Macromolecules **2004,** *37,* 9395−9401

Determination of the Kinetic Parameters of Atom Transfer Radical Polymerizations

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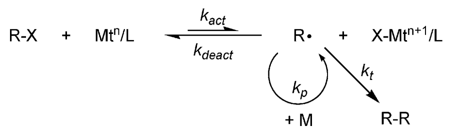
Received February 24, 2004; Revised Manuscript Received August 13, 2004

ABSTRACT: In an attempt to find a novel catalyst system for atom transfer radical polymerization (ATRP), a parameter estimation method based on nonlinear regression was developed to evaluate various catalyst systems by determining kinetic parameters of polymerization. From our model system considering small molecular atom transfer addition reaction, we found that equilibrium constant of atom transfer reaction could be successfully determined using our parameter estimation method. However, the each value of activation rate constant and deactivation reaction constant is hard to be determined ubiquitously because of the poor sensitivities of them and the local minima trapping. By applying second minimization algorithm, the parameter estimation algorithm achieves higher propensity to reach global minimum, yet not all the time. The simulation results using kinetic rate constants determined by our method shows better agreement with the experimental data than that using literature values. This is because the current method uses fewer assumptions than other literature methods in determining rate constants. We also demonstrated the determination of kinetic constants in the polymerization of styrene and MMA using various metal catalysts, and the simulations using these kinetic constants agree well with the experimental data.

I. Introduction

A number of controlled radical polymerization methods have been developed during the past decade.[1−6] Even though it has rather short history, this new concept has provided lots of new and advanced applications of radical polymerization techniques. The key kinetic feature of controlled radical polymerizations is the reduction of the concentration of active chain ends by establishing dynamic equilibrium between active radicals and dormant species. In turn, this reduced radical concentration suppresses the rate of the bimolecular termination reactions. Moreover, the termination reactions between activated radical species are suppressed by the persistent radical effect.[7] Of the various controlled radical polymerizations, atom transfer radical polymerization (ATRP) involves metal complexes as media of halogen atom transfer between dormant chains and active radicals (eq 1).



(1)

Various metals and ligands have been used as catalysts for ATRP.[4,5,8−16] Determining the kinetic parameters of the polymerization using these catalysts allows for the quantification of their efficiency. In ATRP, there are at least two important kinetic parameters. The first is the equilibrium constant ($K_{\mathrm{eq}} = k_{\mathrm{act}}/k_{\mathrm{deact}}$) of the atom transfer reaction, which determines the concentration of active radicals propagating at any one time with the reaction. The second important kinetic parameter is the ratio of the deactivation rate constant (k_{deact}) to propagation rate constant (k_{p}), which should have a high value in order to produce polymers having low polydispersities.

Several research groups have attempted to determine kinetic parameters in ATRP using pseudo-first-order kinetics,[17−22] isolation of activation or deactivation step in ATRP process,[23−25] or the analytical solution of the persistent radical effect.[26] Most of works used either ATRP itself for the systems showing good control or special experimental setup which is not under polymerization conditions.

In this paper, we introduced an alternative method to determine kinetic parameters. Ideally, it is possible to determine kinetic parameters of ATRP systems, which are not following pseudo-first-order kinetics, using real polymerization data. The purpose of using this method is on our goal to find a relationship between the characteristics of a catalyst system and its efficiency as an ATRP catalyst. Parameter estimation algorithms have been widely used in the kinetic studies of chemical reactions, including polymerization systems.[27−29] The parameter estimation algorithm has many advantages: The estimation algorithm can use all experimental data carried out under different conditions and allows the estimation of all the parameters of the model. Moreover, the model involves fundamental parameters of the process, and there is no limitation on the number and character of estimatable parameters. In this work, we are going to apply this parameter estimation algorithm to determine important rate constants of ATRP, including K_{eq}, k_{act}, and k_{deact}. Furthermore, the method developed herein should be useful for any type of polymerization system.

II. Results and Discussion

Model Reactions. The first step of developing an algorithm is to establish the model reactions that fully

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10.1021/ma049627i CCC: $27.50

