &\qquad\qquad \text{(at small } t\text{)} \end{aligned} \qquad (13)$$

where k_{deg} is the rate constant of spontaneous degradation of galvinoxyl with $k_{deg}[Gal]_0 = 5.5 \times 10^{-7}\ M\ s^{-1}$ (110 °C).

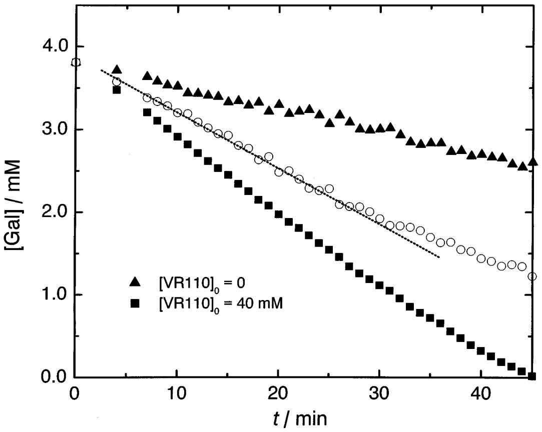

Figure 2. Plot of [Gal] vs *t* for the styrene/*t*BB/galvinoxyl/VR110 system (110 °C): $[Gal]_0 = 3.8$ mM; $[VR110]_0 = 0$ (▲) and 40 mM (■); [styrene]/[*t*BB] = 50/50 v/v. The symbol (○) shows the decay due to the decomposition of VR110 only (see text). The dotted line is the best-fit representation of the data points (○).

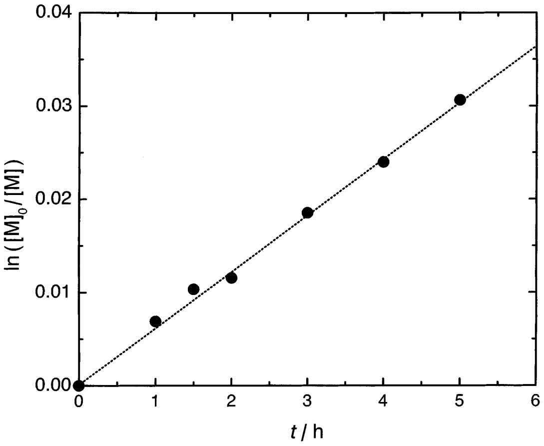

Figure 3. Plot of $\ln([M]_0/[M])$ vs *t* for the styrene/*t*BB/PS−Br(P_0−X)/Cu(I)Br/Cu(II)Br_2/dHbipy system (110 °C): $[P_0{-}X]_0$ = 13 mM; $[Cu(I)Br]_0$ = 10 mM; $[Cu(I)Br_2]_0$ = 2.8 mM; $[dHbipy]_0$ = 38.4 mM; [styrene]/[*t*BB] = 50/50 v/v. The dotted line is the best-fit representation of the data points.

The k_p in Table 1 is the IUPAC recommended value,[35] and the k_a is the one previously determined by the GPC curve-resolution method.[19] Since there are no reported data of K_{AT} and k_t applicable to the present analysis, we estimated them from the stationary-state experiments using eqs 8 and 9. Namely, to estimate K_{AT}, we carried out the polymerization including the PS−Br adduct ($[P_0{-}X]_0$ = 13 mM: see Experimental Section), Cu(I)Br ($[A]_0$ = 10 mM), and a sufficiently large amount of Cu(II)Br_2 at $t = 0$ ($[XA]_0$ = 2.8 mM) at 110 °C, where eq 8 is expected to hold. To ensure a perfect solubility of the copper species, the ligand dHbipy was added in excess (3 times the molar amount of the copper species) in all related experiments. Figure 3 shows the plot of $\ln([M]_0/[M])$ vs *t*. The plot was linear, as expected. From the slope of the straight line, we have $K_{AT} = 2.4 \times 10^{-8}$. This value is to be compared to the one (3.9×10^{-8}) reported by Matyjaszewski et al. for the corresponding styrene/diphenyl ether (50/50 v/v) system (at 110 °C).[18]

To estimate k_t, we examined the system with $[P_0{-}X]_0$ = 13 mM, $[A]_0$ = 10 mM, and $[VR110]_0$ = 40 mM. In this system, R_i hence *b* is large enough that eq 9 should hold. In fact, as shown in Figure 4, the first-order plot may be approximated by a linear relation after *t* =

