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Online Monitoring of 4-Vinylbenzene sulfonic acid Sodium Salt – Acrylamide Copolymerization in Water

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Summary: 4-Vinylbenzene sulfonic acid sodium salt (VB) – Acrylamide (Aam) homopolymerization and copolymerization reactions with various feed ratios were performed in water at 60 °C. All reactions were monitored online, by an Automatic Continuous Online Monitoring of Polymerization (ACOMP) system. The concentrations of the two comonomers in their monomeric form, as well as their concentrations incorporated into polymer, were obtained from the monitored data. It was seen that Aam homopolymerization was faster than VB and both homopolymerization rates were higher than copolymerization rates at any combination. In the reactions with 1.5%, 5% and 10% (mol) VB, VB was completely depleted and further reaction was Aam homopolymerization. In the copolymerizations with 5 to 50% initial VB content, the plots of VB fraction in the remaining monomer mixture versus conversion exhibited a corner at 10–30% conversion. This corner showed that the behavior of the reaction changed abruptly at this point. In the first stage of the reactions, the composition was seen to be almost constant with almost no composition drift whereas in the second part, the VB fraction decreased monotonically. Monomer reactivity ratios (MRR) were calculated by error in variables (EVM) method. Since the reactions gave two distinguishable regions, the reaction part before and after the corner were evaluated separately. Therefore, the monomer reactivity ratios were found as $r_{Aam} = 0.34 \pm 0.07$, $r_{VB} = 0.40 \pm 0.21$ for the part before and $r_{Aam} = 0.2 \pm 0.04$, $r_{VB} = 9.0 \pm 0.8$ for the part after the corner.

Keywords: copolymerization; online monitoring; polyelectrolytes; reactivity ratio; water soluble polymers

Introduction

The field of applications of VB polymers has rapidly grown in recent years and reached large-scale industrial uses due to its micelle forming properties in emulsions and slurries, binders and flocculants. It is used in biotechnology and medicine to take advantage of complex formation properties with proteins, microencapsulation of biological objects, formation of polyelectrolyte multilayers, and the formation of DNA complexes in gene therapy.[1–9]

Because of counterion condensation there is no advantage in using charge densities beyond one charged unit per Bjerrum length. For this reason, copolymers of VB with an uncharged monomer like Aam are commonly used instead of homopolyelectrolytes.

Continuous monitoring of copolyelectrolyte formation is vital in elucidating copolyelectrolyte behavior. Recently, Florenzano and coworkers have developed an online technique called automatic continuous monitoring of polymerization (ACOMP). This technique has been applied to study radical chain polymerization of vinyl pyrrolidinone[10] and acrylamide,[11] urethane

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formation and many other homopolymerization systems.[12–18]

Copolymerization of styrene with methyl methacrylate and Aam with acrylic acid were monitored and the reaction parameters were obtained from online data.[19–20] ACOMP technique allows data to be obtained continuously during the reaction. In on-line techniques a large amount of data are obtained for each experiment resulting in more accurate determination of reaction parameters.

The composition and properties of the resulting copolymer depends not only on the feed composition but also on the reactivities of individual monomers. When the penultimate effects are not important and under quasi steady state (QSS) conditions, the copolymerization is governed by the well-known Mayo-Lewis equation.[21]

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

where [a] and [b] are the molar concentrations of the two monomers, $r_a = k_{aa}/k_{ab}$ and $r_b = k_{bb}/k_{ba}$ are the monomer reactivity ratios (MRR). The k's are the rate constants for the relevant reactions. Many linear[22,23] and nonlinear[24–37] methods have been developed to obtain these reactivity ratios. Most of the modern methods, known as error in variables methods (EVM)[33–37] take the variations in all measured quantities into account in estimating the reactivity ratios. In this work VB - Aam copolymerization is studied by the ACOMP method. The data are analyzed by EVM and the MRRs are obtained from the evolution of monomer concentrations.

Experimental Part

Aam and VB were obtained from Fluka. Copolymerizations were initiated in aqueous solution at 60 °C, with 2,2′-Azobis(2-amidinopropane)dihydrochloride (V50, Fluka). The copolymerizations were monitored with ACOMP. Figure 1 shows raw ACOMP data for the copolymerization reaction W2 in Table 1, where each step is indicated; baseline stabilization period, baseline of pure monomer, point of initiator addition, and the polymerization period.

