

Monomer and Radical Reactivity Ratios in 4-Vinylbenzenesulfonic Acid Sodium Salt–Acrylamide Copolymerization in 0.1M NaCl Solution

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ABSTRACT: Reaction kinetics and composition of 4-vinylbenzenesulfonic acid sodium salt (VB)–acrylamide (Aam) copolymerization in 0.1M NaCl solution are investigated. Data obtained by the automatic continuous monitoring of copolymerization system, up to 80% conversion, are analyzed by an “error-in-variables method” developed for obtaining the reactivity ratios by on-line monitoring. Monomer reactivity ratios are found as $r_{\text{Aam}} = 0.085 \pm 0.020$, $r_{\text{VB}} = 2.0 \pm 0.33$. Although the terminal model describes the composition data well, it is seen to be inconsistent with the reaction rates. This discrepancy is attributed to implicit penultimate effects and using the recently developed calculation method, effective radical reactivity ratios are found as $s_{\text{VB}} = 0.26$ and $s_{\text{Aam}} = 0.027$, and both

composition and rate data fit the implicit penultimate model extremely well. On-line monitored data showed that in the reactions where the VB was completely consumed, the subsequent Aam homopolymerization was very rapid; thus, the reaction showed definitely two rate regimes, before and after VB depletion. Acrylamide take up rate also showed these two rate regimes. We conclude that low conversion results can be misleading and reactions must be monitored up to a high conversion for a robust control of composition and reaction kinetics. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 850–856, 2011

Key words: copolymerization; polyelectrolytes; radical polymerization; water soluble polymers

INTRODUCTION

Poly (vinylbenzenesulfonic acid sodium salt) (VB) has many applications ranging from large-scale industrial uses in emulsions, slurries, binders, and flocculants to applications in biotechnology and medicine.^{1–7} Applications originate from its polyelectrolytic nature. Because of counter ion condensation, the charge density on a polymer chain cannot exceed one charged unit per Bjerrum length. Properly prepared copolymers of polyelectrolytes provide the same electrolytic properties as the homopolyelectrolyte, and VB is often used in the form of copolymer with nonionic monomers like acrylamide.

Under quasi steady state conditions and when the penultimate effects are not important, the copolymerization is governed by eq. (1).⁸

$$\frac{d[a]}{d[b]} = \frac{[a]}{[b]} \left(\frac{r_a[a] + [b]}{[a] + r_b[b]} \right) \quad (1)$$

Here [a] and [b] are the molar concentrations of the

monomers, $r_a = k_{aa}/k_{ab}$ and $r_b = k_{bb}/k_{ba}$ are the monomer reactivity ratios (MRRs) and the k s are the rate constants for the relevant propagation reactions. The first index denotes the terminal unit of the macro radical, and the second index denotes the monomer added. The composition and properties of copolymers depend not only on the feed composition but also on the reactivities of individual monomers. Many methods have been developed to determine these ratios. Modern methods, known as “error-in-variables methods” (EVMs), take the variations of all measured quantities into account while estimating them.^{9–11}

In many copolymerization systems, eq. (1) cannot describe the composition of the resulting copolymer. In these systems, the selectivities of the radicals depend not only on the terminal unit of the chain radical but also on its penultimate unit. Four MRRs are needed to describe the evolution of the copolymer composition. The dependence of the MRRs on the penultimate unit of the chain is known as the “explicit penultimate effect.” It was noted that for many systems, while the terminal model adequately describes the copolymer composition, the reaction rate predicted by this model does not agree with the experimental results.^{12–15}

According to the terminal model, copolymerization rate is given by eq. (2a).¹⁶

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$$-\frac{d[m]}{dt} = \frac{(r_a X + 1)X + (X + r_b)}{(X + 1)(r_a X/k_{aa} + r_b/k_{bb})} [M^*][m] \quad (2a)$$