Scheme 1. Model Reactions of ATRP of Styrene

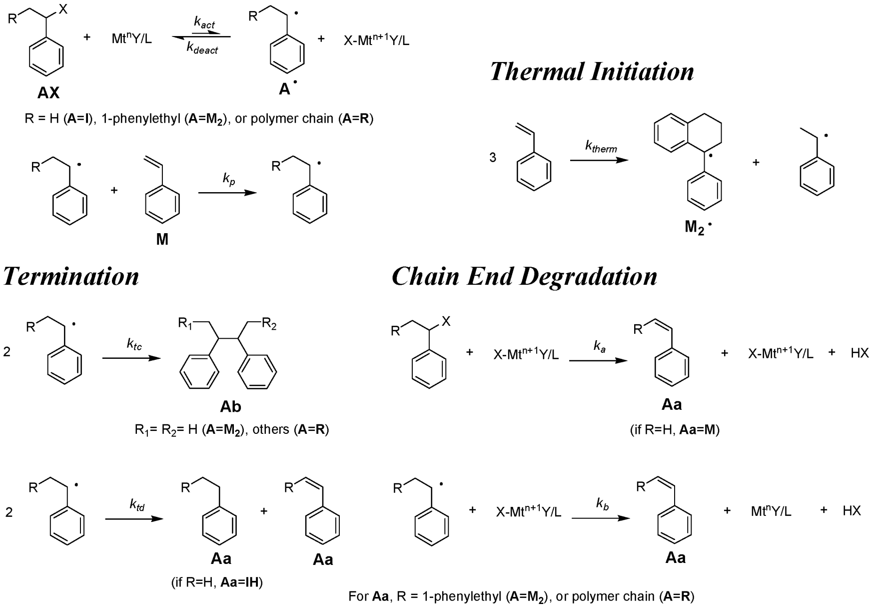


Table 1. Values of the Parameters Used in the Simulation

k_{act} (M^{-1} s^{-1})[18]	0.45	k_{td} (M^{-1} s^{-1})[34]	1.0×10^8
k_{deact} (M^{-1} s^{-1})[18]	1.1×10^7	k_{therm} (M^{-1} s^{-1})[34]	4.8×10^{-11}
k_p (M^{-1} s^{-1})[34]	1.6×10^3	k_a (M^{-1} s^{-1})[33]	1.0×10^{-4}
k_{tc} (M^{-1} s^{-1})[34]	1.0×10^9	k_b (M^{-1} s^{-1})[35]	1.63×10^3

as possible describe the polymerization reactions. One of the merits of our current approach is that it is possible to incorporate every possible reaction into this model. Scheme 1 outlines the general model for the polymerization of styrene used in our analysis. Included are the following reactions and associated rate constants/coefficients: (a) activation and deactivation of the dormant and active species (k_{act}, k_{deact}, and K_{eq}), (b) propagation (k_p), (c) thermal initiation (k_{therm}), (d) termination of two radicals by both combination and disproportionation (k_{tc}, k_{td}), and (e) chain end degradation (k_a, k_b). Simulations using this model show the good agreements with the other simulation results by Fischer[30] and Matyjaszewski[31] and also agree well with the experimental data.

Parameter Estimation Algorithm. We used the MINPACK package for the parameter estimation steps.[32] The MINPACK is a universal package composed of many subsolvers designed to address different problems. However, in addition to make the necessary choices with the MINPACK package, we had to modify the program to make it suitable for our purposes. Therefore, prior to applying this modified program to real problems, we had to check the validity of the algorithm to ensure that the rate constants can be determined successfully with this new package. To properly test this package, we used fabricated experimental data points that were generated by using literature values of rate constants (Table 1).[18,33−35] A series of initial "poor guesses" for the rate constants were refined using an iterative regression approach in direction to minimize the difference (merit function, Φ) between the experimental values and the simulated values using the set of rate constants. The goodness of fit was then evaluated by determining how close the calculated values matched the rate constants used to generate the data.

For accuracy and reliability of the parameter estimation approach, it is desirable to have data that relates to as many of the individual mechanistic steps as possible. In the polymerization itself, the pertinent data are the concentration of the monomer, molecular weight, and polydispersity of resulting polymer. It is, however, difficult to simulate molecular weight and polydispersity of polymer because of the complex nature of the polymerization. We therefore used a simplified model system for this phase of the study. Specifically, small molecular atom transfer radical addition (ATRA) reactions were used as our test bed. We used high initial concentrations of both initiator ([IX]/[M] = 4) and metal complexes ([IX]/[Mt^n] = 10). Under these reaction conditions, the concentration of the important components, including initiator (IX), dimeric dormant species (M$_2$X), and the termination dimeric product of initiator radical (M$_2$b), could be determined using standard characterization methods. It should be noted that because our model systems run at high catalyst concentrations and low monomer concentrations, the effect of the chain end degradation reactions becomes very important.

Table 2 shows the first results of the parameter estimation. We started with several initial guesses having diverse values to identify the global minimum. The regression results showed that for all rate constants different final values resulted in fits of the data that were indistinguishable from one another. However, the ratio of k_{act} and k_{deact}, the equilibrium constant K_{eq}, converged quite well to the original value for most of the initial guesses. This result implied that although we could not successfully estimate each of the individual rate constants, it is possible to determine the K_{eq} from our model reactions and reaction conditions.

