Hierarchical Data Analysis of a Replicate Experiment in Emulsion Terpolymerization

Marc A. Dubé and Alexander Penlidis
Dept. of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

A systematic study of the terpolymerization of butyl acrylate/methyl methacrylate/vinyl acetate (BA/MMA/VAc) was conducted. Complete replication of an emulsion terpolymerization experimental run was performed in a 5-L stainless-steel batch pilot-plant reactor. The polymers produced were characterized for conversion, terpolymer composition, molecular weight averages, and average particle size. A hierarchical (nested) data analysis was performed on the experimental data to ascertain various sources of error and to allow for comments to be made regarding the data quality.

Introduction

The growing interest in multicomponent polymerizations from both industry and academia has uncovered the need for a more systematic approach to the study of such systems. The aim of such a study is the understanding of the fundamental physicochemical phenomena and hence, the production of improved paints, adhesives, waxes, coatings, and plastisols. The approach consists of using mathematical modeling and experimental kinetics along with rigorous statistical experimental designs to examine all levels of the multicomponent polymerization. That is, one first studies the homopolymerization systems, followed by each of the copolymerization systems and continues with the multicomponent polymerization system(s). Also, the study of each system is undertaken in bulk, then in solution, and finally, in the emulsion mode. Extensive data collection and careful sample characterization through the full conversion range serve to maximize the information content of the experiments and are an integral part of the systematic approach. The data may then be compared to a mechanistic model that will in turn uncover any lack of process understanding and thus direct further experimentation. It is by breaking down the multicomponent system into its more straightforward parts that a fundamental understanding of each of these parts is achieved. Of course, the task is simplified if results from comprehensive kinetic studies are already available in the open literature for the systems of interest. In that case, one may run replicates of the literature studies or perform complementary studies at different experimental conditions. This approach finally leads to a more thorough view of the multicomponent system.

From previous work, a better understanding about the more straightforward components of the BA/MMA/VAc terpolymerization system was developed (viz., bulk and solution homo-, co-, and terpolymerization, and emulsion homo- and copolymerization) (Dubé and Penlidis, 1995a,b,c). This eventually led naturally to a comprehensive study of the emulsion terpolymerization of BA/MMA/VAc (Dubé and Penlidis, 1996; Dubé et al., 1996).

After committing so much time and effort to an experimental program, it is dangerous to neglect making a thorough assessment of the quality of the data. The situation becomes even worse when the data are to be used for parameter estimation and for comparison with model predictions. In experimental data, there is always some amount of noise or variation induced by known and/or unknown disturbances. Part of these disturbances can be attributed to measurement error. At times, measurement error can obscure important process variable effects and at other instances it may mislead the experimenter into identifying effects or patterns that do not exist.

Polymer properties, such as molecular weight, are often determined from indirect measurements that are subject to experimental and instrumental errors. These errors will propagate through the model used to relate the properties to the measurements. Therefore, it is important to identify the sources of error in order to minimize the uncertainty and to use proper estimation procedures.

Correspondence concerning this article should be addressed to A. Penlidis.
Current address of M. A. Dubé: Dept. of Chemical Engineering, University of Ottawa, 161 Louis Pasteur St., P.O. Box 450, Station A, Ottawa, Ontario K1N 6N5, Canada.

Researchers are often asked about the error in their measurements. Typically, the error quoted is that from the operating manual of the particular measurement instrument that is being used. This, of course, neglects all other sources of variability and is, in every sense of the word, incorrect.

To properly ascertain what the sources and magnitudes of errors in the data were in this long-term experimental study, a replicate experiment was conducted and subjected to extensive characterization using a nested or hierarchical measurement design (Box et al., 1978). In this way, the quality (reproducibility, precision) of the data in the whole study were properly assessed. We believe that such a step should be the culmination of every study on experimental kinetics.

Experimental Studies

Reagent purification

Purification of reagents was performed by classic methods (Stickler, 1987; Dubé et al., 1990). The butyl acrylate and methyl methacrylate monomers (Aldrich Chemical Co. Inc.), were washed three times with a 10% sodium hydroxide solution, washed three times with deionized water, dried over calcium chloride, freshly distilled under vacuum at most 24 hours before use and stored at -10°C. The vinyl acetate monomer (Aldrich Chemical Co. Inc.) was distilled under vacuum at most 24 hours before use and stored at -10°C. Distillations were performed in a Yamato RE-51B rotary evaporator. The first 20 to 50 mL of distillate were discarded (distillate bottoms). Oxygen, being a highly reactive inhibitor, was removed from the reaction mixture prior to the polymerizations by nitrogen sparging.

All of the solvents used during characterization of the polymers (ethanol, chloroform-d, tetrahydrofuran (THF)) were employed as packaged without further purification. The ammonium persulfate (APS) initiator, the sodium metabisulfite (SMBS) reducing agent, the iron sulfate heptahydrate (Fe) component, the sodium bicarbonate (Na bicarb) buffer, the *n*-dodecyl mercaptan (NDM) chain transfer agent (CTA) (all from Aldrich Chemical Co. Inc.), and the Aerosol MA-80 (AMA-80) and Aerosol OT-75 (AOT-75) emulsifiers (Cyanamid Canada Inc.) were also used as received without further purification.

Polymerization method

The experiments were conducted isothermally in a jacketed 5-L stainless-steel pilot plant batch reactor. The reactor configuration has been described elsewhere (Dubé and Penlidis, 1995c; Dubé, 1994).

Polymerization proceeded by first charging the various reagents into the reactor with the exception of the initiator solution (APS in water). The initiator solution was deoxygenated by sparging with nitrogen for ~10 min and then charged to a loading cell. The reactor top head was secured. Agitation of the reactor contents was started (300 rpm) and the reactor contents were heated while being sparged with nitrogen for about 10 minutes. When the reactor contents reached the desired temperature, the initiator was charged into the reactor. This corresponded to time zero. Samples were taken from the reactor (~10 mL) at various time intervals in order to produce a well-defined conversion vs. time curve. A few drops of hydroquinone solution were added to each sample; the sample was shaken and then placed in an ice bath. pH measurements were taken on each sample. Gravimetric analysis was performed on a ~2-mL aliquot of each sample. The latex samples were then dried in an oven to constant weight and were analyzed for composition by proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy and for molecular weight by gel permeation chromatography (GPC). Some of the latex samples were analyzed for particle size using a disk centrifuge.

Run 11 was chosen for replication, as it appeared to represent the entire sequence of experiments. For more details on the experimental runs and their coding, see Dubé and Penlidis (1996). The length of time required to complete run 11 and its particle-size range were also considered in the selection of the replicate experiment. That is, it was preferable to run an experiment that took less than, say, 8 hours and one in which the particles were quite large in order to shorten the particle size analysis time. The recipe for the replicate run (run 19) is shown in Table 1. The recipe for the original run 11 (expressed in units of phm or parts per hundred parts monomer by mass) is also shown in the table. The run took place in the pilot plant reactor isothermally at 50°C.