In this equation, X is the ratio of concentrations of the two monomer species ($X = [a]/[b]$), $[m]$ is the total monomer concentration ($[m] = [a] + [b]$), and $[M^*]$ is the total concentration of chain radicals ($[M^*] = [A^*] + [B^*]$), where A^* and B^* are macroradicals with a and b monomers as their terminal units. Note that k_{aa} and k_{bb} are the homopolymerization rate constants for the monomers a and b ;

$$-\frac{d[a]}{dt} = k_{aa}[A^*][a] \quad (2b)$$

$$-\frac{d[b]}{dt} = k_{bb}[B^*][b] \quad (2c)$$

As the terminal model is concerned with the propagation step, it would seem natural to account for the discrepancy by variation of the termination rate constant. However, Fukuda has noted that as the termination step is diffusion controlled, the termination rate constant for the copolymer is expected to lie between those of the two homopolymers. Fukuda et al.¹⁷ attributed this behavior to kinetic effects of the penultimate unit and named it "implicit penultimate effect" (IPE). They proposed the implicit penultimate model, where the penultimate unit has no effect on the selectivity of the radical, but it influences its stability. Thus, it has no effect on the composition of the copolymer but influences the reaction rate. The theoretical and experimental evidence for IPE are detailed in review articles of Fukuda et al.¹⁸ and Coote and Davis.¹⁹ In the implicit penultimate model, in addition to the MRRs, there are two ratios, $s_a = k_{aaa}/k_{baa}$ and $s_b = k_{bbb}/k_{abb}$, known as the radical reactivity ratios (RRRs), which influence the reaction rate. Here, the first index denotes the penultimate unit, the second index denotes the terminal unit of the chain, and the third index denotes the monomer. The RRRs are determined by intermittent polymerization methods such as the rotating sector method. Currently, the best method for determining them is the pulse laser polymerization technique.²⁰⁻²² With IPE, the reaction rate is

$$-\frac{d[m]}{dt} = \frac{k_{aa}}{r_a} \frac{(r_a X + 1)((r_a X + 1)X + (X + r_b))}{(X + 1)(r_a X^2 + (1/s_a + Z/s_b)X + r_b Z)} [M^*][m], \quad (3)$$

where X , $[m]$, and $[M^*]$ are as defined above and $Y = (r_a X + 1)/(X + r_b)$ and $Z = (k_{aaa} r_b/k_{bbb} r_a) Y$. The IPE model reduces to the terminal model if $s_a = s_b = 1$.

Most of the above mentioned work is performed at low conversions, and the theoretical models are verified by low conversion experiments. On the other hand, industrial applications require high efficiency and high conversions. As conversion increases, the working conditions vary: viscosity increases, feed composition drifts, and due to the exothermic nature of polymerization, the temperature may increase. For these reasons reactions must be monitored up to high conversion for reliable data. Note that monitoring is not equivalent to high conversion data but yields the evolution of the concentrations throughout the experiment.

The "automatic continuous monitoring of polymerization" (ACOMP) technique allows composition and rate data to be harvested continuously during the reaction. Various copolymerizations including styrene-methyl methacrylate,²³ acrylamide-acrylic acid,²⁴ and VB-acrylamide^{25,26} were monitored by this technique.

Other recent methods for monitoring copolymerization reactions and obtaining the reactivity ratios from on-line data are the spectroscopic methods.²⁷⁻²⁹ On-line ¹H NMR spectroscopy has also been used to calculate MRRs.³⁰⁻³³ An on-line method was developed for terpolymerization.³⁴ In on-line techniques, large amount of data are obtained for each experiment resulting in more accurate determination of reaction parameters. On-line techniques give not only the composition data but also the time rate of monomer consumption. Only a few reactions are sufficient to obtain the MRRs.

Sünbül et al.³⁵ have developed an EVM based method to calculate the MRRs from on-line monitored data. They have also proposed a calculation method to estimate the effective RRRs from the same data.³⁶ Total monomer concentration $[m]$ versus time data obtained during the whole reaction are fitted to the eq. (3). The MRRs obtained from eq. (1) and the homopolymerization rates from eqs. (2b) and (2c) are used to estimate the effective RRRs by scanning the s_a and s_b parameter space to find the best fit values. Although the method gives effective RRR values, where the influence of the variation of the termination rate constant is not separated from the variation of the propagation rate constant, these estimates are useful for many practical applications. Parameters representing the average values for the whole process are usually more useful than the values obtained at low conversion. Availability of parameters that can predict the composition and the rate in copolymerization is essential to industry. In previous work on VB-Aam copolymerization, kinetics in water,²⁶ polyelectrolytic properties, conductivity, and molar mass of VB-Aam copolymers in water and in 0.1M NaCl solution²⁵ were investigated. However, those studies did not include kinetics of VB-Aam copolymerization in saline solution.