There were several possible explanations for this unsuccessful parameter estimation scheme. The first reason is the sensitivities of the rate constants. If one reaction has a very small influence on the overall course of the reaction, it is hard to determine the rate constant corresponding to that step. The sensitivities of each of the rate constants could be checked by plotting the contour map of the merit function. We are attempting to estimate five different rate constants in ATRP, which means that the real contour map of our problem is 5-dimensional. Because it is impossible to visualize a 5-dimensional contour map, we simplified the problem into a series of 1-dimensional representations by holding

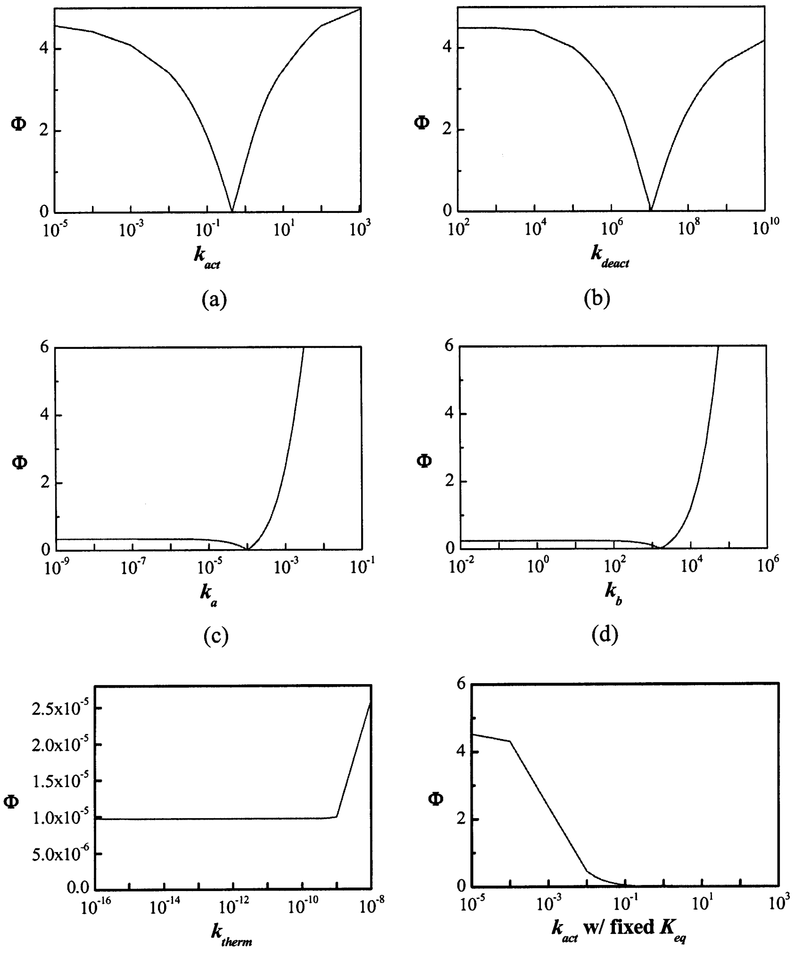
Table 2. Effect of the Initial Guess on the Estimated Parameters

initial guesses					estimated parameters						
k_{act}	k_{deact} ($\times 10^{-7}$)	k_a ($\times 10^4$)	k_b ($\times 10^{-3}$)	k_{therm} ($\times 10^{11}$)	k_{act}	k_{deact} ($\times 10^{-7}$)	k_a ($\times 10^4$)	k_b ($\times 10^{-3}$)	k_{therm} ($\times 10^{11}$)	K_{eq}	Φ
0.5	0.5	0.5	0.5	0.5	0.34	0.82	1.49	0.58	0.01	4.10×10^{-8}	2.76×10^{-2}
1	1	1	1	1	0.91	2.24	1.27	1.02	0.92	4.07×10^{-8}	1.41×10^{-2}
5	5	5	5	5	2.42	8.12	0.00	10.53	5.61	2.98×10^{-8}	8.99×10^{-1}
0.5	1	5	1	0.5	0.72	1.77	1.14	1.32	0.00	4.08×10^{-8}	7.05×10^{-3}
1	5	0.5	5	1	2.22	5.49	0.00	2.88	0.39	4.04×10^{-8}	1.44×10^{-1}
5	0.5	1	0.5	5	0.01	0.02	1.82	0.01	0.00	5.64×10^{-8}	2.65×10^{-1}
			original values		0.45	1.10	1.00	1.63	1.00	4.09×10^{-8}	

other four rate constants fixed at the original values. This is not a true contour map, but it does allow us to get an idea about the sensitivities of each of the rate constants. From Figure 1, we can immediately see that k_{act} and k_{deact} are very sensitive and show a big difference on value of merit function around the original values (Figure 1a,b), k_a and k_b are less sensitive (Figure 1c,d), and k_{therm} is extremely insensitive to the system (Figure 1e). One additional note is that when k_{act} or k_{deact} changes, K_{eq} also changes along with it because the other parameter is fixed at a constant value. In other words, the very sensitive parameter is not k_{act} or k_{deact} itself but the ratio of the two, K_{eq}. Figure 1f is the contour map generated by changing k_{act} with a fixed value of K_{eq}. In this case, the value k_{deact} must also change along with k_{act} in order to have the same value of K_{eq}. With a fixed value of K_{eq}, k_{act} is not so sensitive, and the contour map shows a smooth valley around the original value.

