Reactivity Ratios of Acrylamide–Vinyl Pyrrolidone Copolymerization System Obtained by Sequential Sampling

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ABSTRACT: Free-radical copolymerization of vinyl pyrrolidone and acrylamide was performed in water at 60°C. Their copolymerization reactions were continued up to high conversions and reaction mixture sampled sequentially during the reaction. The compositions of the aliquots were measured by UV spectroscopy, and their polymer contents were obtained by gravimetry. Data are evaluated by a recent error in variables method developed for sequential sampling. Reactivity ratios are found as $r_A = 2.03 \pm 0.14$, $r_{VP} = 0.09 \pm 0.02$. Analysis of the data up to 45% conversion by the Extended Kelen Tüdös method gave consistent results. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3822–3827, 2006

Key words: copolymerization; reactivity ratio; EVM; on-line monitoring; vinyl pyrrolidone; acrylamide

INTRODUCTION

Water-soluble polymers have a growing area of application due to their environmentally benign nature. Vinyl pyrrolidone and acrylamide are among the most frequently used members of this family, and their homo- and copolymers have found wide use from mining to pharmaceuticals as flocculants, thickeners, and drag reduction agents.[1]

Properties of copolymers depend on their composition, which in turn depends on the reactivity ratios of the comonomers as well as the feed mixture. The Mayo–Lewis copolymerization equation[2]

$$d[A]/d[B] = \{[A]/[B]\}\{(r_a[A] + [B])/([A] + r_b[B])\}$$

(1)

gives the ratio of the intake rates of the two monomers when the monomer concentrations and the reactivity ratios r_a and r_b are known. Reliable values of the reactivity ratios are necessary to completely understand and control the copolymerization systems.[3]

In determining the reactivity ratios, several experiments with different monomer feed compositions are performed. In traditional methods, these experiments are terminated at a low to moderate conversion (5–50%), and the composition of the polymer is analyzed. Each experiment gives a single datum. The reactivity ratios are determined by a linear or nonlinear analysis of the data. Nonlinear methods, especially the powerful error in variables (EVM) techniques, are gradually displacing the older linearized methods.[4–10]

Several experimental methods obtain multiple data points from each experiment.[11–15] In these methods, the reaction medium are sampled either continuously or periodically, or the data are taken directly from the reaction vessel. As the monomer take up rates at each sampling point are recorded, these methods allow greater amount of data to be obtained from each experiment and enable the obtaining of the reactivity ratios from only three or four reactions. In these methods, it is usual to use data obtained throughout the whole reaction, at high conversion as well as at low and moderate conversion.

In the sequential sampling method of Paril et al.,[15] used in this work, evolutions of the monomer and polymer compositions and conversion are obtained from UV spectrometric and gravimetric measurements performed on aliquots periodically withdrawn from the reaction medium. The data are then fitted to a numerical solution of eq. (1). Errors in both the gravimetric and spectroscopic measurements are taken into account in the EVM analysis.

TABLE I
Reaction Compositions at Different Experiments

No of exp.	A (g)	VP (g)	ACV (g)	Water (g)
75/25	1.5	0.5	0.02	100
50/50	1	1	0.02	100
25/75	0.5	1.5	0.02	100

TABLE II
ε Values of the Materials at 235 nm in $Vl/(g/g)$

	ε
A	$0.18 \ 10^6$
PA	$0.026 10^6$
VP	$32.30 \ 10^6$
PVP	$1.86 \ 10^6$
ACV	$4.96 \ 10^6$

In this work, free-radical solution copolymerization of water, the soluble monomers acrylamide (A), and 1-vinyl-2-pyrrolidone (VP) was studied up to high conversion by sequential sampling. The reaction compositions are given in Table I. The data are also analyzed by the traditional Extended Kelen Tüdös (EKT) method up to 45% conversion.[16,17]