TABLE I
Reactor Conditions for VB–Aam Copolymerization in 0.1M NaCl Solution

Experiment No.	% VB	c_{VB} (mol/L)	c_{Aam} (mol/L)	c_{Total} (mol/L)	V50 (mol/L)	pH _{initial}	pH _{initiator}	pH _{final}
1	100	0.3636	0	0.3636	2e-3	9.41	8.45	7.82
2	75	0.2727	0.0909	0.3636	2e-3	10.3	9.21	8.93
3	50	0.1808	0.1818	0.3626	2e-3	9.34	8.57	8.03
4	25	0.0909	0.2727	0.3636	2e-3	9.26	8.27	8.08
5	10	0.0364	0.3272	0.3636	2e-3	8.72	7.67	7.90
6 ^a	0	0	0.3636	0.3636	2e-3	8.86	7.96	8.18

^a In the Experiment 6, medium pH was set to the level of other experiments by adding NaOH.

In this work, the composition and kinetics of VB–Aam copolymerization in 0.1M NaCl solution are investigated. In 0.1M NaCl solution, polyelectrolytic effects are suppressed and reactions have followed completely different regimes from those performed in water. The MRRs are obtained by EVM using the [VB] *versus* [Aam] data. Even though the terminal model satisfies the composition data, rate data show a very interesting behavior that definitely shows the existence of the IPE. The effective RRRs are estimated from the monomer concentration *versus* time data using Sünbül's method.³⁶

EXPERIMENTAL

VB–Aam copolymerizations were initiated with 2,2'-Azobis(2-amidinopropane) dihydrochloride (V50) at 60°C. All chemicals were from Aldrich and used as received. The copolymerizations were monitored

with ACOMP. The system and the experimental details are described in Ref. 25.

In these experiments, 0.1M NaCl solution was used as both the system solvent and the carrier solvent. During the experiments, a continuous stream was withdrawn from the reactor and was diluted approximately 100-fold by the carrier solvent before passing through the detectors. The concentrations in the figures refer to the diluted sample stream in the detector train. The amounts of monomers and initiator are given in Table I. The table also shows the pH values of the system before initiator addition (pH_{initial}), after initiator addition (pH_{initiator}), and at the end of the reaction (pH_{final}).

RESULTS AND DISCUSSION

The VB fraction in the monomer mixture, f_{VB} , is shown in Figure 1(a), as a function of total conversion.