During the replicate run (run BMV 19), 24 samples were taken at time intervals that coincided with a step of about 5% in conversion from 0% to 100% inclusive. This accounted for 21 of the samples. Of these 21 samples, those that represented the 35, 65, and 95% conversion levels were taken at the 82, 197, and 600 minute marks, respectively. These times coincided with the sampling times of run 11 for conversions of 36.988, 64.160, and 94.559, respectively. This permitted direct comparison of those particular samples with those of run 11 for the purpose of calculating batch-to-batch variability. The three remaining samples were each taken *immediately* after the samples taken at 82, 197, and 600 min. This allowed for the characterization and subsequent analysis of variance to be conducted in a hierarchical fashion (see Box et al., 1978, p. 572). This sampling method was used in order to check for constant variance throughout the run. That is, multiple samples were taken near the beginning, the middle, and the end of the polymerization and the variances of the characterization methods for each sample were compared at each point.

Table 1. BA/MMA/VAc Emulsion Replicate Runs 19 and 11: Ingredients

Ingredient	Mass g	Vol. L	Conc. mol/L	Run 19 phm	Run 11 phm
BA	441.27	0.4937	—	29.963	29.989
MMA	443.13	0.4727	—	30.089	29.990
VAc	588.32	0.6359	—	39.948	40.021
Water	2,400.68	2.4007	—	163.010	163.174
APS	1.0321	—	0.001884	0.0701	0.0701
SMBS	0.8644	—	0.001894	0.0587	0.0585
Fe	0.1252	—	0.000187	0.00850	0.00873
Na bicarb	1.0337	—	0.005125	0.0702	0.0700
AMA-80	14.81	—	0.015881	1.006	1.002
AOT-75	14.75	—	0.013820	1.002	1.013
NDM	1.47	—	0.003025	0.0998	0.0999
Total	3,907.49	4.0029	—	—	—

Product characterization

The gravimetric analysis was based on total polymer. Approximately a 1- to 2-mL aliquot was transferred from the sample vial into a preweighed glass dish and weighed. Contents of the dish were then dried to a constant weight in an oven (~ 40°C). The % solids was subsequently calculated by:

$$\% \text{ solids} = \frac{\begin{pmatrix}\text{wt. of dried sample and}\\ \text{dish} - \text{wt. of empty dish}\end{pmatrix}}{\begin{pmatrix}\text{wt. of dish and}\\ \text{sample} - \text{wt. of empty dish}\end{pmatrix}} \times 100.$$

The sample also contained solid materials other than polymer, so these materials (emulsifier, initiator, etc.) were taken into account in order to calculate conversion. The samples were corrected for the nonpolymeric solid content by knowledge of the initial charge to the reactor. The conversion was calculated by:

$$x = \frac{\left[\left(\frac{\%\text{ solids}}{100}\right) - \text{wt. fraction initiator} - \text{wt. fraction emulsifier}\right]}{(\text{wt. fraction monomer initially})}.$$

A 300-MHz AC Bruker Fourier-Transform ^{1}H-NMR spectrometer was used to measure polymer composition. Analysis was carried out in deuterated chloroform (chloroform-d) (~ 2% (w/v) solutions) at room temperature. The relative amounts of monomer bound in the polymer were estimated from the areas under the appropriate absorption peaks of the spectra. Good peak separation was achieved, thus allowing the unambiguous interpretation of the results (Dubé and Penlidis, 1995b; Dubé, 1994).

A Waters Associates GPC was used to measure molecular weight averages. Three Waters Ultrastyragel columns (10^3, 10^4 and 10^6 Å) were installed in series. Tetrahydrofuran (THF), Caledon reagent grade, degassed and filtered, was used as the eluent. Samples were prepared in THF (~ 0.2% w/v solutions) and filtered through 0.45-μm filters to remove any high molecular weight gel. Polymer elution was detected with a Waters R401 differential refractometer (DRI). Data were recorded using a 12-bit AD/DA data capture card installed in a 386-33-MHz IBM-compatible computer. Software for data collection, storage and manipulation was written in QuickBASIC at the University of Waterloo (Scott et al., 1992).

The particle size and size distribution of the latexes were measured using an ICI-Joyce Loebl Disk Centrifuge (Devon et al., 1991). The output was recorded by a Brookhaven Instruments DCP-1000 Data System. Water was used as the spin fluid, and the density gradient was produced using methanol. The latexes were diluted to approximately 1 wt. % in a mixture of 80/20 water/methanol by volume. Approximately 0.2-mL samples were injected and spin rates were chosen such that the peak eluted in a reasonable time period (< 1 h).

Theoretical Background

The uncertainty in some of the data was calculated using rules summarized by Reilly (1992) for manipulating uncertain numbers. The rules are based on the well-known formula for the propagation of variance (Davies and Goldsmith, 1977). First, the uncertainty in a sum or difference of numbers is the square root of the sum of the squares of the uncertainties in the individual numbers:

$$u(x_1 \pm x_2 \pm \cdots \pm x_n) = \left\{\sum_{i=1}^{n} [u(x_i)]^2\right\}^{1/2}, \qquad (1)$$

where x_i represents the number and $u(x_i)$ represents the uncertainty in it.

For products and quotients the rule is as follows: Let

$$y = x_1 \overset{\times}{\div} x_2 \overset{\times}{\div} \cdots \overset{\times}{\div} x_n. \qquad (2)$$

Then

$$y \pm u(y) = y\left\{1 \pm \left[\sum_{i=1}^{n}\left(\frac{u(x_i)}{x_i}\right)^2\right]^{1/2}\right\}. \qquad (3)$$

That is, the relative uncertainty in a product or quotient is the square root of the sum of the squares of the relative uncertainties in the individual numbers.

For the uncertainty in a general function $f(x_1, x_2, \ldots, x_n)$, the general rule gives

$$u(f) = \left[\sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_i}u(x_i)\right)^2\right]^{1/2}. \qquad (4)$$

The formula for the propagation of variance is in general only approximately true. It depends on a linearization of the function $f(x_1, x_2, \ldots, x_n)$. Hence, Eq. 1 is strictly correct, but Eqs. 3 and 4 are approximate. This approximation is good, however, as long as the relative error in the x's is not too large ($\leq$ 20%; Davies and Goldsmith, 1977).

A nested (hierarchical) design was used to estimate the components of variance in each measurement (Box et al., 1978). Three levels of the nested design were examined in this study. The lowest level was the test (T) level, which represented the measuring instrument or analytical error. This was examined by performing replicate analyses. The next level was the homogeneity level (H), which tested the error in analyzing different portions of the samples. The highest level was the sampling level (S). This final level compared the difference between two supposedly identical samples. T was defined as the number of replicate analyses, H was defined as the number of times the sample was split, and S was the number of samples.