EXPERIMENTAL

Acrylamide (Sigma, Steinheim, Germany) and vinyl pyrrolidone (Fluka, Steinheim, Germany) monomers were copolymerized with initiator 4,4'-Azobis (4-cyanopentanoic acid) (ACV, Fluka) in deionized water under nitrogen atmosphere at 60°C in a constant temperature bath. The copolymerization reactions were performed at 75%A-25%VP, 50%A-50%VP, 25%A-75%VP, initial weight compositions. To obtain error bars, the 50%A-50%VP reaction was repeated three times. Samples were withdrawn at determined times, and a small portion of chilled methanol was added to quench the reaction. A portion of each sample was dried in a vacuum oven at room temperature until the constant weight. Gravimetry gives the overall conversion.

$$[PA]_t + [PVP]_t = [Copol]_t \qquad (2a)$$

The rest was diluted for UV absorption measurements. UV Spectrophotometer was used for the absorption measurements (Shimadzu 150–02 double beam). Both comonomers have a double bond per monomer, which disappears during polymerization. The UV measurements give,

$$e_A[A]_t + e_{PA}[PA]_t + e_{VP}[VP]_t$$
$$+ e_{PVP}[PVP]_t + e_{ACV}[ACV]_t$$
$$= \text{Absorbance (at 235 nm)} \qquad (2b)$$

where e represents the molar extinction coefficient for the relevant material, determined immediately prior to each experiment, to avoid instrument drifts.

The conservation laws

$$[A]_t + [PA]_t = [A]_i \qquad (2c)$$
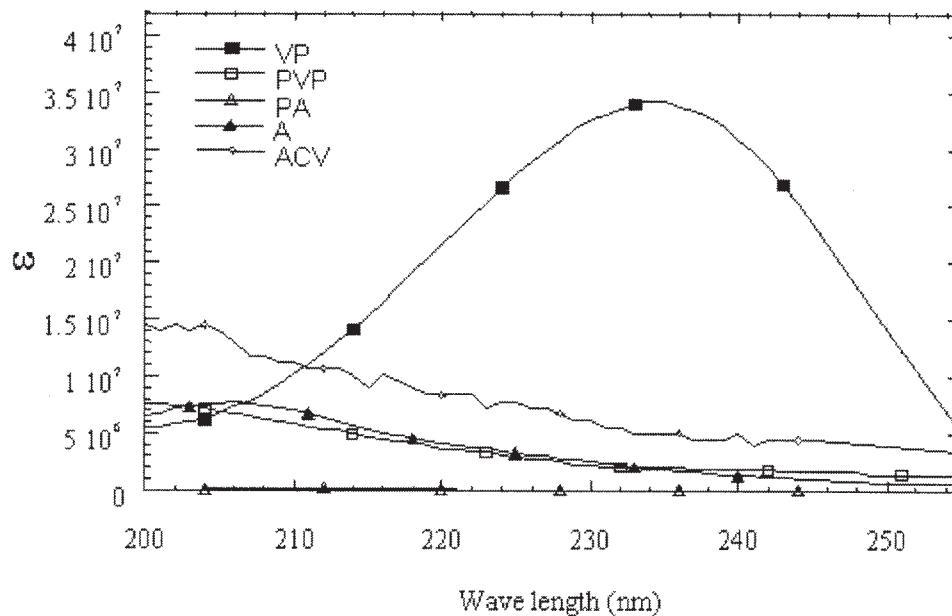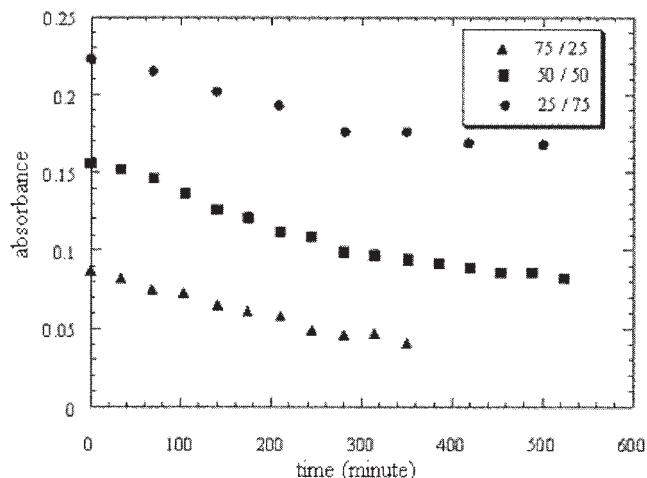

Figure 1 ε values for monomers, polymers, and initiator.