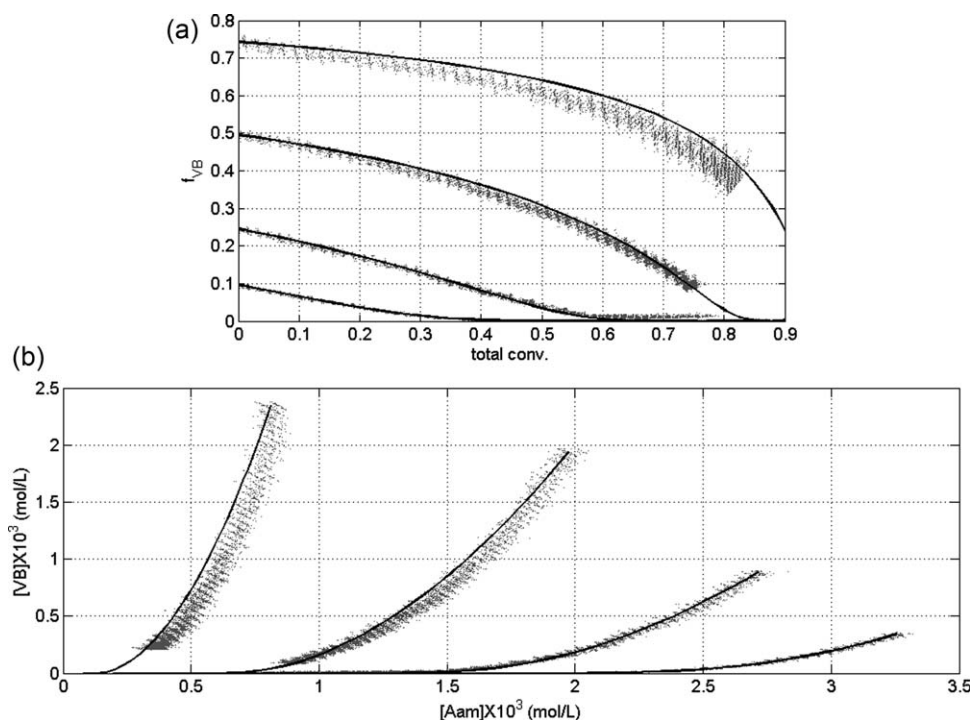


Figure 1 (a) VB fraction in remaining monomer, f_{VB} , *versus* total conversion. The data (top to bottom) are 75, 50, 25, and 10% VB experiments. (b) VB concentration *versus* Aam concentration. The data (left to right) are 75, 50, 25, and 10% VB experiments. The concentrations (mol/L) refer to the values in the detector train.

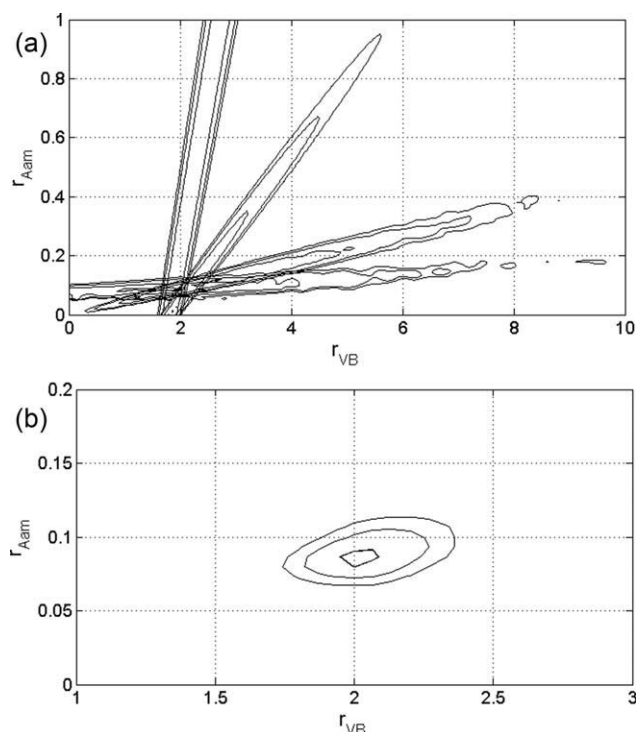


Figure 2 (a) Confidence contours for MRRs for individual experiments. (b) Combined confidence contours for MRRs for all copolymerization experiments.

It is decreasing monotonically in all experiments and there is no azeotropic point. This result, without any calculation, indicates that $r_{VB} > 1 > r_{Aam}$. The VB concentration *versus* Aam concentration data, shown in Figure 1(b), is fitted to a numerical solution of the copolymerization eq. (1) to generate the confidence contours of the individual experiments in Figure 2(a) and the combined results of all copolymerization experiments in Figure 2(b). The MRRs are found as $r_{Aam} = 0.085 \pm 0.020$ and $r_{VB} = 2.0 \pm 0.33$. In Figure 1(a,b), the continuous lines are the predictions of the terminal model. It is known that the MRRs of charged units depend on reaction conditions such as pH and ionic strength (IS), and these conditions differ not only among reactions with different initial compositions but also during individual reactions, due to such effects as counterion condensation. Small deviations between experimental data and theoretical solid line can be attributed to variations of experimental conditions. Considering these effects, the terminal model gives a very good description of the polymer composition.