Three related (variance) quantities were calculated: V_T, V_H, and V_S. The observations were defined as $y_{sh1}, y_{sh2}, \ldots, y_{sht}$, that is, the T replicated analytical tests made on the hth portion of the sth sample. Averages for each hth portion were defined as $\bar{y}_{sh}$. The pooled estimate of the test component of the variance was

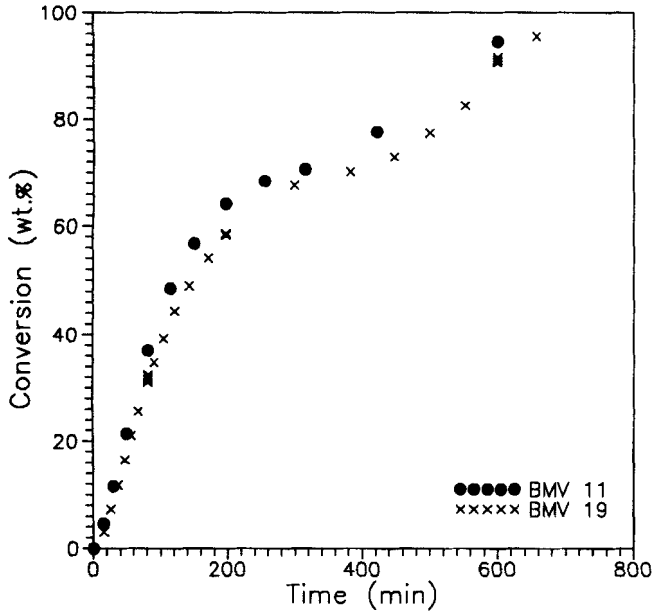

Figure 1. BA/MMA/VAc emulsion runs 11 and 19: conversion vs. time.

$$V_T = \frac{\sum_s \sum_h \sum_t (y_{sht} - \bar{y}_{sh})^2}{SH(T-1)}, \quad (5)$$

which was an estimate of $\hat{\sigma}_T^2$ having $SH(T-1)$ degrees of freedom.

To calculate V_H, the H portion averages, $\bar{y}_{s1}$, $\bar{y}_{s2}$, ..., $\bar{y}_{sn}$, were calculated for the sth sample. Next, the average, $\bar{y}_s$, was calculated from the portion averages. Pooling the variances for all the samples gave

$$V_H = \frac{\sum_s \sum_h (y_{sh} - \bar{y}_s)^2}{S(H-1)}. \quad (6)$$

V_H was *not* an estimate of σ_H^2 alone, because each sample was represented by an average of T test analyses. Thus, V_H was actually an estimate of $\sigma_H^2 + (\sigma_T^2/T)$.

Finally, to calculate V_S, the S sample averages, $\bar{y}_1$, $\bar{y}_2$, ..., $\bar{y}_s$, and a grand average, $\bar{y}$, were calculated. The quantity

$$V_S = \frac{\sum_{s=1}^{S} (y_s - \bar{y})^2}{S-1} \quad (7)$$

was thus an estimate of $\sigma_S^2 + (\sigma_H^2/H) + (\sigma_T^2/HT)$.

For the gravimetric analyses, $T = 0$ (the error in the balance was known), $H = 4$, and $S = 2$. For the molecular weight and composition analyses $T = 4$, $H = 4$, and $S = 2$. For the particle-size analyses, $T = 3$, $H = 3$, and $S = 2$. From these numbers, the reader can readily appreciate that the characterization of the replicate experiment took considerable time and an enormous effort.

Conversion Results

The gravimetric results are presented in Table 2 and Figure 1. The error analysis concentrated on samples 8, 9, 15, 16, 22 and 23. Samples 9, 16 and 23 were taken immediately (zero time delay) after samples 8, 15, and 22, respectively. Four aliquots of approximately 2 mL each were taken from each of the six samples and weighed into separate petri dishes for a total of 24 separate gravimetric analyses.

Using Eqs. 1 and 3, the analytical error in a representative sample (sample 17) was calculated. Thus, the percent solids of sample 17 expressed with the estimate of analytical error

Table 2. BA/MMA/VAc Emulsion Run 19: Gravimetric Results

Sample	Time min	Solids wt. %	Conversion wt. %	Sample	Time min	Solids wt. %	Conversion wt. %
1	1	0.000	0.000	15b	197	22.925	58.512
2	16	2.031	3.074	15c	197	22.991	58.685
3	26.5	3.604	7.247	15d	197	22.844	58.296
4	37	5.308	11.769	16a	197	22.843	58.293
5	47	7.073	16.452	16b	197	22.895	58.430
6	57	8.800	21.034	16c	197	22.974	58.640
7	67.666	10.534	25.634	16d	197	22.982	58.662
8a	82	12.570	31.037	17	299	26.352	67.603
8b	82	12.775	31.581	18	382	27.313	70.153
8c	82	12.707	31.401	19	447	28.348	72.900
8d	82	12.850	31.779	20	500	30.036	77.378
9a	82	12.740	31.448	21	552	31.982	82.541
9b	82	13.080	32.390	22a	600	35.173	91.009
9c	82	13.039	32.281	22b	600	35.024	90.614
9d	82	12.983	32.134	22c	600	35.035	90.641
10	90.5	13.959	34.723	22d	600	35.089	90.784
11	105	15.668	39.257	23a	600	35.144	90.931
12	121	17.566	44.292	23b	600	35.239	91.184
13	142.5	19.332	48.978	23c	600	35.254	91.223
14	170.5	21.266	54.109	23d	600	35.393	91.591
15a	197	22.970	58.630	24	657	36.875	95.524

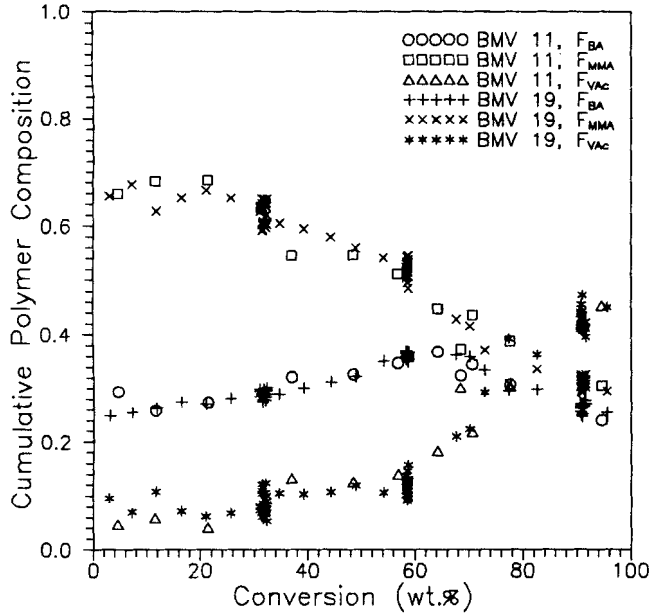

Figure 2. BA/MMA/VAc emulsion runs 11 and 19: cumulative average polymer composition vs. conversion.