The second explanation as to the failing of this parameter estimation scheme is the possibility of correlation between parameters. If there is a correlation between parameters, then they are not truly independent variables and could not be determined at the same time. Being correlated, the individual values of k_{act} and k_{deact} were at best poorly estimated, but the ratio of them was successfully determined. This bolsters the idea that some correlation between two parameters may exist.

The third possibility is that the system gets trapped within local minimum before reaching the global minimum. We used two different convergent tests on the parameter estimation algorithm. The first test was



(a) (b)

(c) (d)

(e) (f)

Figure 1. One-dimensional contour maps. Φ is the merit function to be minimized during the calculation. (a) Activation rate constant, k_{act}; (b) deactivation rate constant, k_{deact}; (c) rate constant for degradation reaction of the halide chain ends, k_a; (d) rate constant for degradation reaction of the radical chain ends, k_b; (b) thermal initiation rate constant, k_{therm}; and (e) activation rate constant, k_{act}, with fixed equilibrium constant, K_{eq}.

Table 3. Parameter Estimation Using the Algorithm of Sequential Use of MINPACK and DSM

initial guesses					estimated parameters						
k_{act}	k_{deact} ($\times10^{-7}$)	k_a ($\times10^{4}$)	k_b ($\times10^{-3}$)	k_{therm} ($\times10^{11}$)	k_{act}	k_{deact} ($\times10^{-7}$)	k_a ($\times10^{4}$)	k_b ($\times10^{-3}$)	k_{therm} ($\times10^{11}$)	K_{eq}	Φ
1	1	1	1	1	0.44	1.07	1.00	1.63	0.00	4.09×10^{-8}	1.00×10^{-4}
5	5	5	5	5	0.46	1.13	1.00	1.63	0.00	4.09×10^{-8}	8.03×10^{-5}
0.5	1	5	1	0.5	0.46	1.13	1.00	1.63	1.68	4.09×10^{-8}	9.20×10^{-5}
1	5	0.5	5	1	0.46	1.12	1.00	1.63	0.01	4.09×10^{-8}	4.76×10^{-5}
5	0.5	1	0.5	5	0.46	1.12	1.00	1.63	0.05	4.09×10^{-8}	1.04×10^{-4}
			original values		0.45	1.10	1.00	1.63	1.00	4.09×10^{-8}	

Table 4. Effect of Experimental Noise on the Estimated Parameters

σ	k_{act}	k_{deact} ($\times10^{-7}$)	k_a ($\times10^{4}$)	k_b ($\times10^{-3}$)	k_{therm} ($\times10^{11}$)	K_{eq}	Φ
0.02	0.50	1.21	1.11	1.39	0.00	4.12×10^{-8}	1.35×10^{-1}
0.05	0.09	0.21	1.17	1.33	0.78	4.28×10^{-8}	3.37×10^{-1}
original values	0.45	1.10	1.00	1.63	4.80	4.09×10^{-8}	

Table 5. Parameter Estimation Using Less Experimental Data

initial guesses					estimated parameters						
k_{act}	k_{deact} ($\times10^{-7}$)	k_a ($\times10^{4}$)	k_b ($\times10^{-3}$)	k_{therm} ($\times10^{11}$)	k_{act}	k_{deact} ($\times10^{-7}$)	k_a ($\times10^{4}$)	k_b ($\times10^{-3}$)	k_{therm} ($\times10^{11}$)	K_{eq}	Φ
0.5	0.5	0.5	0.5	0.5	0.34	0.82	1.00	1.64	0.00	4.09×10^{-8}	8.25×10^{-5}
1	1	1	1	1	0.86	2.10	1.01	1.60	1.08	4.10×10^{-8}	1.37×10^{-4}
5	5	5	5	5	0.28	0.69	0.99	1.65	0.25	4.09×10^{-8}	1.47×10^{-4}
0.5	1	5	1	0.5	0.64	1.57	1.00	1.61	0.00	4.09×10^{-8}	8.85×10^{-5}
1	5	0.5	5	1	4.12	10.05	1.01	1.59	0.07	4.10×10^{-8}	2.57×10^{-4}
5	0.5	1	0.5	5	12.79	2.29	0.21	0.57	0.00	5.57×10^{-7}	1.20×10^{-1}
			original values		0.45	1.10	1.00	1.63	1.00	4.09×10^{-8}	

designed to check how close the simulated data matched the experimental data, and the second one checked how small the step length in a single cycle is. A very small step length means no practical improvement in convergent values, and further calculation is wasted. If the convergence test meets the first criteria, there is a higher probability of reaching the global minimum. However, convergence on the second test, which was the case for most of our calculation, would indicate a high probability of local trapping.

