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A systematic approach to the study of multicomponent polymerization kinetics—the butyl acrylate/methyl methacrylate/vinyl acetate example: 1. Bulk copolymerization

Marc A. Dubé and Alexander Penlidis*
Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada
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A systematic study of the terpolymerization of butyl acrylate/methyl methacrylate/vinyl acetate (BA/MMA/VAc) is being conducted. In the first stage of this study, bulk copolymerizations of BA/MMA, BA/VAc and MMA/VAc were performed. The polymers produced were characterized for conversion, composition and molecular weight. For the vinyl acetate-containing copolymerizations, during the first period of the reaction the acrylic monomer virtually 'homopolymerized' and thus the reaction exhibited the characteristics of a 'solution' polymerization with the vinyl acetate acting as the 'solvent'. Typical solution polymerization behaviour, i.e. a dampened autoacceleration or gel effect, was in evidence for the first period of the reaction. After the virtual depletion of the acrylic monomer, the remaining vinyl acetate polymerized and exhibited its own characteristic gel effect. We refer to this phenomenon as the 'double gel effect'. Estimates of the copolymerization reactivity ratios were calculated and were found to predict copolymer composition accurately through the full conversion range for each copolymer system. Extremely high-molecular-weight polymer was produced attesting to the high degree of branching in these copolymer systems.

(Keywords: reactivity ratios; copolymerization kinetics; BA/MMA/VAc terpolymerization)

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 modelling and experimental kinetics 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 the bulk, then in solution and finally in the emulsion mode. The data are then compared to a mechanistic model, which will in turn uncover any lack of process understanding and thus direct further experimentation. It is by breaking down (decomposing) 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.

This paper describes the first stage of such a systematic approach for the study of the butyl acrylate/methyl methacrylate/vinyl acetate (BA/MMA/VAc) terpolymerization. Methyl methacrylate[1–5] and vinyl acetate[6–11] bulk and solution homopolymerizations have already been studied at many different conditions, and hence pursuing an investigation of these systems again was not necessary. Butyl acrylate, however, has not received a large amount of experimental attention and a study of its bulk polymerization kinetics was performed[12]. Of the three copolymer pairs of interest (viz. BA/MMA, BA/VAc, MMA/VAc), only one recent study on the solution polymerization of MMA/VAc[13] can be considered as comprehensive.

In this paper, we report the estimation of reactivity ratios for each of the three copolymer systems as well as kinetic data for the full conversion range.

EXPERIMENTAL

Purification of reagents

Purification of reagents was performed by classic methods[14,15]. The initiator 2,2′-azobisisobutyronitrile

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* To whom correspondence should be addressed

(AIBN) (Polysciences Inc.) was recrystallized three times from absolute methanol. The monomers butyl acrylate and methyl methacrylate (Aldrich Chemical Co. Inc.) were washed three times with a 10% sodium hydroxide solution, washed three times with distilled water, dried over calcium chloride and freshly distilled under vacuum at most 24 h before use and stored at −10°C. The monomer vinyl acetate (Aldrich Chemical Co. Inc.) was distilled under vacuum at most 24 h before use and stored at −10°C. All of the solvents used over the course of the experiments and for characterization of the copolymers (toluene, ethanol, chloroform-d, tetrahydrofuran (THF)) were used as packaged without further purification.

Reactivity ratio experiments

The experiments were carried out in borosilicate glass ampoules (capacity ~10 ml). The monomers and initiator were weighed and then pipetted into the ampoules. The ampoules were degassed by several vacuum-freeze–thaw cycles and subsequently submerged in a 60°C water bath for a recorded time interval. The ampoules were then weighed, submerged in liquid nitrogen, scored, broken and the contents poured into a 10-fold excess of ethanol. The empty ampoules were then reweighed. The precipitated copolymer was dried in a vacuum oven at 40°C until a constant weight was reached.