(the error from the balance) was 26.3518 ± 0.000721. Similarly, the percent conversion of sample 17 was 67.6035 ± 0.0200. Thus the variance for the percent conversion based only on the analytical error was $\hat{\sigma}_I^2 = 0.0004$.

From Eq. 6, the homogeneity component of the variance was found to be $\hat{\sigma}_H^2 = 0.071725$. The sampling component of the variance was calculated using Eq. 7, as $\hat{\sigma}_S^2 = 0.08392475$.

From the preceding calculations, it can be seen that the error from the balance was minimal. Also, there did not appear to be any significant errors due to the homogeneity of the samples nor due to any sampling errors. The sampling error had the largest amount of variability. The overall error calculated by adding the three components of error was $\hat{\sigma}_x^2 = 0.1560$. This translates into a 95% confidence interval of ± 0.77 (when x is expressed as wt. %, for example, sample 2 in Table 2 has a conversion of 3.074 ± 0.77 wt. %). This demonstrates that the experimental procedures and analytical techniques that influenced the calculation of conversion were very consistent and accurate.

One can see in Figure 1 that the reproducibility was good. Yet, the difference in conversion between the two runs cannot be explained by the variability of the data alone. Based on the preceding error analysis, it can be stated that differences in conversion were not due to the analytical technique. The differences are likely due to slight differences in the recipes (see Table 1). Another possible source of error was the evaporation of monomer both during the weighing of the recipe and during the gravimetric analysis. The error analysis given previously indicates that the procedures were consistent based on the low variability of the results. Dissolved oxygen may have been a factor, although no apparently significant induction times were exhibited in these two runs (runs 11 and 19).

Table 3. BA/MMA/VAc Emulsion Replicate Run 19: Composition Results

Sample	Conversion wt. %	$\bar{F}_{BA}$	$\bar{F}_{MMA}$	$\bar{F}_{VAc}$
2	3.074	0.249	0.655	0.096
3	7.247	0.255	0.676	0.070
4	11.769	0.264	0.628	0.108
5	16.452	0.275	0.652	0.072
6	21.034	0.271	0.666	0.062
7	25.634	0.281	0.651	0.068
8a1	31.037	0.299	0.628	0.073
8a2	31.037	0.285	0.636	0.079
8a3	31.037	0.295	0.626	0.079
8a4	31.037	0.285	0.633	0.081
8b1	31.581	0.275	0.609	0.116
8b2	31.581	0.285	0.594	0.121
8b3	31.581	0.279	0.635	0.086
8b4	31.581	0.291	0.630	0.079
8c1	31.401	0.290	0.606	0.104
8c2	31.401	0.288	0.603	0.109
8c3	31.401	0.292	0.641	0.068
8c4	31.401	0.289	0.650	0.061
8d1	31.779	0.291	0.605	0.104
8d2	31.779	0.286	0.645	0.068
8d3	31.779	0.291	0.649	0.061
8d4	31.779	0.299	0.629	0.072

Table 4. BA/MMA/VAc Emulsion Replicate Run 19: Composition Results

Sample	Conversion wt. %	$\bar{F}_{BA}$	$\bar{F}_{MMA}$	$\bar{F}_{VAc}$
9a1	31.448	0.288	0.591	0.121
9a2	31.448	0.290	0.649	0.061
9a3	31.448	0.289	0.640	0.071
9a4	31.448	0.288	0.633	0.079
9b1	32.390	0.298	0.603	0.100
9b2	32.390	0.290	0.620	0.090
9b3	32.390	0.297	0.650	0.053
9b4	32.390	0.302	0.621	0.077
9c1	32.281	0.295	0.621	0.084
9c2	32.281	0.289	0.635	0.077
9c3	32.281	0.289	0.642	0.069
9c4	32.281	0.284	0.641	0.074
9d1	32.134	0.278	0.598	0.123
9d2	32.134	0.289	0.605	0.105
9d3	32.134	0.295	0.638	0.066
9d4	32.134	0.289	0.643	0.068
10	34.723	0.290	0.605	0.105
11	39.257	0.301	0.595	0.103
12	44.292	0.313	0.580	0.107
13	48.978	0.323	0.560	0.118
14	54.109	0.352	0.542	0.106
15a1	58.630	0.363	0.508	0.129
15a2	58.630	0.360	0.546	0.094
15a3	58.630	0.360	0.547	0.093
15a4	58.630	0.355	0.523	0.122
15b1	58.512	0.358	0.496	0.146
15b2	58.512	0.361	0.532	0.107
15b3	58.512	0.366	0.520	0.114
15b4	58.512	0.356	0.530	0.114

Terpolymer Composition Results

As described earlier, an aliquot of approximately 5 mL of each sample was poured into ethanol in order to precipitate the latex and wash it of any excess emulsifier. Then, for each of samples 8, 9, 15, 16, 22 and 23 (see Table 2), four separate

Table 5. BA/MMA/VAc Emulsion Replicate Run 19: Composition Results

Sample	Conversion wt. %	$\bar{F}_{BA}$	$\bar{F}_{MMA}$	$\bar{F}_{VAc}$
15c1	58.685	0.359	0.516	0.125
15c2	58.685	0.359	0.532	0.109
15c3	58.685	0.369	0.529	0.103
15c4	58.685	0.364	0.526	0.110
15d1	58.296	0.359	0.504	0.137
15d2	58.296	0.368	0.531	0.101
15d3	58.296	0.357	0.518	0.125
15d4	58.296	0.360	0.524	0.116
16a1	58.293	0.370	0.510	0.120
16a2	58.293	0.356	0.516	0.128
16a3	58.293	0.358	0.505	0.137
16a4	58.293	0.360	0.512	0.128
16b1	58.430	0.360	0.511	0.129
16b2	58.430	0.365	0.544	0.091
16b3	58.430	0.356	0.534	0.110
16b4	58.430	0.370	0.517	0.113
16c1	58.640	0.358	0.525	0.117
16c2	58.640	0.359	0.533	0.108
16c3	58.640	0.360	0.517	0.124
16c4	58.640	0.351	0.517	0.132
16d1	58.662	0.357	0.486	0.157
16d2	58.662	0.362	0.538	0.100
16d3	58.662	0.366	0.535	0.099
16d4	58.662	0.353	0.515	0.132
17	67.603	0.363	0.428	0.210
18	70.153	0.360	0.416	0.224
19	72.900	0.335	0.372	0.293
20	77.378	0.297	0.310	0.393
21	82.541	0.299	0.337	0.364