Finding a global minimum is, in general, a difficult problem. Two standard strategies are widely used: (i) find local minima starting from widely varying starting values of the independent variables (perhaps chosen quasi-randomly) and then pick the most extreme of these (if they are not all the same); or (ii) perturb a local minimum by taking a finite amplitude step away from it and then monitor the response of the routine to see whether it arrives at a better point or "always" return to the same one. At first, we attempted to find global minimum using the second method. However, it was hard to determine the suitable amplitude of perturbation from the local minimum. In the next trial, instead of taking finite amplitude steps away from the values generated from the MINPACK algorithm, we applied a secondary minimization algorithm as a perturbation. The secondary minimization algorithm has to be of a different character from the first MINPACK algorithm, and it does not have to be a particularly accurate minimization algorithm. In our strategy, the accuracy is derived from the first MINPACK algorithm because it is a special minimization algorithm developed for the parameter estimation problem. We used a simple minimization algorithm, the "downhill simplex method (DSM)", as our perturbation source.[36]

Table 3 shows the results of the parameter estimation of ATRP using this new algorithm. From all of the initial guesses used, the algorithm successfully found the original values of the kinetic parameters except k_{therm}.

Table 6. Result of Parameter Estimation Using Literature Data

	k_{act}	k_{deact}	k_b	k_{therm}	K_{eq}
this work	0.58	3.90×10^{6}	6.62	1.93×10^{-9}	1.481×10^{-7}
literature	0.45	1.10×10^{7}	1.00×10^{4}		4.091×10^{-8}

As we have seen before, the k_{therm} has too low of a sensitivity to be estimated even with this new algorithm. With the new algorithm, we were successful in estimating not only K_{eq} but also each value of k_{act} and k_{deact}. The merit functions also had much smaller values than those of the older algorithm that used only the MINPACK package. One thing to be noted is that the termination of the new algorithm was signaled not by how small the merit function becomes, but by how small the step or change of the merit function is. Therefore, the possibility of being trapped in a local minimum was not completely eliminated in the new algorithm.

Effect of Experimental Error. In generating simulated experimental data, we did not include experimental errors. However, real experimental data never result in a perfectly smooth curve, and there is always measurement error incorporated. Therefore, it is worthwhile to check the behavior of parameter estimation approach when the data are affected by experimental errors. The experimental errors can be either or both random, statistical errors and/or systematic errors, such as wrong temperatures, poor fixing of starting time, or the wrong calibration of measurement apparatus. Because systematic errors are not the general case, our concern was limited to statistical errors. We used a Gaussian random number generator with a standard deviation, σ. The parameter estimation results show that as σ is increased, the merit function of best fit is increased, and the estimated values of kinetic parameters deviate from the original values. However, K_{eq} is again successfully converged to the original value for all cases (Table 4). Hence, accurate results require accurate input.

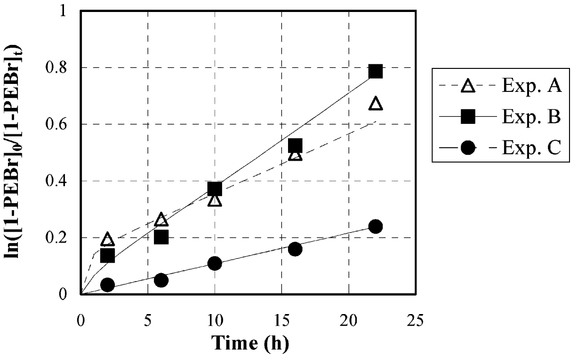


Figure 2. First-order kinetic plot of 1-phenylethyl bromide (1-PEBr) consumption in the ATRA of styrene; experimental data[33] (points) and simulation with estimated kinetic parameters (lines). Experiment A: $[\text{I-PEBr}]_0 = 0.20$ M; $[\text{Mt}^n/\text{L}]_0 = 0.05$ M. Experiment B: $[\text{1-PEBr}]_0 = 0.20$ M; $[\text{Mt}^n/\text{L}]_0 = 0.05$ M; $[\text{X-Mt}^{n+1}/\text{L}]_0 = 0.03$ M. Experiment C: $[\text{I-PEBr}]_0 = 0.20$ M; $[\text{X-Mt}^{n+1}/\text{L}]_0 = 0.03$ M.