The design of the experiments followed the criterion proposed by Tidwell and Mortimer[16], which is based on the sensitivity of the reactivity ratio estimates to the errors encountered in the determination of copolymer composition. Their recommended design is to run several replicates at two different monomer feed compositions. According to the criterion, the initial mole fractions of the monomer designated as monomer 1 are given by:

$$f'_{10}=2/(2+r_1) \qquad (1)$$

and

$$f''_{10}=r_2/(2+r_2) \qquad (2)$$

Initial guesses for the reactivity ratios r_1 and r_2 needed by the above equations were obtained from a recalculation of reactivity ratios based on literature data using an error-in-variables model (EVM) microcomputer program developed specifically for the estimation of reactivity ratios[17]. For our study, the values for the initial guesses, their source and the resulting design points are shown in *Table 1*. Throughout this paper, monomer 1 refers to the first monomer mentioned, e.g. for BA/MMA, monomer 1 refers to BA.

Four replicate runs at each design point were performed to mass conversions not exceeding 5%. The conversion was based on total polymer and was measured by gravimetry. The resulting copolymers were isolated as described above and analysed for cumulative polymer composition by proton nuclear magnetic resonance (^{1}H n.m.r.) spectroscopy.

Table 1 Experimental design: reactivity ratio estimation

Copolymer	Source	r_1	r_2	f'_{10}	f''_{10}
BA/MMA	Ref. 18	0.507	2.375	0.798	0.543
BA/VAc	Ref. 19	3.393	0.0565	0.371	0.0275
MMA/VAc	Ref. 20	17.340	0.0253	0.103	0.0125

Full conversion range experiments

The experiments performed through the full range of conversion were carried out in borosilicate glass ampoules of length 10 cm and of outer diameter 1.7 cm. The initial monomer feed was prepared by weighing the monomers and initiator into a flask and pipetting the contents into several numbered ampoules. The ampoules were then treated exactly as in the reactivity ratio experiments. Some of the higher-conversion samples (>60%) were either in a glassy or rubbery state and hence the extraction of residual monomer from them was not possible using the same methods as for low-conversion samples. Upon removing these high-conversion ampoules from the water bath, the ampoules were frozen, broken and the frozen polymer/monomer mixture was weighed. These high-conversion samples were placed in toluene at −10°C until dissolved, precipitated in a 10-fold excess of ethanol and finally dried to constant weight in a vacuum oven at 40°C.

Full conversion range experiments were run for the three copolymer pairs at 60°C. The BA/VAc copolymerization was run at a feed mole fraction of BA of 0.798 and initiator concentration of 0.000 54 mol l^{-1}. The MMA/VAc copolymerization was run at a feed mole fraction of MMA of 0.3 and initiator concentration of 0.01 mol l^{-1}. A 2^2 factorial experiment as well as a replicate run were performed in the case of the BA/MMA copolymer. The design factors and their levels were as follows: initiator concentration 0.01 and 0.005 mol l^{-1}, monomer feed (mole fraction BA) 0.163 and 0.439. The replicate run conditions were at 0.005 mol l^{-1} initiator and 0.439 mole fraction of BA.

Conversion was determined by gravimetry and was based on total polymer. The isolated copolymers were analysed for cumulative polymer composition by ^{1}H n.m.r. spectroscopy and for cumulative number- and weight-average molecular weight by gel permeation chromatography (g.p.c.).

Characterization

For this study, a 300 MHz AC Bruker Fourier-Transform ^{1}H n.m.r. spectrometer was used. Analysis was carried out in deuterated chloroform (~2% (w/v) solutions) at room temperature. The relative amounts of monomer bound in the copolymer were estimated from the areas under the appropriate absorption peaks of the spectra. For the case of the BA/MMA system, the spectral peaks for the $-OCH_2$ group in BA were located at ~4.0 ppm and the $-OCH_3$ group in MMA was at ~3.6 ppm. The BA/VAc system spectra exhibited peaks for the α hydrogen in VAc at ~4.9 ppm and the $-OCH_2$ group in BA at ~4.0 ppm. Finally, for the MMA/VAc case, the spectra showed peaks for the α hydrogen in VAc at ~5.0 ppm and the $-OCH_3$ group in MMA at ~3.6 ppm. *Figure 1* shows sample spectra for the BA/MMA system and is representative of the good peak separation that was achieved. All our spectra exhibited good peak separations, thus allowing the unambiguous interpretation of the results. For the sake of brevity, sample spectra for the other two copolymers are not shown. The reader can find more details in reference 21.