Table 6. BA/MMA/VAc Emulsion Replicate Run 19: Composition Results

Sample	Conversion wt. %	$\bar{F}_{BA}$	$\bar{F}_{MMA}$	$\bar{F}_{VAc}$
22a1	91.009	0.270	0.321	0.409
22a2	91.009	0.253	0.302	0.445
22a3	91.009	0.266	0.325	0.409
22a4	91.009	0.272	0.321	0.407
22b1	90.614	0.263	0.323	0.414
22b2	90.614	0.256	0.302	0.442
22b3	90.614	0.256	0.304	0.440
22b4	90.614	0.272	0.315	0.413
22c1	90.641	0.272	0.318	0.410
22c2	90.641	0.256	0.315	0.429
22c3	90.641	0.267	0.317	0.416
22c4	90.641	0.266	0.316	0.418
22d1	90.784	0.265	0.314	0.421
22d2	90.784	0.264	0.325	0.411
22d3	90.784	0.250	0.294	0.456
22d4	90.784	0.270	0.319	0.411
23a1	90.931	0.271	0.299	0.430
23a2	90.931	0.270	0.297	0.433
23a3	90.931	0.248	0.279	0.473
23a4	90.931	0.271	0.293	0.436
23b1	91.184	0.267	0.317	0.416
23b2	91.184	0.268	0.317	0.415
23b3	91.184	0.268	0.318	0.415
23b4	91.184	0.269	0.311	0.420
23c1	91.223	0.270	0.319	0.411
23c2	91.223	0.270	0.313	0.418
23c3	91.223	0.266	0.320	0.414
23c4	91.223	0.272	0.315	0.413
23d1	91.591	0.278	0.309	0.413
23d2	91.591	0.278	0.327	0.396
23d3	91.591	0.272	0.303	0.424
23d4	91.591	0.272	0.317	0.411
24	95.524	0.255	0.295	0.451

pieces of dried polymer from each precipitation were dissolved in chloroform-d and placed in separate ^{1}H-NMR tubes for a total of 24 tubes (not including those samples from the remainder of the run). Each of the ^{1}H-NMR tubes was analyzed four times. The composition results are shown in Tables 3 through 6 and are plotted in Figure 2. $\bar{F}_i$ in Tables 3 through 6 denote the cumulative mole fraction of monomer i bound in the terpolymer.

Separate error analyses were performed for the mole fraction of each component of the polymer (BA, MMA, and VAc), although it is noted that the errors were not independent. From Eq. 5, the analytical component of the variance was found to be $\hat{\sigma}_T^2 = 3.399 \times 10^{-5}$ for BA, 2.191×10^{-4} for MMA, and 2.980×10^{-4} for VAc. Therefore, the mole fraction of monomer bound in the polymer varied by ± 0.0114 for BA, by ± 0.0290 for MMA and by ± 0.0338 for VAc (with 95% confidence) based solely on the ^{1}H-NMR measurement. These are typical NMR measurement errors (Scott et al., 1993).

Using Eq. 6, the homogeneity component of the variance was found to be $\hat{\sigma}_H^2 = 2.163 \times 10^{-6}$ for BA, and $\hat{\sigma}_H^2 = 6.010 \times 10^{-6}$ for VAc. The variance for MMA was negligible relative to the instrument error. The sampling component of the variance was calculated using Eq. 7 to be $\hat{\sigma}_S^2 = 3.557 \times 10^{-6}$ for BA. The variances for MMA and VAc were negligible.

It is evident that the error from the ^{1}H-NMR analysis is the dominant one. This supports the sampling and sample preparation techniques used in the experiments. That is, the low values for the homogeneity and sampling components of the variance indicate that the samples were homogeneous and that the drift in polymer composition was not rapid enough to affect the measurements. Figure 2 demonstrates the good reproducibility of the terpolymer composition data and gives a good idea about the expected scatter due to the analytical error of the measuring instrument. The overall errors expected in composition, expressed as 95% confidence intervals of the mole fractions, were ± 0.0118 for BA, ± 0.0290 for MMA, and ± 0.0342 for VAc.

A similar but less involved examination of the ^{1}H-NMR measurement was performed for ethylene/vinyl acetate copolymers by Scott (1992), who calculated a standard deviation of $\sigma = 1.13$ wt. %. This compares well with the values in this study (converted to wt. %): $\hat{\sigma} = 0.77$ wt. % for BA, $\hat{\sigma} = 1.48$ wt. % for MMA, and $\hat{\sigma} = 1.50$ wt. % for VAc.

Molecular Weight Results

For molecular weight analysis, a sample from each of the four gravimetric analyses was taken for each of samples 8, 9, 15, 16, 22 and 23. Thus, for each of samples 8, 9, 15, 16, 22, and 23, there were four vials of filtered, dissolved polymer in THF. Four separate aliquots from each of the vials were injected into the GPC setup and analyzed for molecular weight. All the other remaining samples were analyzed once. The molecular weight results are shown in Tables 7 and 8 and are plotted in Figure 3.

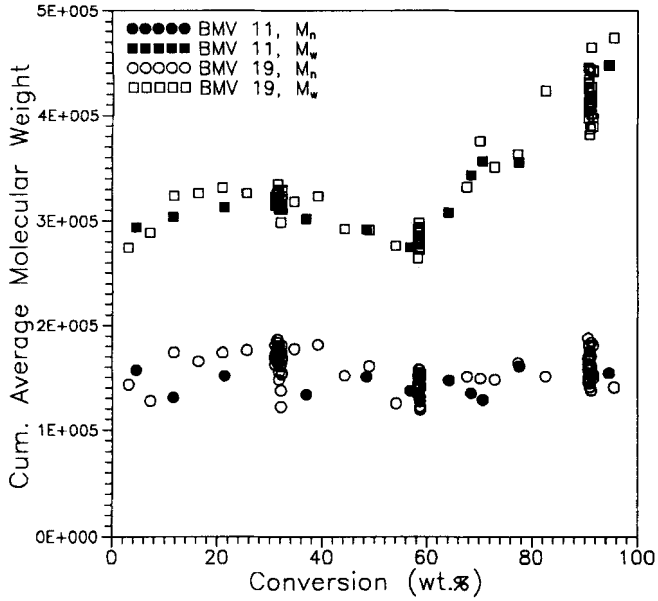

Figure 3. BA/MMA/VAc emulsion runs 11 and 19: cumulative number- and weight-average molecular weight vs. conversion.

Error analyses were performed for both the cumulative number- and weight-average molecular weights ($\overline{M}_n$ and $\overline{M}_w$). From Eq. 5, the analytical component of the variance was found to be $\hat{\sigma}_T^2 = 1.28 \times 10^8$ for $\overline{M}_n$, and 1.47×10^8 for $\overline{M}_w$. This translates into an error of $\pm 22{,}175$ for $\overline{M}_n$ and of $\pm 23{,}764$ for $\overline{M}_w$ (with 95% confidence) based solely on the GPC instrument. This is well within typical values.