The UV signals increase during the pure monomer flow period, whereas the LS and viscosity scarcely change. During the poly-

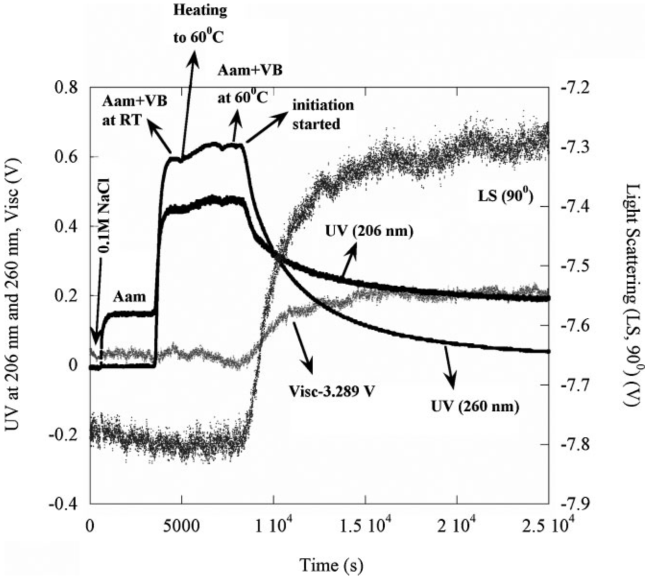

Figure 1.
Raw ACOMP signals for W2 experiment.

Table 1.
VB – Aam copolymerization in water.

Exp. No.	%VB (mol)	C_{VB} (mol/L)	C_{Aam} (mol/L)	C_{Total} (mol/L)	initiator V50 (mol/L)	$pH_{initial}$ - $pH_{aft\ init.\ addition}$ -pH_{final}
W 1	100	0.1818	0	0.1818	3.8e-3	9.02 - 8.07 - 7.86
W 2	50	0.1818	0.1818	0.3636	2e-3	9.68 - 8.50 - 7.89
W 3	25	0.09088	0.2727	0.3636	2e-3	9.21 - 8.44 - 7.97
W 4	15	0.055	0.3091	0.3640	2e-3	8.73 - 7.57 - 7.57
W 5	10	0.03640	0.3272	0.3636	2e-3	8.57 - 7.38 - 7.95
W 6	5	0.01821	0.3453	0.3636	2e-3	7.71 - 6.81 - 8.21
W 7	1.5	0.00546	0.3582	0.3636	2e-3	5.91 - 5.14 - 6.61
W 8	0	0	0.1818	0.1818	2e-3	6.30 - 5.91 - 6.33

merization reaction the loss of the double bonds of each comonomer as it incorporates into polymer leads to (differentially) decreasing UV absorption, while the viscosity and LS signals increase with increasing polymer concentration. The ACOMP technique itself and its application to VB-Aam system have been adequately described.[38] 0.1M NaCl was used as the carrier solvent. The amounts used, pH's measured at the beginning of the experiment, after the initiator addition and at the end of reaction are given in Table 1.

Results and Discussion

Figure 2 shows the total conversion versus time data for all reactions. In all cases Aam homopolymerization is faster than VB, and both homopolymerization rates are higher than copolymerization rates at any combination.

Figure 3 shows the evolution of instantaneous VB fraction in the monomer mixture. In the later parts of the reactions, VB enters the copolymer more readily than Aam does and it is depleted faster.

In the reactions W5, W6, W7 (Table 1) where VB is completely consumed further reaction is Aam homopolymerization. As Aam homopolymerization is faster than the copolymerization rate, the reaction rate increases after this point as in Figure 2. This acceleration is a consequence of the reaction becoming homopolymerization due to complete depletion of the VB monomer.