The reactivity ratios of the VB–Aam system were also studied by Gao et al.³⁷ They found $r_{VB} = 0.27$ and $r_{Aam} = 2.21$. However, they did not quote the pH values, salt concentrations, and conversion in their experiments. As Rintoul and Wandrey^{38,39} have shown, the reactivity ratios and even which monomer is more reactive depend strongly on the pH of the medium in copolymerizations involving one

ionic and one nonionic species. The MRRs also depend on the total IS of the medium and whether the polymer concentration is above or below c_p^* in experimental conditions,²⁶ where the overlap concentration, $c_p^* = 1/R_G^3$, corresponds to one polymer coil in a volume equal to the cube of the radius of gyration.⁴⁰ For this reason, results cannot be compared with each other unless the studies are performed under same conditions.

Figure 3 shows the evolution of total conversion with time. Aam homopolymerization is faster than VB, and both homopolymerization rates are higher than copolymerization rates at any combination. Figure 4 is the logarithmic plot of remaining monomer concentration *versus* time for the copolymerization experiments (Experiments 2–5). The average values of the effective rate constant k_{eff} calculated from the slopes, for every 5000 s of the reaction are plotted in Figure 5. As seen from Figure 5, the effective rate constant for 75% VB reaction decreases exponentially with time. This is due to the reduction of the initiator concentration, which was found to have a life time of ~ 2500 s in the reaction conditions. A similar decrease in the reaction rate is seen in the first 5000 s of the 50 and 25% VB reactions; however in the 50% case, the rate of decrease moderates in the later part of the reaction. In the 25% VB case, the rate of decrease is actually reversed and the reaction is faster in the last 5000 s. A similar speeding up occurs in the 10% VB reaction, but in this case the acceleration occurs after 5000 s. In all the cases, the acceleration corresponds to complete depletion of the VB. The subsequent reaction is Aam homopolymerization and is much faster. In the 50% VB experiment, the VB is not completely depleted and the moderation of the rate of decrease seen in this

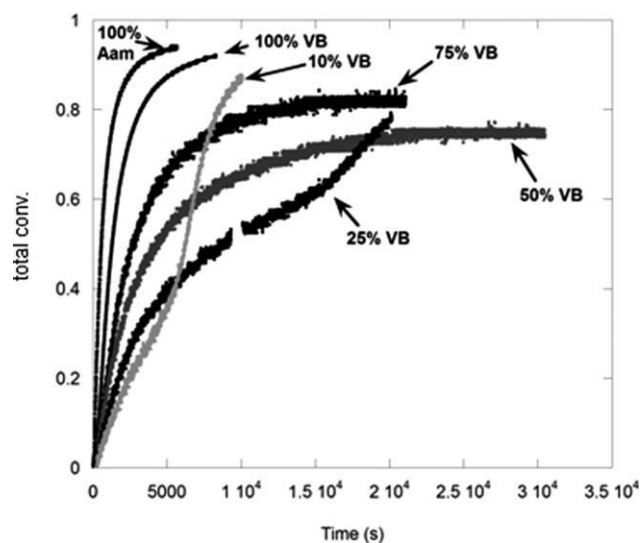


Figure 3 Conversion *versus* time plots for all experiments.

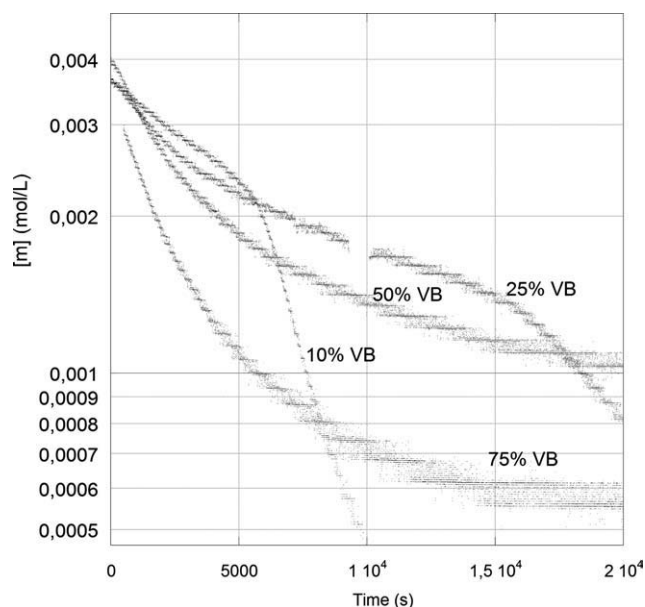


Figure 4 Logarithmic plot of remaining monomer concentration *versus* time for the copolymerization experiments (Experiments 2–5). The concentrations refer to the values in the detector train.

experiment is due to the early stages of this effect. As seen from eq. (3), when the VB fraction is close to zero or one, that is, the feed composition is almost purely a single monomer, the IPE has no impact on the rate. Thus, complete depletion of the more reactive monomer (in this case the VB) results in the IPE being turned off.