Using Eq. 6, the homogeneity component of the variance was found to be $\hat{\sigma}_H^2 = 2.59 \times 10^7$ for $\overline{M}_n$, and $\hat{\sigma}_H^2 = 3.65 \times 10^6$ for $\overline{M}_w$. The sampling component of the variance was calculated using Eq. 7 to be $\hat{\sigma}_S^2 = 2.925 \times 10^6$ for $\overline{M}_n$ while that for $\overline{M}_w$ was negligible. As in the case for the NMR, the GPC instrument is the greatest source of error in the results. These results support the sampling and sample preparation techniques used in the experiments. Again, the samples were homogeneous (based on the low value of the homogeneity component of variance), and the molecular weight changes during the course of the polymerization were not rapid (based on the low value of the sampling component of variance). Figure 3 demonstrates remarkable reproducibility of the molecular weight data and shows the expected scatter due mostly to the analytical error of the measuring instrument. Using all sources of known error, the 95% confidence intervals are $\pm 24{,}061$ for $\overline{M}_w$ and $\pm 24{,}543$ for $\overline{M}_n$.

In a separate test of the GPC techniques used in this study, a round-robin GPC analysis was performed in our laboratory and three different industrial laboratories operated by ICI, Worldwide. The results showed only minor differences between the various laboratories, thus, confirming the accuracy of the analytical techniques employed in this study. A number of samples were sent to ICI/Glidden (USA) for GPC analysis to compare directly with the results in this study. The ICI/Glidden results are shown in Table 9 along with our results. ICI/Glidden used both a conventional GPC and a

Table 7. BA/MMA/VAc Emulsion Replicate Run 19: Molecular Weight Results

Sample	Conversion wt. %	$\overline{M}_n$	$\overline{M}_w$	Sample	Conversion wt. %	$\overline{M}_n$	$\overline{M}_w$
2	3.074	143,186	274,714	9c1	32.281	152,876	315,049
3	7.247	127,457	288,892	9c2	32.281	167,458	320,187
4	11.769	174,101	323,894	9c3	32.281	180,489	314,900
5	16.452	165,391	326,084	9c4	32.281	173,236	320,414
6	21.034	173,812	331,530	9d1	32.134	137,467	312,310
7	25.634	176,355	326,297	9d2	32.134	122,092	298,554
8a1	31.037	171.830	320,819	9d3	32.134	161,555	313,717
8a2	31.037	167,662	320,766	9d4	32.134	162,860	315,711
8a3	31.037	162,198	314,729	10	34.723	177,322	318,437
8a4	31.037	180,743	323,168	11	39.257	181,541	323,436
8b1	31.581	167,650	316,060	12	44.292	151,677	292,722
8b2	31.581	177,906	328,456	13	48.978	160,723	291,236
8b3	31.581	178,335	334,699	14	54.109	125,238	276,250
8b4	31.581	163,192	317,966	15a1	58.630	143,484	273,621
8c1	31.401	166,068	314,988	15a2	58.630	141,053	290,000
8c2	31.401	172,635	319,937	15a3	58.630	147,853	280,717
8c3	31.401	173,330	323,099	15a4	58.630	147,047	281,961
8c4	31.401	177,076	325,946	15b1	58.512	152,768	284,070
8d1	31.779	180,597	329,699	15b2	58.512	132,432	277,825
8d2	31.779	147,875	311,384	15b3	58.512	148,435	279,355
8d3	31.779	176,623	325,578	15b4	58.512	143,062	298,073
8d4	31.779	155,273	315,451	15c1	58.685	120,065	275,157
9a1	31.488	169,416	318,703	15c2	58.685	119,125	272,650
9a2	31.488	183,795	326,065	15c3	58.685	122,359	273,649
9a3	31.488	186,679	322,897	15c4	58.685	139,381	281,204
9a4	31.488	178,147	319,454	15d1	58.296	151,735	282,664
9b1	32.390	169,219	323,623	15d2	58.296	144,990	292,531
9b2	32.390	154,217	310,999	15d3	58.296	137,826	278,168
9b3	32.390	166,808	328,146	15d4	58.296	139,743	282,904
9b4	32.390	170,135	329,549				

Table 8. BA/MMA/VAc Emulsion Replicate Run 19: Molecular Weight Results

Sample	Conversion wt. %	$\overline{M}_n$	$\overline{M}_w$	Sample	Conversion wt. %	$\overline{M}_n$	$\overline{M}_w$
16a1	58.293	142,098	279,232	22b3	90.614	157,717	413,338
16a2	58.293	132,998	264,665	22b4	90.614	149,731	445,580
16a3	58.293	151,075	290,319	22c1	90.641	162,884	397,463
16a4	58.293	135,154	278,492	22c2	90.641	169,415	411,144
16b1	58.430	149,059	283,773	22c3	90.641	169,729	430,137
16b2	58.430	138,923	282,966	22c4	90.641	145,079	404,792
16b3	58.430	157,475	290,609	22d1	90.784	154,035	422,215
16b4	58.430	138,769	280,403	22d2	90.784	156,881	424,802
16c1	58.640	127,210	279,485	22d3	90.784	180,929	434,867
16c2	58.640	143,413	294,130	22d4	90.784	160,815	411,413
16c3	58.640	150,048	288,485	23a1	90.931	144,578	381,618
16c4	58.640	156,904	286,110	23a2	90.931	147,273	411,770
16d1	58.662	154,344	280,153	23a3	90.931	140,900	409,600
16d2	58.662	149,616	279,329	23a4	90.931	167,171	407,327
16d3	58.662	131,576	278,481	23b1	91.184	137,486	417,302
16d4	58.662	152,890	290,590	23b2	91.184	158,395	415,685
17	67.603	150,875	332,346	23b3	91.184	153,046	401,693
18	70.153	149,126	375,729	23b4	91.184	170,348	412,769
19	72.900	148,018	351,579	23c1	91.223	183,955	465,078
20	77.378	163,872	363,215	23c2	91.223	154,086	427,023
21	82.541	151,033	423,517	23c3	91.223	160,981	402,131
22a1	91.009	156,712	444,090	23c4	91.223	159,207	412,660
22a2	91.009	157,409	387,411	23d1	91.591	148,709	390,111
22a3	91.009	175,101	407,757	23d2	91.591	181,019	442,975
22a4	91.009	175,519	418,865	23d3	91.591	153,436	398,133
22b1	90.614	168,612	431,173	23d4	91.591	151,976	441,944
22b2	90.614	188,050	426,454	24	95.524	140,455	474,172

GPC/Viscometer. For samples 8a, 15a and 22a an average value was reported for our results.

The analyses from ICI are the same as the results from this study within experimental error. This is another confirmation of the reproducibility and accuracy of the data in this study.

Particle Size and Number Results

For each of samples 15, 16, 22, and 23, three separate dilution vials were prepared. That is, as explained earlier, several drops of latex were diluted in a vial containing a methanol/water mixture. Therefore, there was a total of 12 dilution vials for samples 15, 16, 22, and 23. Three separate aliquots from each of the vials were injected into the disk centrifuge for particle-size analysis. All of the other samples (12 through 24) were analyzed once. The lower conversion samples, samples 1 through 11, were not characterized for particle size. Average particle size and number results are shown in Tables 10 and 11. $\overline{D}_n$ in Tables 10 and 11 denotes the number-average particle size, whereas N_p stands for the number of particles per liter of water. The particle size-results are plotted in Figure 4.