Figure 2 Evolution of absorbance at 235 nm for different compositions during the copolymerization.

$$[VP]_t + [PVP]_t = [VP]_i \tag{2d}$$

together with spectroscopic and gravimetric results give the concentrations of both monomer species and their corresponding units in the copolymer as functions of time. Here, $[A]_i$, $[VP]_i$ are the initial concentrations of the monomers. [Copol] denotes the total copolymer concentration in the sample; PA and PVP denote the A and VP monomeric units in the copolymer, respectively; and the subscript t denotes the sample withdrawn at time t.

For a given pair of reactivity ratios r_a and r_b, and initial concentrations $[a]_i$ and $[b]_i$, the theoretical value of $[a]$ corresponding to the experimental $[b]_{exp}$ and the parameters r_a and r_b $[a]_{the}$ ($[b]_{exp}$, $[a]_i$, $[b]_i$, r_a, r_b) is obtained by numerically solving the copolymerization eq. (1) by the fourth-order Runge Kutta method with variable step size. This value is then compared with the experimental $[a]_{exp}$ obtained from the same aliquot. The procedure produces a $\chi^2(r_a \ r_b)$ value by,

$$Q = ([a]_{exp} - [a]_{the}([b]_{exp}, [a]_i, [b]_i, r_a, r_b)) \tag{3a}$$

$$\chi^2 = \sum_i^{n(\text{data})} \sum_j^{n(\text{exp})} Q_{ij}^2 / \text{Var}(Q_{ij}) \tag{3b}$$

Here, the index "j" denotes the experiment number, and the index "i" represents the data point on that experiment. The sum involves all data points in all of the experiments.

The error terms arise from the measurements and the calibration constants. In practice, the dominant errors are those in the measurements of the samples.

Only the drift of the instrument, between the calibration and the measurements, contributes the calibration errors. Performing the calibration and the measurements at the same time minimized these errors. The calculation of the variations is given in Ref. 14.

RESULTS

Ultraviolet absorption spectra of A, PA, VP, PVP, and ACV are given in Figure 1. The absorption at 235 nm is dominated by VP. The ε values at 235 nm are given in Table II.

The decrease of the UV absorption spectra due to the disappearance of the C=C bonds in the monomers during the reaction and the increase of the conversion are shown in Figures 2 and 3, respectively.

The polymer and monomer concentrations of the aliquots were calculated from eq. (2). The results are in given Figures 4–6.

The EKT method takes the composition drift into account. For this reason, it is valid for moderate conversion as well as low conversion data. Data obtained at up to 45% conversion are used in this analysis.

In the Figure 7, the points in each of the three groups show the data obtained for samples removed from an experiment as the reaction proceeds. The EKT plot gives the reactivities as $r_A = 2.08 \pm 0.04$ and $r_{VP} = 0.12 \pm 0.04$ with a = 0.43. The points lie on a straight line, which indicates that the copolymerization equation is valid and explicit penultimate effects are not significant for this pair of monomers.
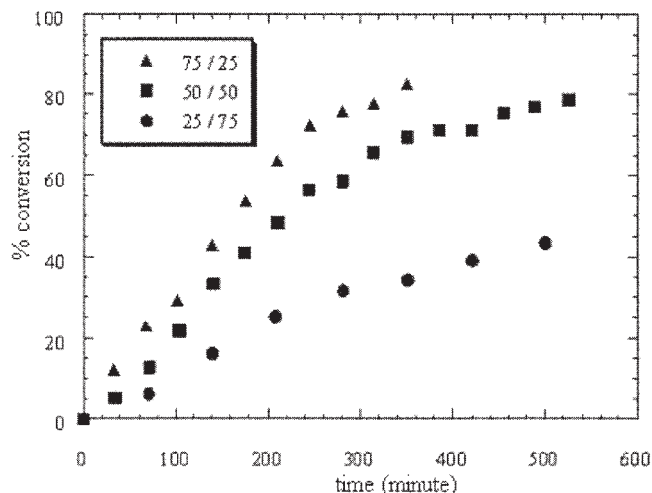