These kinetic results cannot be understood on the basis of terminal model kinetics. The absence of analogous rate increases in the 50 and 75% VB reactions (Experiment 2 and 3), and the coincidence of

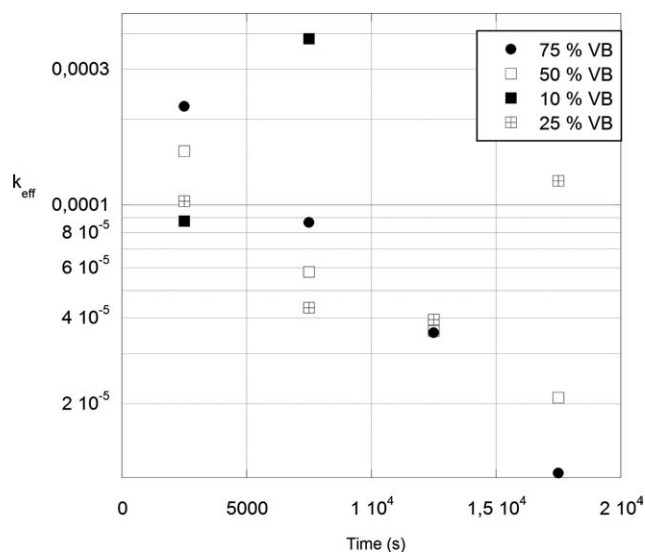


Figure 5 The average value of the effective rate constant k_{eff} , calculated from the slopes in Figure 4, for every 5000 s of the reaction.

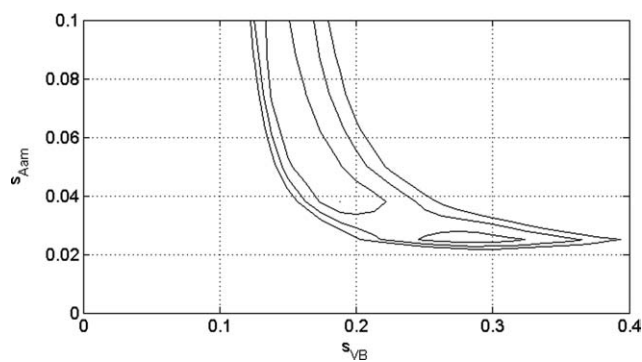


Figure 6 The map of χ^2 as a function of the fit parameters, the best fit values are $s_{\text{VB}} = 0.26$ and $s_{\text{Aam}} = 0.027$.

the onset of the acceleration with the depletion of VB indicate that this effect is due to the existence of IPE with small effective RRRs.

To estimate the effective RRRs, total monomer concentration [m] *versus* time data are fitted to the eq. (3) using the method of Sünbül et al.³⁶ The $k_{\text{aaa}}[\text{A}^*]$ and $k_{\text{bbb}}[\text{B}^*]$ values obtained from the 100% Aam and 100% VB curves in the Figure 3 and $r_{\text{Aam}} = 0.085$ and $r_{\text{VB}} = 2.0$ obtained by EVM are used to find the effective RRRs. The composition drift and the decrease of the initiator concentration during the reactions are taken into account in the numerical integrations because the reaction periods are longer than the initiator lifetime. The χ^2 value is obtained by comparing numerical results with on-line data. This procedure is repeated with all values of s_a and s_b within the scanning range. A map of χ^2 as a function of the two fit parameters is generated and the best fit values shown in Figure 6 are $s_{\text{VB}} = 0.26$ (+0.09–0.16) and $s_{\text{Aam}} = 0.027$ (+0.09–0.006). Plotting the χ^2 contours as a function of ss rather than the $(1/s)$ distorts the figure and results in the so-called “banana plot.” For this reason, the error intervals are not symmetric.