Table 9. Comparison of Molecular Weight Analyses with Industrial Laboratory

	This Work		ICI GPC		ICI GPC/Visc.	
Sample	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w$
4	174,101	323,894	152,000	286,000	176,000	343,000
8a	170,608	319,871	158,000	292,000	183,000	319,000
12	151,677	292,722	141,000	271,000	153,000	300,000
15a	144,859	281,575	127,000	261,000	177,000	342,000
19	148,018	351,579	157,000	332,000	146,000	309,000
22a	166,185	414,531	150,000	368,000	136,000	348,000

From Eq. 5, the analytical component of the variance of the particle size was found to be $\hat{\sigma}_T^2 = 8.753 \times 10^{-7}$. This translates into an error of ± 0.001834 μm (or ± 18.34 Å) (with 95% confidence) based solely on the disk centrifuge.

Using Eq. 6, the homogeneity component of the variance was found to be $\hat{\sigma}_H^2 = 1.976 \times 10^{-6}$. The sampling component of the variance was negligible in comparison to the other sources of error. Unlike the previous characterizations (composition, molecular weight, etc.), the homogeneity component of the variance was the largest source of variability in the particle size results. This heterogeneity may be due even to minor coagulation during the preparation of the samples. Latexes are easily destabilized in the presence of alcohols.

Figure 4 demonstrates fairly good reproducibility of the average particle-size data. The overall error in the particle sizes is ± 0.00331 μm (or ± 33.1 Å or $\pm 0.331 \times 10^{-6}$ cm) (with 95% confidence). These results support the sampling and sample preparation techniques used in the experiments. However, in the future, it may be advisable to add more emulsifier to the diluted latexes in order to enhance their stability.

PH Results

The results of the pH measurement are shown in Table 12 and are plotted in Figure 5. From the figure it is evident that the pH was adequately reproducible.

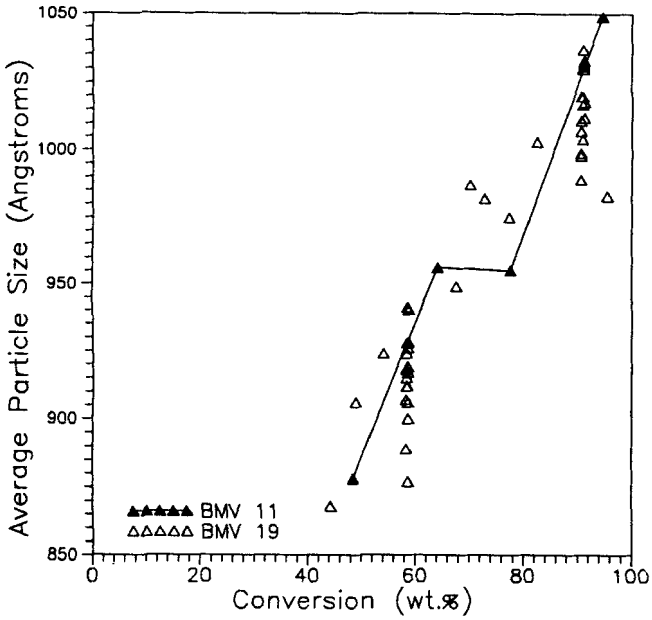

Figure 4. BA/MMA/VAc emulsion runs 11 and 19: particle size vs. conversion.

Batch-to-Batch Variability

In a previous publication, prior variances were estimated for the four responses of interest in a Bayesian design of experiments (Dubé et al., 1996). Having chosen three identical sampling times in the replicate run, it was possible to calculate new estimates of the variances for all but the batch time response. The batch time response variance could not be calculated, as it required identical conversions, *not* identical sampling times.

For the molecular weight response, a new estimate of the variance was estimated as 3.2×10^8 compared to the prior estimate of 9×10^8. Using a chi-squared test at a confidence level of 95%, the variances did not differ significantly, and hence, altering the prior estimate was not justified. This was also the case for the composition variance, the new estimate being 0.00126, while the prior estimate was 0.0025. Of course, the confidence intervals in both these cases were quite large owing to the low degrees of freedom (2) in the estimation of the variances from the replicate experiment.

Table 10. BA/MMA/VAc Emulsion Replicate Run 19: Particle Size and Number of Particles

Sample	Conversion wt. %	$\bar{D}_n$ 10^6 cm	N_p 10^{-17} No./L Water
12	44.292	8.680	6.962
13	48.978	9.060	6.778
14	54.109	9.240	7.084
15a1	58.630	8.770	8.990
15a2	58.630	9.000	8.315
15a3	58.630	9.060	8.151
15b1	58.512	9.280	7.568
15b2	58.512	9.120	7.976
15b3	58.512	9.410	7.266
15c1	58.685	9.400	7.304
15c2	58.685	9.280	7.591
15c3	58.685	9.280	7.600
16a1	58.293	8.890	8.589
16a2	58.293	9.070	8.074
16a3	58.293	9.180	7.789
16b1	58.430	9.120	7.964
16b2	58.430	9.240	7.662
16b3	58.430	9.150	7.882
16c1	58.640	9.260	7.634
16c2	58.640	9.170	7.862
16c3	58.640	9.190	7.811
17	67.603	9.490	8.182
18	70.153	9.870	7.545

Table 11. BA/MMA/VAc Emulsion Replicate Run 19: Particle Size and Number of Particles

Sample	Conversion wt. %	$\bar{D}_n$ (10^6 cm)	N_p 10^{-17} No./L Water
19	72.900	9.820	7.936
20	77.378	9.750	8.566
21	82.541	10.003	8.395
22a1	91.009	10.030	8.516
22a2	91.009	10.037	8.326
22a3	91.009	10.030	8.511
22b1	90.614	9.990	9.285
22b2	90.614	9.890	9.560
22b3	90.614	9.980	9.304
22c1	90.641	10.007	9.078
22c2	90.641	10.011	8.952
22c3	90.641	10.020	8.730
23a1	90.931	10.020	8.762
23a2	90.931	10.017	8.839
23a3	90.931	10.004	9.160
23b1	91.184	10.032	8.479
23b2	91.184	10.030	8.530
23b3	91.184	10.031	8.505
23c1	91.223	10.018	8.841
23c2	91.223	10.033	8.461
23c3	91.223	10.012	8.995
24	95.524	9.830	10.026

Conclusions

An integral step in any experimental program should be the assessment of the quality and reproducibility of the data. This is often recommended but rarely done. This exercise, while time-consuming, was an important step in the "systematic approach" that was implemented in this study.

The error in the various measurements in this study can be expressed as $x\pm0.77$ wt. %, $\bar{F}_{BA}\pm0.0118$, $\bar{F}_{MMA}\pm0.0290$, $\bar{F}_{VAc}\pm0.0342$, $\bar{M}_n\pm24543$, $\bar{M}_w\pm24061$, and $\bar{D}_n\pm33.1$ Å.