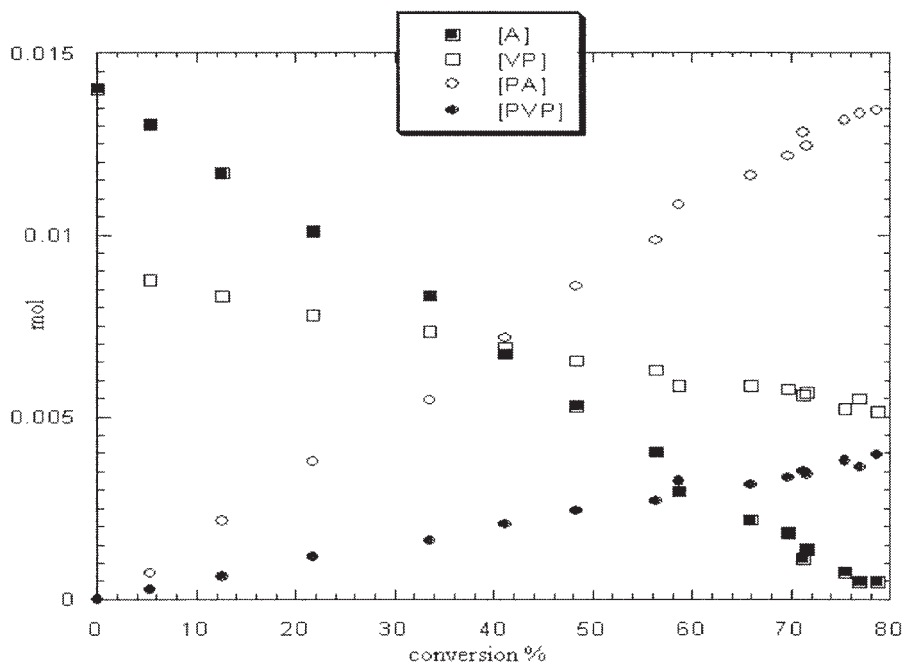**Figure 3** Evolution of conversion for different compositions during copolymerization.

Figure 4 Evolution of composition during 25/75 copolymerization.

A χ^2 map was obtained by comparing data obtained at up to 80% conversion with numerical results. Complete parameter space (r_{VP}, r_A) was swept and contours corresponding to (0.5, 1, and 2) σ levels were plotted (Fig. 8). The results are consistent with EKT analysis in that the error boxes largely overlap (r_A = 2.03 ± 0.14, r_{VP} = 0.09 ± 0.02).

In previous work, Chatterjee and Burns, with reactions performed at 60°C using cumene hydro peroxide initiator and an unspecified linear least squares data
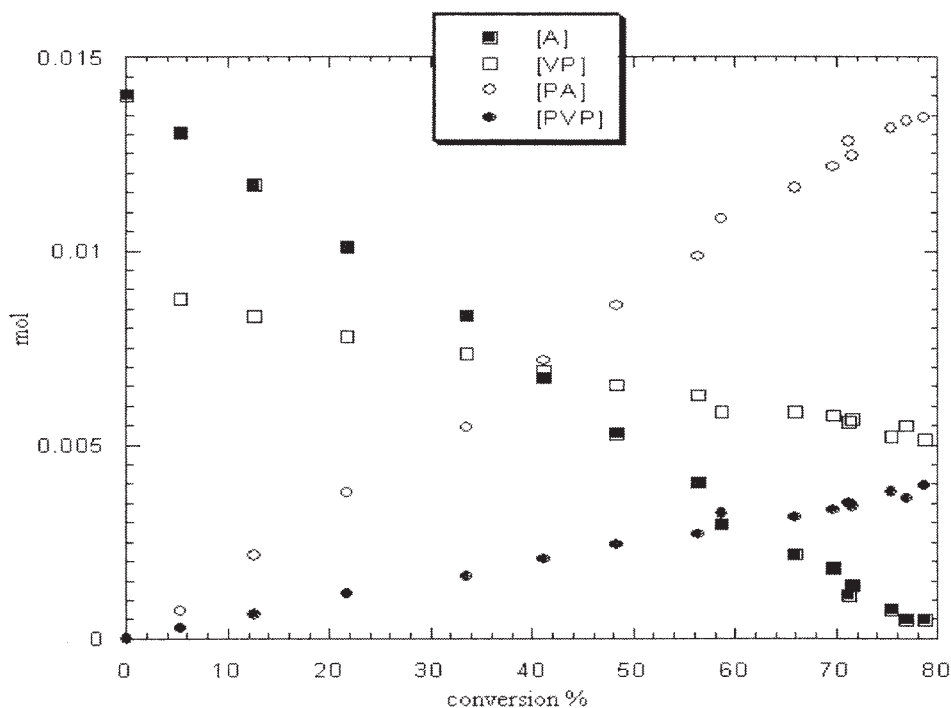