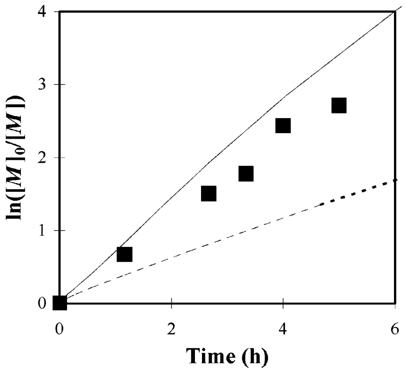


Figure 3. First-order kinetic plot of monomer consumption in the ATRP of styrene; experimental data[17] (points) and simulation (lines; - - -, with the literature values of kinetic parameters (Table 1) and —, with estimated kinetic parameters using our method): $[\text{styrene}]_0 = 8.7$ M; $[\text{1-PEBr}]_0 = 0.087$ M; $[\text{CuBr}]_0 = [\text{dNbpy}]_0/2 = 0.087$ M.

Effect of the Size of the Experimental Data Set. Not only is the success of the parameter estimation highly dependent on the quality of the data, it is also dependent on the size of the data set. It is practically impossible to get concentration profiles of all the components in the model. We chose {IX, M, M_2X, M_2b} as the set of observable variables because we thought that they would be easy to determine by normal analytical methods. In some cases, however, the concentrations of dimeric species, M_2X and M_2b, are still too small to be measured unambiguously by any analytical method. It was thus advisable to check how the accuracy of estimated parameters is affected when there is a limit on the available data. As a check, we used the observable variables {IX, M}, as components constitute the main portion of reaction mixture. Table 5 shows the results of parameter estimation using these two observable variables. It can be seen from the table that the value of K_{eq} converges to the original value for most of initial guesses. Even though it was not as good as before, each of the values of estimated parameters also approach the original values.

Application to Available Literature Data. Before applying the algorithm to the real data, it was first applied to the literature data. Most of the available literature data are on polymerization rather than ATRA reactions. Matyjaszewski et al. tried to determine the chain end degradation rate constants using high initiator concentration.[33] We used these same reaction data to determine the kinetic parameters. Table 6 shows the results of parameter estimation. The calculated values showed some differences from the literature values. However, the values were close to the ones ($k_{act} = 0.45$, $k_{deact} = 5 \times 10^6$) used in simulation that shows excellent agreement with real experimental data.[31] Figure 2 is the plot of simulated data using estimated rate constants. The simulation matches the real experimental data with excellent accuracy. The polymerization results also plotted in Figure 3. The experimental data were taken from the literature.[17] The simulated data using newly estimated rate constants by the parameter estimation algorithm show good agreement with the experimental data.

Determination of Kinetic Constants in ATRP for Various Polymerization Systems. Among the various characterization methods, we used gas chromatography (GC) to measure the observable variables. GC is simple, fast, and highly sensitive characterization method and does not require any pretreatment of the sample such as removal of the metal catalysts. If GC having a mass detector (GC-MS) is used, it is easy to identify each peak. The method development for GC is also relatively simple, and quantitative analysis can be done using internal standard without previous calibration. For the peak identification in the GC spectrum using an FID detector, model compounds were prepared by separate syntheses. We synthesized the dimeric compounds by the atom transfer−propagation reaction (M_2X) and by the combinational termination reaction between initiator radicals (M_2b).

Next we demonstrated the application of the parameter estimation approach to several atom transfer reaction systems. The system includes the atom transfer reactions of styrene and MMA using $\text{FeBr}_2/\text{PnBu}_3$ and $\text{RuCl}_2(\text{PPh}_3)_3/\text{Al(O-}i\text{Pr)}_3$ as catalysts.[37] Table 7 shows the one example of parameter estimations. For all cases of parameter estimation, convergence to the global minima was not achieved from any initial guesses. Instead, by combining the first strategy to find the global minimum, picking the most extreme among the many local minima starting from widely varying initial values of the parameters chosen quasi-randomly, we determined the values of the kinetic parameters ($K_{eq} = 5.40 \times 10^{-8}$). Moreover, in most cases, we could observe some level of convergence to the values of the kinetic