A Waters Associates Gel Permeation Chromatograph was used to measure molecular-weight averages. Three Waters Ultrastyragel columns (10^3, 10^4 and 10^6 Å) were

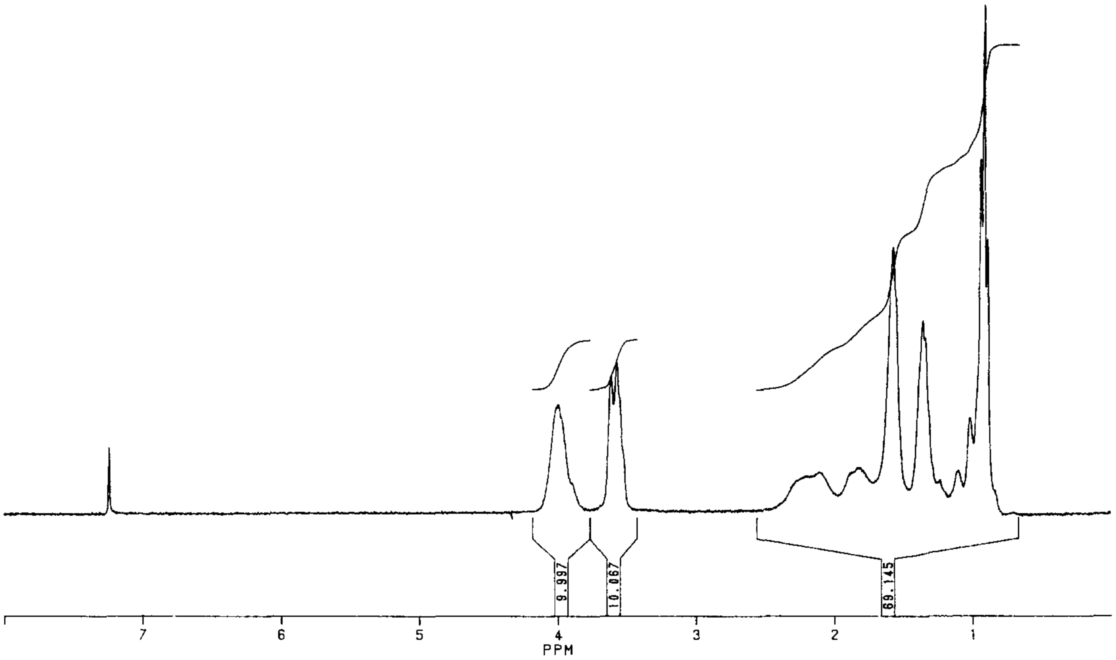

Figure 1 BA/MMA, ${}^1H$ n.m.r. spectrum

installed in series. Tetrahydrofuran (THF) (Caledon reagent grade), degassed and filtered, was used as the eluent. Samples were prepared in THF (~0.2% 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[22].

RESULTS

Reactivity ratio estimation

The monomer feed, final conversion and copolymer composition for each sample are shown in *Tables 2–4* for the three copolymer pairs.

The analysis of the data was performed using two different computational tools. First, the data were analysed using a program developed 'in house' known as RREVM[17]. RREVM employs the Mayo–Lewis equation:

$$\frac{F_1}{F_2}=\frac{(r_1[M_1]+[M_2])[M_1]}{([M_1]+r_2[M_2])[M_2]} \tag{3}$$

where F_1 and F_2 are the overall instantaneous mole fractions of monomer 1 and monomer 2 in the copolymer, respectively, and $[M_i]$ is the concentration of monomer i in the reaction mixture. RREVM considers the measurement error in both the dependent and independent variables, i.e. the copolymer composition and the feed composition, respectively.