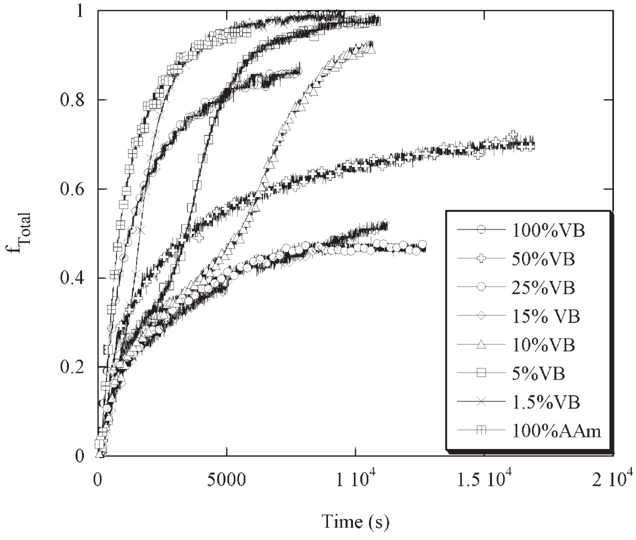

Figure 2.
Conversion versus time plots for VB-Aam copolymerization.

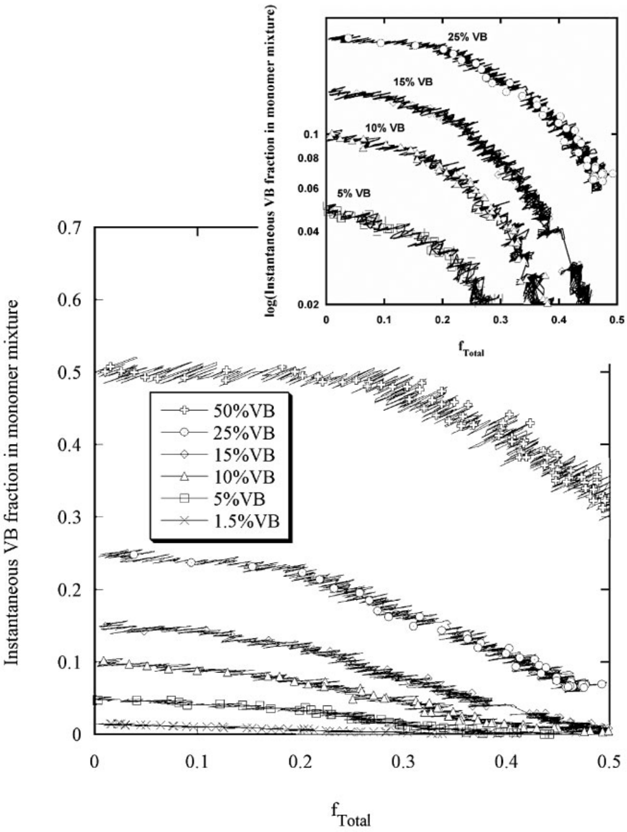

Figure 3.
Instantaneous VB fraction versus total conversion.

During the copolymerizations with 5 to 50% VB, VB fraction in each monomer mixture versus conversion curve went through a "corner" at 10–30% conversion depending on the VB content as seen in Figure 3 and its inset. This corner indicates that the behavior of the reaction changes abruptly at this point. This sudden change in the reaction kinetics and the monomer reactivities is probably due to reaching the c^* overlap concentration. Beyond this point the whole reaction vessel is within the coils of the polymers already formed so that the electrostatic repulsion between the macro radical and the charged VB monomer is suppressed. The reactivity of VB increases substantially after the corner.

For nonelectrolytic monomers the reactivity ratios are almost independent of solvent characteristics. However the reactivity ratios of charged monomers depend strongly on the pH and less strongly on the total ionic strength of the solution.[20,39,40] In general, the reactivity of a monomer decreases as it becomes ionized. This behavior can be understood as a result of the electrostatic repulsion between the ionic monomer and the charged polymer coil. Because of the charge on the polyion the concentration of coions (monomeric ions) in and around it are diminished and the concentration of the counterions is enhanced. Uncharged species, including the uncharged monomers are not affected. The situation is analogous to heterogeneous polymerization, where the overall monomer concentration and the concentration at the locus of polymerization can differ.[41–44]