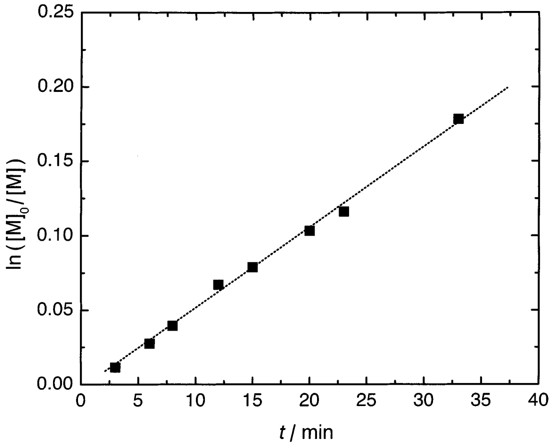

Figure 4. Plot of $\ln([M]_0/[M])$ vs t for the styrene/tBB/PS−Br(P_0−X)/Cu(I)Br/dHbipy/VR110 system (110 °C): $[P_0\text{−}X]_0 = 13$ mM; $[\text{Cu(I)Br}]_0 = 10$ mM; $[\text{dHbipy}]_0 = 30$ mM; $[\text{VR110}]_0 = 40$ mM; [styrene]/[tBB] = 50/50 v/v. The dotted line is the best-fit representation of the data points.

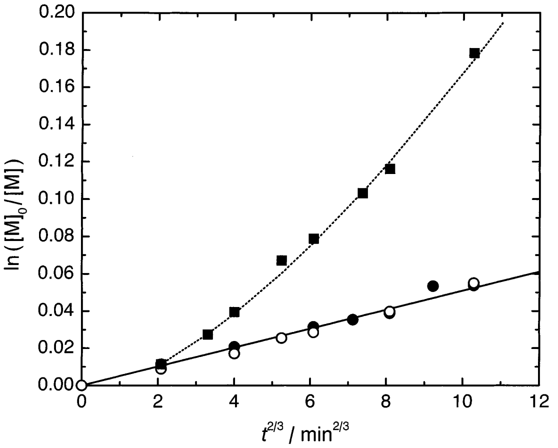

Figure 5. Plot of $\ln([M]_0/[M])$ vs $t^{2/3}$ for the styrene/tBB/PS−Br(P_0−X)/Cu(I)Br/dHbipy system (110 °C): $[P_0\text{−}X]_0 = 13$ mM; $[\text{Cu(I)Br}]_0 = 10$ mM; $[\text{dHbipy}]_0 = 30$ mM; [styrene]/[tBB] = 50/50 v/v. The experiment was duplicated (● and ○). The solid line shows eq 7 with the independently determined rate constants (Table 1). The data points in Figure 4 (■) are replotted against $t^{2/3}$. (The dotted line is the reproduction of the one in Figure 4 in the $t^{2/3}$ plot.)

3 min, and the slope of the line gives $k_t = 3.6 \times 10^8$ M^{-1} s^{-1}. This k_t value should be regarded as a certain mean value applicable to an early stage of polymerization initiated with a polystyryl adduct with $M_n = 1200$. Notably, this is the first experimental observation that an ATRP system follows eq 9. Conventional radical initiators have been used in many reverse ATRP,[36] but no attempts have been made to increase $[P^\bullet]$ up to the stationary state.

Quantitative Comparison of Theory and Experiment. By using these parameters, we tested eqs 7, 10, and 11 on an absolute scale. To test the rate eq 7 ($R_i = [XA]_0 = 0$), we examined the system with $[P_0\text{−}X]_0 = 13$ mM and $[A]_0 = 10$ mM. As will be justified below, thermal initiation is entirely negligible in the examined time range (<35 min) due to a sufficiently high dilution of styrene with tBB. Figure 5 shows the results. The duplicated experimental points (circles) are well reproduced by the $t^{2/3}$-dependent linear line predicted by the theory (solid line), confirming the validity of the theory on an absolute scale.