The data in this study were shown to be reproducible. The analytical and experimental techniques used were justified and accurate. These conclusions led to a corollary regarding the various inferences made about the data throughout the study. The trends indicated in the various plots throughout this study are real and are not artifacts due to error. In particular, the "two-stage rate" phenomenon (see, for instance, Figure 1, and Dubé and Penlidis, 1995a–c, 1996, for details) is a real phenomenon detected in the conversion, composition, and molecular weight plots.

The reader may have noted that throughout this article, the presentation of the plotted data did not include any error bars. This was purposefully done in order to keep the plots free from unnecessary clutter. Clearly, the analysis presented

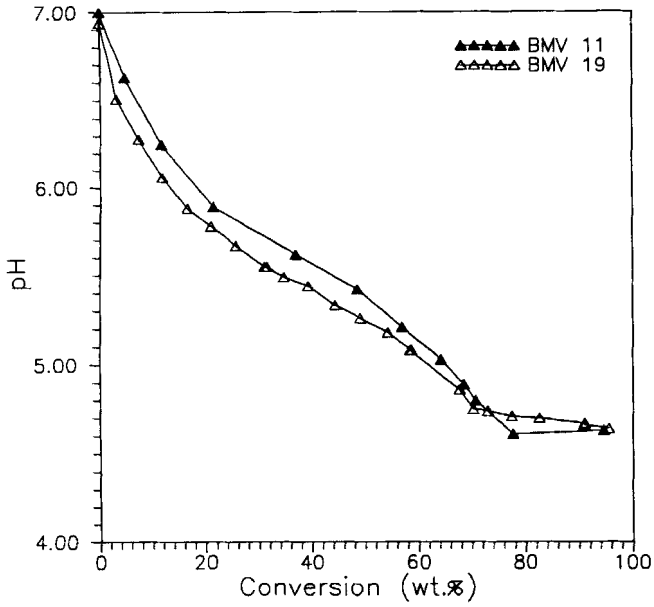

Figure 5. BA/MMA/VAc emulsion runs 11 and 19: pH results.

herein overcompensates for the lack of error bars in the various plots.

Acknowledgments

Financial support from the Natural Sciences and Engineering Research Council (NSERC) of Canada is gratefully acknowledged. Support of this work by ICI, Worldwide, is greatly appreciated. The assistance of Professor Tom Duever is greatly appreciated.

Literature Cited

Box, G. E. P., W. G. Hunter, and J. S. Hunter, *Statistics for Experimenters: An Introduction to Design, Data Analysis and Model Building*, Wiley, Toronto (1978).

Davies, O. L., and P. L. Goldsmith, *Statistical Methods in Research and Production*, Longman, New York (1977).

Devon, M. J., T. Provder, and A. Rudin, "Measurement of Particle Size Distributions with a Disc Centrifuge. Data Analysis Considerations," *Particle Size Distribution: II. Assessment and Characterization*, T. Provder, ed., ACS Symp. Ser. (1991).

Dubé, M. A., "A Systematic Approach to the Study of Multicomponent Polymerization Kinetics," PhD Thesis, Univ. of Waterloo, Waterloo, Ont., Canada (1994).

Dubé, M. A., and A. Penlidis, "A Systematic Approach to the Study of Multicomponent Polymerization Kinetics: The Butyl Acrylate/Methyl Methacrylate/Vinyl Acetate Example I. Bulk Copolymerization," *Polymer*, **36**, 587 (1995a).

Table 12. BA/MMA/VAc Emulsion Replicate Run 19: pH Results

Sample	Conversion Wt. %	pH	Sample	Conversion Wt. %	pH
1	0.000	6.94	13	48.978	5.26
2	3.074	6.51	14	54.109	5.18
3	7.247	6.28	15	58.630	5.08
4	11.769	6.06	16	58.293	5.08
5	16.452	5.88	17	67.603	4.86
6	21.034	5.78	18	70.153	4.75
7	25.634	5.67	19	72.900	4.74
8	31.037	5.55	20	77.378	4.71
9	31.488	5.55	21	82.541	4.70
10	34.723	5.49	22	91.009	4.67
11	39.257	5.44	23	90.931	4.66
12	44.292	5.33	24	95.524	4.64

Dubé, M. A., and A. Penlidis, "A Systematic Approach to the Study of Multicomponent Polymerization Kinetics: The Butyl Acrylate/Methyl Methacrylate/Vinyl Acetate Example: 2. Bulk (and Solution) Terpolymerization," *Macromol. Chem. Phys.*, **196**, 1101 (1995b).

Dubé, M. A., and A. Penlidis, "A Systematic Approach to the Study of Multicomponent Polymerization Kinetics: The Butyl Acrylate/Methyl Methacrylate/Vinyl Acetate Example: 3. Emulsion Homo- and Copolymerization in a Pilot Plant Reactor," *Poly. Int.*, **37**, 235 (1995c).

Dubé, M. A., and A. Penlidis, "Emulsion Terpolymerization of Butyl Acrylate/Methyl Methacrylate/Vinyl Acetate: Experimental Results," *J. Poly. Sci., Poly. Chem. Ed.*, submitted for publication (1996).

Dubé, M. A., A. Penlidis, and K. F. O'Driscoll, "A Kinetic Investigation of Styrene/Butyl Acrylate Copolymerization," *Can. J. Chem. Eng.*, **68**, 974 (1990).

Dubé, M. A., A. Penlidis, and P. M. Reilly, "A Systematic Approach to the Study of Multicomponent Polymerization Kinetics: The Butyl Acrylate/Methyl Methacrylate/Vinyl Acetate Example: IV. Optimal Bayesian Design of Emulsion Terpolymerization Experiments in a Pilot Plant Reactor," *J. Poly. Sci., Poly. Chem. Ed.*, **34**, 811 (1996).

Reilly, P. M., "A Statistical Look at Significant Figures," *Chem. Eng. Educ.*, **26**, 152 (1992).

Scott, P. J., "Ethylene-Vinyl Acetate Semi-Batch Emulsion Polymerization: Kinetics, Reactor Design and Modelling," PhD Thesis, Univ. of Waterloo, Waterloo, Ont., Canada (1992).

Scott, P. J., M. E. Kuindersma, and A. Penlidis, "GPC/HPLC Operating Manual," internal report available from A. Penlidis (1992).

Scott, P. J., A. Penlidis, and G. L. Rempel, "Ethylene-Vinyl Acetate Semi-Batch Emulsion Copolymerization: Experimental Design and Preliminary Screening Experiments," *J. Poly. Sci., Poly. Chem.*, **31**, 403 (1993).

Stickler, M., "Experimental Techniques in Free Radical Polymerization Kinetics," *Makromol. Chem., Macromol. Symp.*, **10/11**, 17 (1987).

Manuscript received Aug. 7, 1995, and revision received Nov. 6, 1995.