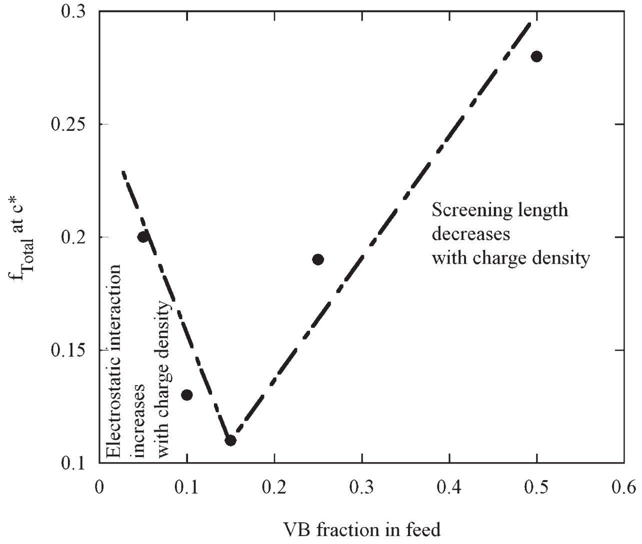

Figure 4.
The conversion at overlap concentration versus VB mol fraction in feed.

Here this effect is probably seen in the first part of the experiment before the corner. If, as surmised above, the corner corresponds to overlap concentration, then the reaction after the corner proceeds essentially completely within the coils and the electrostatic effect decreases. In this stage the local and global concentrations are equal.

Figure 4 shows the conversion at this critical point as a function of VB fraction in the feed. The corner occurred approximately at 11% conversion in the 15% VB experiment. In experiments both at lower and higher VB concentrations it occurred at higher conversions. We can surmise that the coil volume is maximal at this point. Coil

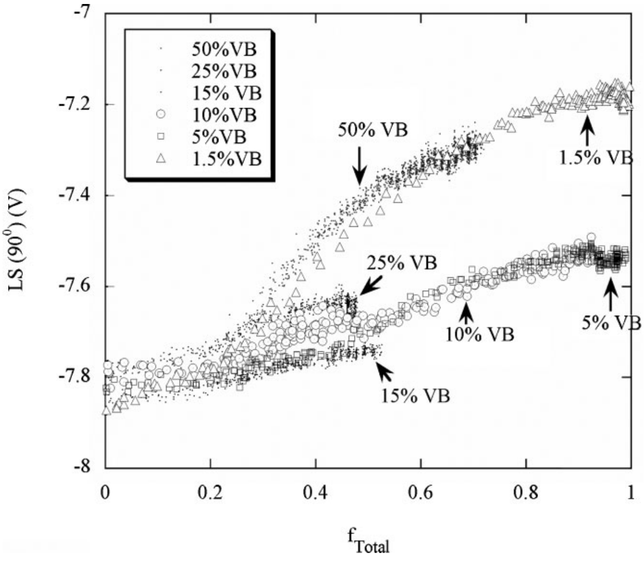

Figure 5.
Raw Light Scattering (90°) data for the experiments.

volume of a polymer depends on its molecular weight and persistence length (PL).

As the molecular weights of these copolymers are similar up to 30% conversion, as seen in the light scattering data in Figure 5, this effect probably originates from differences in PL. PL is a function of Debye screening length and the strength of electrostatic interactions. Figure 4 indicates that the PL is maximum at 15% VB fraction. At higher IS the reduction of the Debye screening length with increasing IS is the dominant effect. Further increase in VB fraction reduces the coil volume. As a