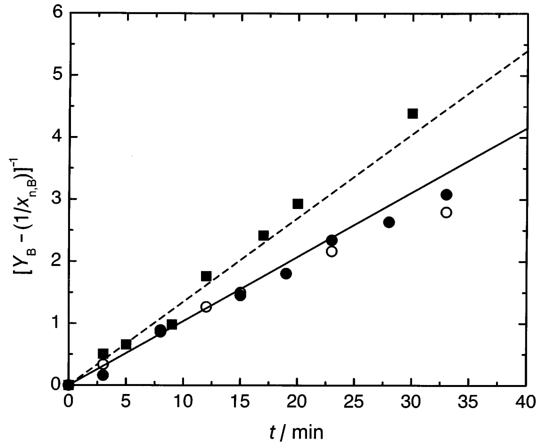

Figure 6. Plot of $[Y_B - (1/x_{n,B})]^{-1}$ vs t for the styrene/tBB/PS−Br(P_0−X)/Cu(I)Br/dHbipy/(VR110) system (110 °C): $[P_0\text{−}X]_0 = 13$ mM; $[\text{Cu(I)Br}]_0 = 10$ mM; $[\text{dHbipy}]_0 = 30$ mM; $[\text{VR110}]_0 = 0$ (● and ○) and 40 mM (■); [styrene]/[tBB] = 50/50 v/v. The solid and broken lines show eqs 10 and 11, respectively, with the independently determined k_a value (Table 1).

Figure 6 shows the comparison of the polydispersity eqs 10 (solid line) and 11 (broken line) with the experiments related to Figure 5 (circles) and Figure 4 (squares). In both systems, satisfactory agreement between theory and experiment was found. The results confirm the theoretical prediction that conventional initiation not only increases the polymerization rate but lowers the polydispersity. Similar observations were previously reported for a nitroxide system.[3] For the system with VR110, it took about 3 min to reach the stationary state (Figure 4). To eliminate the effect of the pre-stationary stage on polydispersity, we obtained the data points in Figure 6 (squares) by regarding the time relevant to the first (smallest t) data point in the stationary state as $t = 0$ and the polymer corresponding to this point as an initiating adduct P_0−X. For more details of this correction, see ref 3.

Justification of the Experimental Conditions. Finally, we examine the propriety of the experimental conditions used above. Figure 7 shows the comparison of the time evolution of z for $R_i > 0$ (solid lines) and $R_i = 0$ (broken line) according to eqs 2 and 6, respectively, where eq 6 is rewritten[3]

$$z^3 = z_0^{\,3} + (3/2)bt \quad (R_i = 0) \tag{14}$$

The experiment with VR110 in Figure 4 was carried out in the range $8 < bt < 90$ with $b = 0.045$ s^{-1}. In this time range, z may be approximated by 1 (Figure 7), and thus the stationary state should be achieved. In the experiment without VR110 in Figure 5, thermal initiation amounts to $b = 1.5 \times 10^{-5}$ s^{-1}. The relevant time range of the experiment corresponds to $bt < 0.03$, where the thermal initiation is totally negligible, as Figure 7 suggests (compare the curves for $R_i > 0$ and $R_i = 0$). The experiment with $[XA]_0 = 2.8$ mM in Figure 3 corresponds to $z_0 = 3.6$ and $bt = 0.26$ after 5 h. The change of z and hence of [XA] is small in this time range (Figure 7), and the system may be regarded as being in a stationary state.

Conclusions

The kinetic theories on ATRP were comprehensively tested by experiments in the copper-mediated styrene

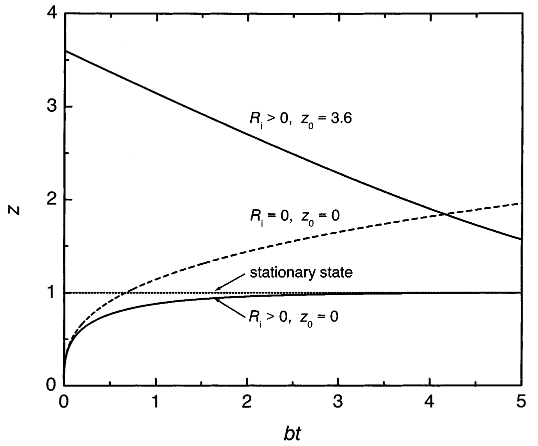

Figure 7. Plot of z vs bt. The solid lines show eq 2 (for $R_i > 0$) and the broken line, eq 14 (for $R_i = 0$). The dotted line represents the stationary state ($z = 1$).

systems at 110 °C. For the system with $R_i = 0$, experiments quantitatively agreed with the theories with respect to both the polymerization rate and polydispersity. The polymerization rate increased to a stationary state by the addition of the conventional initiator VR110. At a given time, polydispersity in the system with VR110 was confirmed to be lower than that in the one without VR110, as the theories predict.

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