Table 7. Estimation of Kinetic Parameters in the ATRA of Styrene Using FeBr$_2$/PnBu3 Catalyst System

initial guesses				estimated parameters					
k_{act}	k_{deact} ($\times 10^{-7}$)	k_a ($\times 10^4$)	k_b ($\times 10^{-3}$)	k_{act}	k_{deact} ($\times 10^{-7}$)	k_a ($\times 10^4$)	k_b ($\times 10^{-3}$)	K_{eq}	Φ
0.5	0.5	0.5	0.5	3.60×10^{-3}	3.21×10^{-3}	2.76×10^{0}	1.34×10^{-1}	1.12×10^{-7}	2.56
1	1	1	1	3.62×10^{-3}	3.29×10^{-3}	2.68×10^{0}	3.74×10^{-2}	1.10×10^{-7}	2.56
5	5	5	5	3.47×10^{-3}	6.43×10^{-3}	1.04×10^{-3}	1.11×10^{1}	5.40×10^{-8}	2.42
0.5	1	5	1	6.67×10^{-2}	1.53×10^{0}	1.04×10^{1}	2.51×10^{0}	4.37×10^{-9}	3.69
1	5	0.5	5	5.09×10^{-1}	1.41×10^{1}	2.53×10^{-3}	7.45×10^{1}	3.62×10^{-9}	3.57
5	0.5	1	0.5	3.45×10^{-3}	6.46×10^{-3}	1.25×10^{-3}	1.12×10^{1}	5.35×10^{-8}	2.42

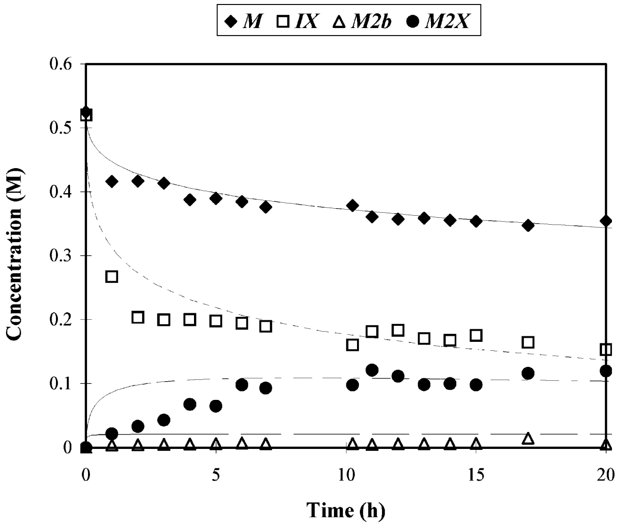


Figure 4. Convolutions of various components over reaction time in the ATRA of styrene in toluene at 110 °C using $FeBr_2/PnBu_3$ catalyst system. Experimental data (points) and simulation with the estimated kinetic parameters (lines): [styrene(M)]$_0$ = 0.52 M; [1-PEBr(IX)]$_0$ = 0.52 M; [$FeBr_2$]$_0$ = [$PnBu_3$]$_0$/3 = 0.05 M.

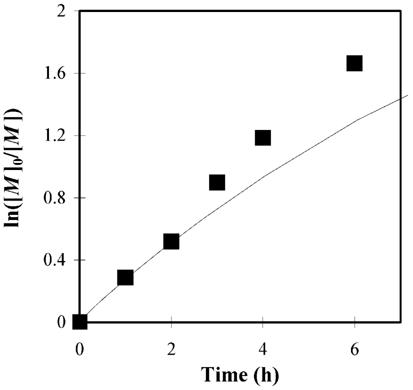


Figure 5. First-order kinetic plot of monomer consumption in the ATRP of styrene at 110 °C using $FeBr_2/PnBu_3$ catalyst. Experimental data[38] (points) and simulation with the estimated rate constants by parameter estimation approach (line): [styrene]$_0$ = 8.7 M; [1-PEBr]$_0$ = 0.043 M; [CuBr]$_0$ = [dNbpy]$_0$/2 = 0.043 M.

parameter at those points. Figure 4 shows the experimental data and the simulations using the estimated kinetic parameters of the convolution of various components over reaction time in the atom transfer reactions of styrene using $FeBr_2/PnBu_3$. The simulation results matched well with the experimental data. Using these estimated kinetic parameters, we also simulated the first-order kinetic plots of monomer conversion as a function of time for the polymerization of styrene using $FeBr_2/PnBu_3$ catalyst and compared with the literature values of the real experimental data (Figure 5).[38] The simulation and the experimental data show excellent agreement, with a deviation at the higher conversion. These results demonstrate that the kinetic rate constants of ATRA or ATRP could be successfully determined by our parameter estimation approaches.