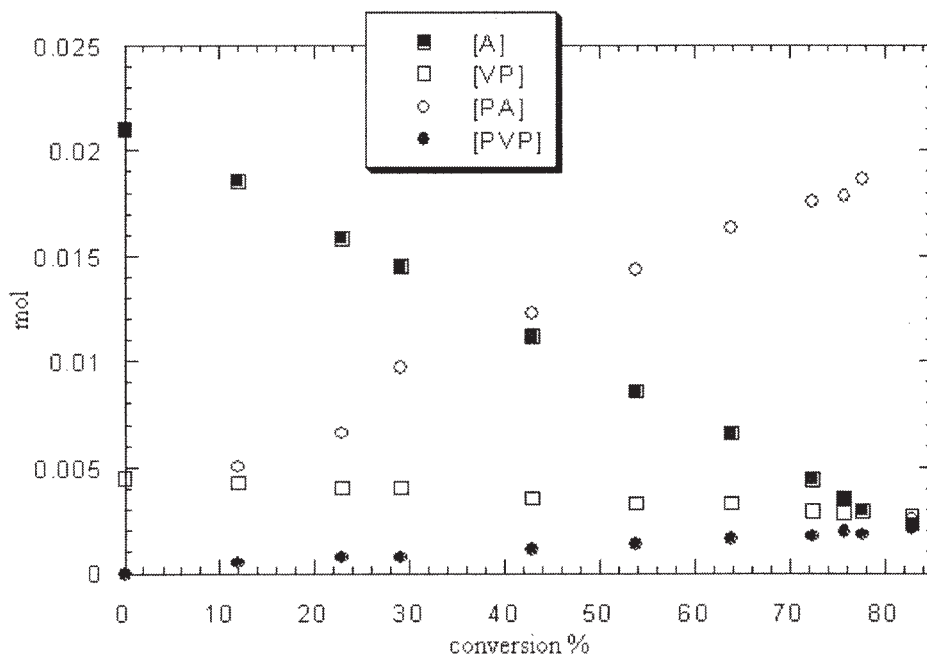**Figure 5** Evolution of composition during 50/50 copolymerization.

Figure 6 Evolution of composition during 75/25 copolymerization.

analysis method, obtained $r_{VP} = 0.17$, $r_A = 0.66$. [18] Bune et al., on the other hand, performed reactions at 35–55°C with potassium persulphate initiator, analyzed sequentially sampled data obtained up to 7% conversion by the Finemann-Ross method, and found $r_{VP} = 0.8$, $r_A = 1.2$. [19]

While all studies show acrylamide to be the more reactive monomer, there are significant quantitative differences among the results. These differences can