Figure 7(a–c) shows the evolution of monomer concentration with time and the predictions of the terminal model and the IPE model with $s_{\text{VB}} = 0.26$ and $s_{\text{Aam}} = 0.027$ for the 75, 50 and 25% VB experiments. The terminal model (lower curves in each figure) clearly fails to satisfy the data. On the other hand, the IPE model fits the results almost perfectly. Figure 7(d) shows the evolution of monomer concentration for the 10% VB experiment and theoretical results with $s_{\text{VB}} = 0.26$ and $s_{\text{Aam}} = 0.020$. The pH in this experiment was lower than the other experiments varying between 7.67 and 7.90. The IS was also the lowest. These factors may be the cause of the lower value of s_{Aam} that fits this experiment.

The residual plots of the 25% VB experiment for the terminal and IPE models are given in Figure 8(a,b), respectively.⁴¹ It is seen that with the terminal model the residuals are an order of magnitude

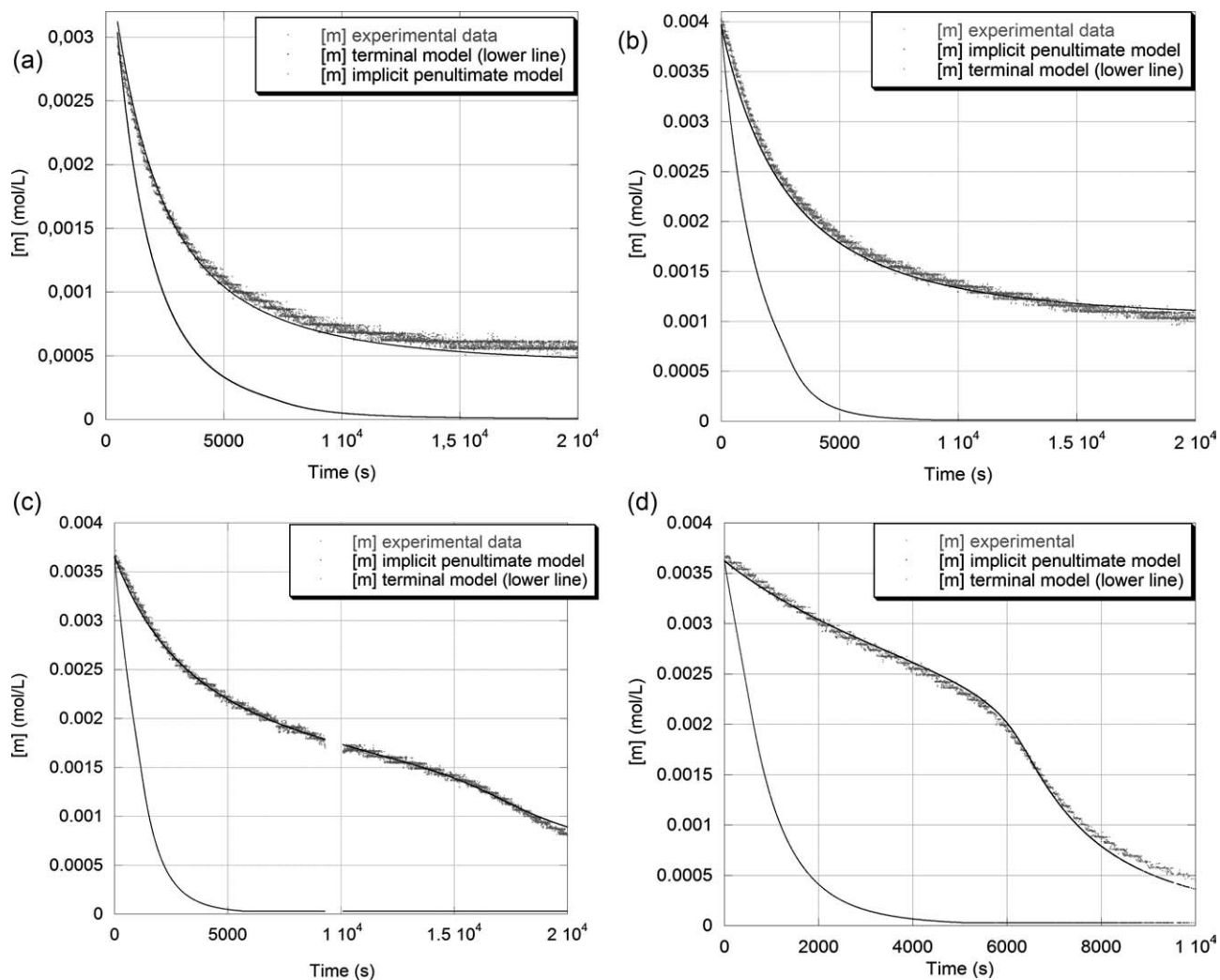


Figure 7 Experimental data and predictions of the terminal and implicit penultimate models for the 75% (a), 50% (b), 25% (c), and 10% (d) VB experiment.

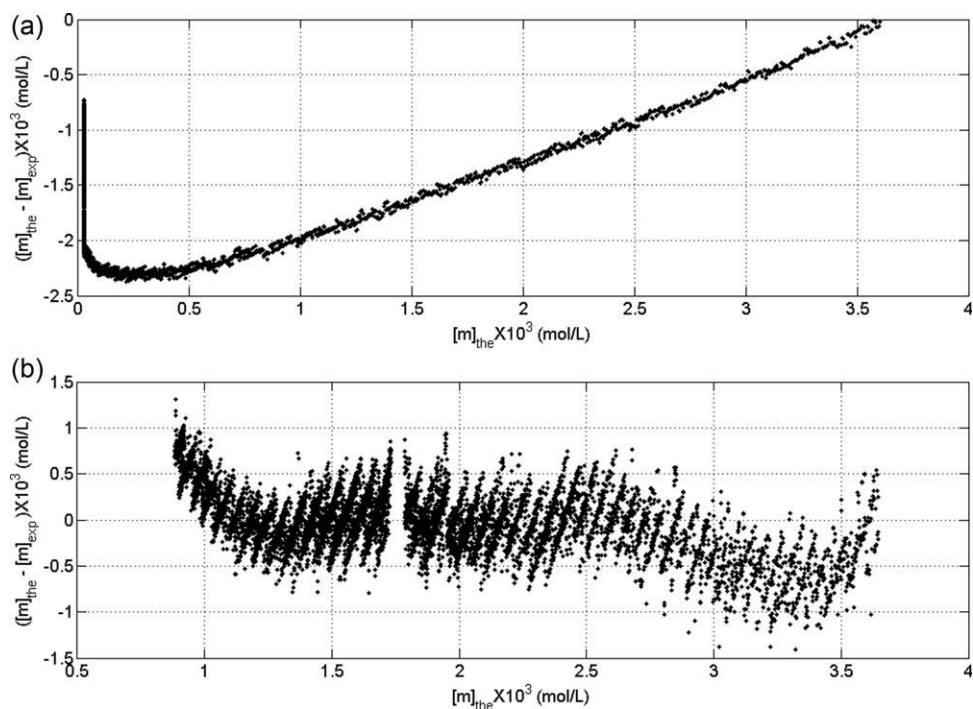


Figure 8 The residual plot of the 25% VB experiment for the terminal model (a) and IPE model (b).

larger than the values predicted by the model. With the IPE model, the residuals are comparable to the scatter. Even in this model, there is a slight deviation during the first and last 10% of the reaction. This is probably due to changes in pH and IS during the reaction. It is well known that pH of the medium affects the MRRs.^{38,39} Although the pH was kept nearly constant during the reactions, Table I shows that small changes occurred. The repulsion between charged coils and charged monomers is screened by the ions in the medium. Because the IS decreases as the ionic monomer is consumed, the reaction kinetics are also affected by the inevitable change in the IS.

CONCLUSION

High conversion reactions are essential especially for copolyelectrolyte production. Continuous on-line monitoring of the copolymerization reactions is a very powerful technique for understanding reaction kinetics and product composition. Here on-line data was used not only to obtain the MRRs, r_a , and r_b but also to determine that IPEs play a role and to estimate the effective RRRs, s_a , and s_b as well. It is seen that the calculated parameters described the reaction course accurately.

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