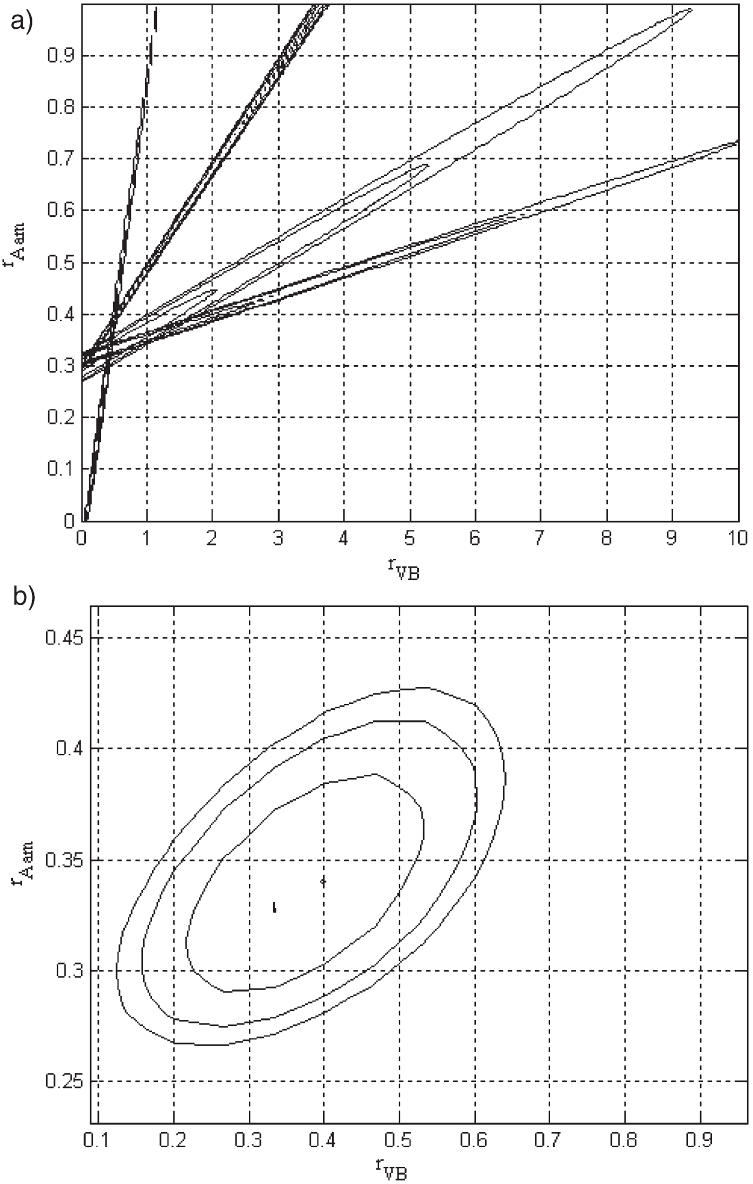

Figure 6.

a. The 1 2 and 3 sigma confidence contours for the MRR for individual experiments. (Early part of the reaction.)

b. The confidence contours for the combined results of experiments. (Early part of the reaction).

result maximum hydrodynamic volume is obtained at 15% VB fraction in our experimental conditions.

Reactivity Ratios

As noted above, the reactions gave two distinguishable regions and the reaction parts before and after the corner were evaluated separately.

In the first phase of the reactions, the composition is almost constant. The valleys in Figures 6a and b show the results before the corner. Figure 6a shows the 1, 2 and 3 σ confidence regions for the individual experiments. The figure is, in effect a Mayo