be due in part to data analysis. The Finemann-Ross method has been shown to be extremely sensitive to a single data point. [8] The different initiators used in the three studies may also have played a role. While the reactivity ratios relate to the propagation step, they depend on the reaction conditions like temperature and solvent. Chatterjee's results show that the dependence is very strong. Different initiators affect the reaction medium differently. Finally, while pre-
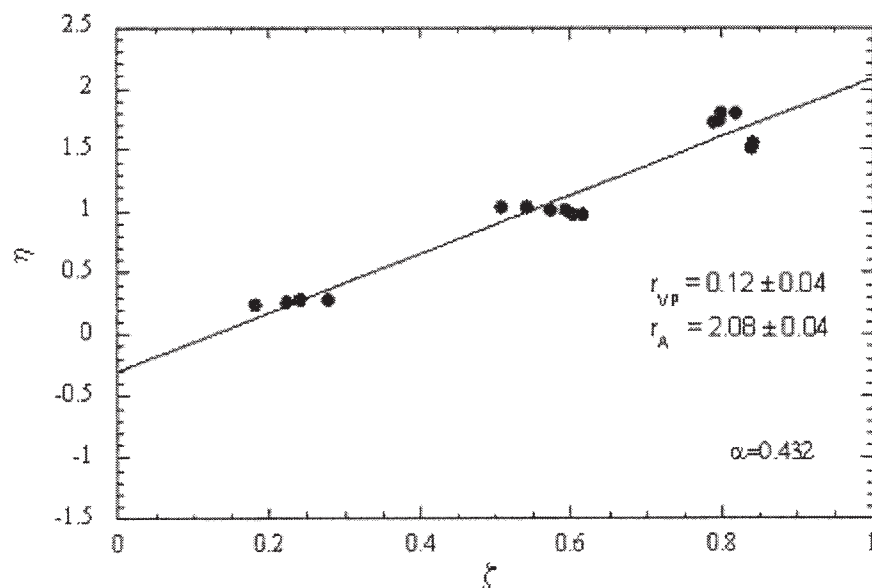

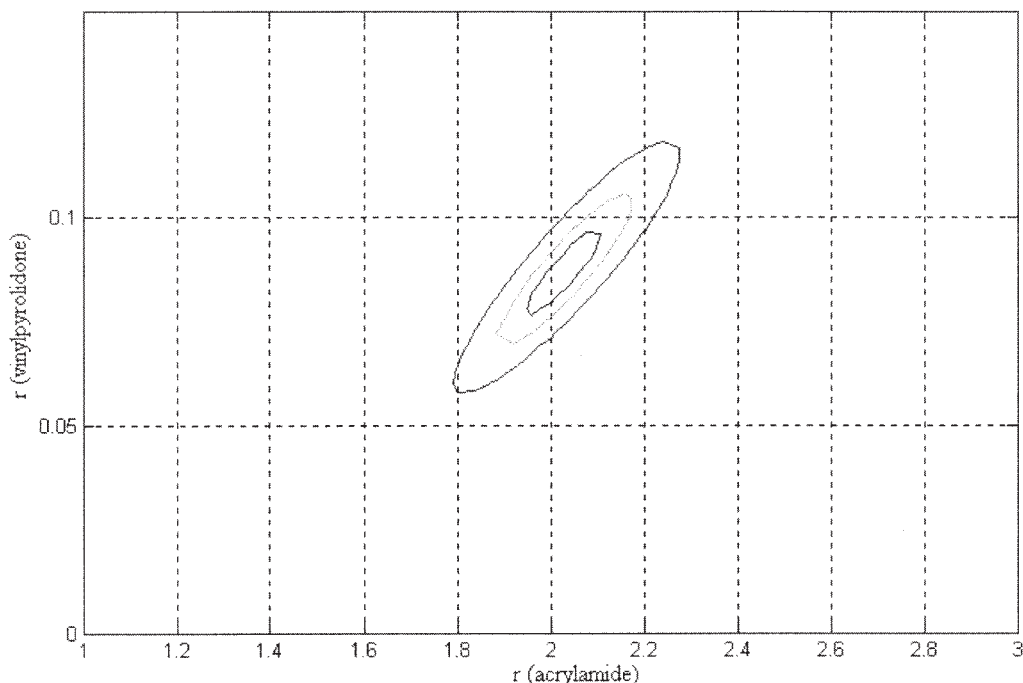**Figure 7** Reactivity ratios found by Extented Kelen-Tüdös method.

Figure 8 The χ^2 contours corresponding to 0.5, 1, and 2σ confidence levels obtained by EVM analysis of sequentially sample data.

vious work used only low conversion data, here data up to 45% conversion evaluated in EKT and up to 80% were used in EVM. Solution properties, such as viscosity, obviously change during the reaction. While low conversion results may be significant due to their purity and intrinsic value, moderate to high conversion results are more relevant to actual practical work using these monomers.

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