III. Conclusion

In this work, we report a new method to evaluate various catalyst systems by determining kinetic parameters of polymerization. We established the model reactions of ATRP including not only the atom transfer reaction and propagation reaction but also other possible side reactions such as termination reaction, thermal initiation reaction, and chain degradation reactions. On the basis of this model, we used a nonlinear regression method to get the important rate constants from atom transfer radical addition reactions. From the test the parameter estimation algorithm using the fabricated experimental data points that were generated by using literature rate constants, we found that it is possible to estimate the equilibrium constant, K_{eq}, of atom transfer reaction. The simulation results using kinetic rate constants determined by parameter estimation algorithm show fairly good agreement with the experimental data. The small discrepancies could come from our assumption that the rate constants are constant throughout the polymerization, which certainly may not be entirely true.[39] It is expected be improved by using more realistic treatment of diffusion-controlled rate constants. We also demonstrated the determination of kinetic constants in the polymerization of styrene and MMA using various metal catalysts, and the simulations using these kinetic constants agree well with the experimental data.

The model we used was successful in estimating K_{eq}, which is one of the main parameters that govern the characteristics of the ATRP. However, it was difficult to determine each value of k_{act} and k_{deact} separately. The value of k_{deact} is important because it is the ratio of k_{deact}/k_p that influences the polydispersity of the polymer sample. Because the model discriminates only between dimeric species and higher oligomeric species, and the polydispersity or the relative population of chains possessing different lengths was not taken into account, k_{deact} was not well estimated by the algorithm. Therefore, to find a model that gives a successful determination of k_{deact}, it is necessary to include factors describing polydispersity into the model. We are currently developing strategies to describe the polymerization in a much simpler way.

IV. Experimental Section

Materials and Characterizations. Gas chromatography (GC) was performed on either a HP 5890 equipped with MS detector or a HP 6890 with a FID detector, using nonpolar HP-5 or medium polar HP-INNOWAX capillary column for the separation.

Materials were obtained from commercial suppliers and used without further purification, unless otherwise noted. Styrene and methyl methacrylate (MMA) were dried over CaH_2 overnight and distilled twice under reduced pressure from CaH_2 prior to use. 1-Phenylethyl bromide (1-PEBr) and methyl α-bromoisobutyrate (MIB-Br) were purchased from Aldrich Chemical and distilled twice under reduced pressure prior to use. Model compounds such as 2,3-diphenylbutane (St-M_2b),[40] 1-bromo-1,3-diphenylbutane (St-M_2X),[41] dimethyl tetramethylsuccinate (MMA-M_2b),[42] and 2-bromo-2,4,4-trimethylpentanedioic acid dimethyl ester (MMA-M_2X) [43,44] for the peak identification in GC were synthesized following the literature with some modification.

Kinetic Study. To a 25 mL Schlenk flask equipped with a magnetic stir bar was charged with initiator (0.5 M), monomer (0.5 M), metal complexes (0.05 M), decane (0.05 M), diphenyl ether (0.005 M), and solvent (toluene) under an inert atmosphere. After removed from the drybox, the reaction flask was put in an oil bath thermostated at 110 °C. At appropriate time intervals, small aliquots were removed from the reaction mixture and placed in liquid nitrogen to stop the reaction. The quenched THF solution was characterized with GC without further purification. The peaks were identified using model compounds in separate runs. The concentrations of monomer

(M) and initiator (IX) were calculated using decane as an internal standard, and the concentrations of dimeric compounds (M_2b and M_2X) were calculated using diphenyl ether as an internal standard.

Simulations. Computer simulations were carried out using Virtual Fortran 4.0 software. We used LSODE (Livermore Solver for Ordinary Differential Equations) FORTRAN solver in ODEPACK developed by Hindmarsh for ATRA and ATRP simulation.[45] The MINPACK package developed at Argonne National Laboratory was used for parameter estimation with some modifications. Among the choices in the package, we used the "lmdif" solver that handles the nonlinear least-squares problem using internally approximate Jacobian matrix calculated by a forward-difference approximation. In simulation of ATRP and ATRA, diffusion-controlled termination reaction was considered since it generated more realistic results in the literature.[31] Termination rate constants were calculated as $k_t(\mathrm{DP}) = k_t(0)\mathrm{DP}^{-(0.65+0.02\mathrm{DP})}$, where $k_t(0)$ is initial termination rate constant and DP is degree of polymerization, calculated from conversion of monomer to polymer ($\mathrm{DP} = \Delta[\mathrm{M}]/[\mathrm{RX}]_0$) and defining the initiator as the first unit.

Supporting Information Available: Results of parameter estimation and comparison of simulation with experimental data for the ATRA of styrene using the $\mathrm{RuCl_2(PPh_3)_3/Al(O\text{-}}i\mathrm{Pr)_3}$ catalyst system, the ATRA of MMA using the $\mathrm{FeBr_2/PnBu_3}$ catalyst system, and the ATRA of MMA using the $\mathrm{RuCl_2(PPh_3)_3/Al(O\text{-}}i\mathrm{Pr)_3}$ catalyst system. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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MA049627I