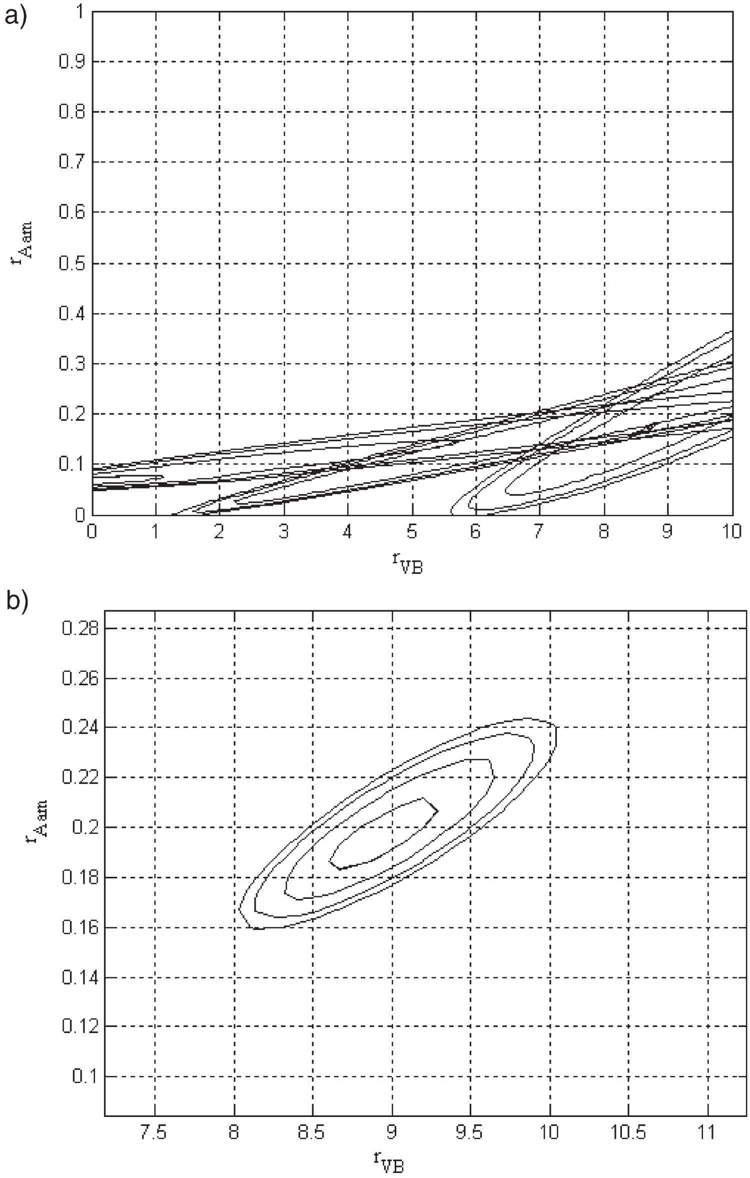

Figure 7.
a. The 1 2 and 3 sigma confidence contours for the MRR for individual experiments. (Late part of the reaction.)
b. The confidence contours for the combined results. (Late part of the reaction).

plot for the online experiment. The lines given by single data points in the Mayo plot are replaced with long ellipsoids given by the several hundred points obtained from each experiment. As the feed composition is slowly evolving these points give the results for the instantaneous polymerization at a given conversion. These ellipsoids do not intersect at exactly the same point. This is because, one of the experimental conditions, namely the ionic strength which depends on the VB concentration is not the same in each experiment, in fact, it changes with conversion, during the experiment itself. For this reason the combined confidence region given in Figure 6b represents the cumulative average over the conditions valid during the early parts of the experiments. The reactivity ratios are found as $r_{Aam} = 0.34 \pm 0.07$, $r_{VB} = 0.40 \pm 0.21$. After the corner, the nature of the reaction changes and the VB fraction starts to drop rapidly with further conversion, indicating a sudden increase in VB reactivity. The reactivity ratios calculated using the data after the corner (shown in Figures 7a and b) gave $r_{Aam} = 0.2 \pm 0.04$, $r_{VB} = 9.0 \pm 0.8$. For the analysis of this part only the experiments with 15-50% VB were used. In the experiments with 1.5–10% VB it is completely consumed and the reaction subsequently proceeds as Aam homopolymerization.

Conclusion

Continuous online monitoring of the copolymerization reactions is a very powerful technique for investigating reaction kinetics. The online data can be used to obtain the reactivity ratios, r_a and r_b. It also provides an insight to understand the changes in the reaction kinetics due to the changing conditions that occur during the reaction as well.

When performing a copolymerization involving a charged comonomer in water one can have unexpected results because the reaction conditions are extremely variable. Here the reactivity ratios obtained from the early part of the experiment would not predict the complete consumption of VB and formation of a VB-Aam copolymer and Aam homopolymer mixture for the 5 and 10% VB experiments. For this reason continuous monitoring of copolymerizations involving a charged monomer is very important.

The reactions changed character midway through the reaction. The salient feature of the set of experiments conducted in water is a sudden change in reaction kinetics, which appears as a corner in the composition versus conversion data. The sudden change in the reaction kinetics in water is probably due to reaching the c^* (overlap) concentration so that further reaction takes place within the coils.

We have obtained indirect evidence that, the maximally expanded copolymer has the composition 15% VB - 85% Aam. Higher VB fractions reduce the Debye screening length because of higher ionic strength and result in reduced chain dimensions.

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