The second analysis was performed with a program that uses the Meyer–Lowry integrated copolymer composition equation:

$$x=1-\left(\frac{f_1}{f_{10}}\right)^{\alpha}\left(\frac{1-f_1}{1-f_{10}}\right)^{\beta}\left(\frac{f_{10}-\delta}{f_1-\delta}\right)^{\gamma} \tag{4}$$

Table 2 Experimental results: BA/MMA copolymerization (step 1)

f_{10}	F_1	Conversion (%)
0.798	0.598	1.084
0.798	0.606	1.146
0.798	0.594	0.896
0.798	0.599	1.194
0.543	0.385	0.433
0.543	0.343	0.357
0.543	0.335	0.406
0.543	0.341	0.297

Table 3 Experimental results: BA/VAc copolymerization

f_{10}	F_1	Conversion (%)
0.371	0.809	3.873
0.371	0.802	4.220
0.371	0.820	3.367
0.371	0.811	3.718
0.0273	0.377	4.808
0.0273	0.377	4.847
0.0273	0.373	4.932
0.0273	0.379	4.854

Table 4 Experimental results: MMA/VAc copolymerization

f_{10}	F_1	Conversion (%)
0.103	0.751	3.786
0.103	0.751	3.782
0.103	0.734	3.972
0.103	0.775	4.124
0.0126	0.312	2.094
0.0126	0.298	2.465
0.0126	0.293	2.671
0.0126	0.296	2.726

Here x denotes monomer conversion, $f_{1 0}$ is the initial mole fraction of monomer 1, f_1 is the mole fraction of monomer 1 and:

$$\alpha = \frac{r_2}{1 - r_2} \tag{5}$$

$$\beta = \frac{r_1}{1 - r_1} \tag{6}$$

$$\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)} \tag{7}$$

$$\delta = \frac{1 - r_2}{2 - r_1 - r_2} \tag{8}$$

This analysis was performed in order to validate the use of the Mayo–Lewis equation for copolymer composition. That is, when comparing the results from both types of analysis, any significant differences would indicate that the composition drift in the samples was too large to use the differential form (Mayo–Lewis) rather than the integrated form (Meyer–Lowry) of the composition equation. The results of the analyses are reported in *Table 5* and discussed below.

Reactivity ratio experiments

Butyl acrylate/methyl methacrylate (BA/MMA). Using a simulation program currently under development, a series of cumulative copolymer composition curves were generated for the BA/MMA system at various monomer feed levels using the reactivity ratios estimated in this work using RREVM (see *Table 5*). This series of curves is plotted in *Figure 2*. From *Figure 2*, it is evident that the use of the differential copolymer composition equation is justified owing to the limited amount of composition drift at low conversions. In fact, the experiments performed for this system were conducted to conversions lower than 1.2% (see *Table 2*).

The results of the parameter estimations using the analyses described earlier are shown in *Table 5*. It is evident from the use of the integrated copolymer composition equation that composition drift did not play a significant role in these experiments. In fact, the minor differences in the reactivity ratio estimates may be attributed to the fact that the integrated equation program does not employ the EVM method (it employs a straightforward non-linear least-squares algorithm).

The 95% posterior probability contour for the reactivity ratio estimates obtained using RREVM is plotted in *Figure 3*. Various reactivity ratio estimates from the literature are shown in *Table 6*. For the cases where the data were published, the results were reanalysed using RREVM and the reactivity ratios are included in the table. The reactivity ratios estimated in this study fall within the range of published values (see *Tables 5* and *6*).

Table 5 Results: reactivity ratio analysis

Copolymer	Analysis	r_1	r_2
BA/MMA	RREVM	0.2976	1.7894
	Integrated equation	0.2936	1.7773
BA/VAc	RREVM	5.9388	0.02622
	Integrated equation	5.9582	0.01443
MMA/VAc	RREVM	24.0254	0.02611
	Integrated equation	26.1975	0.01526

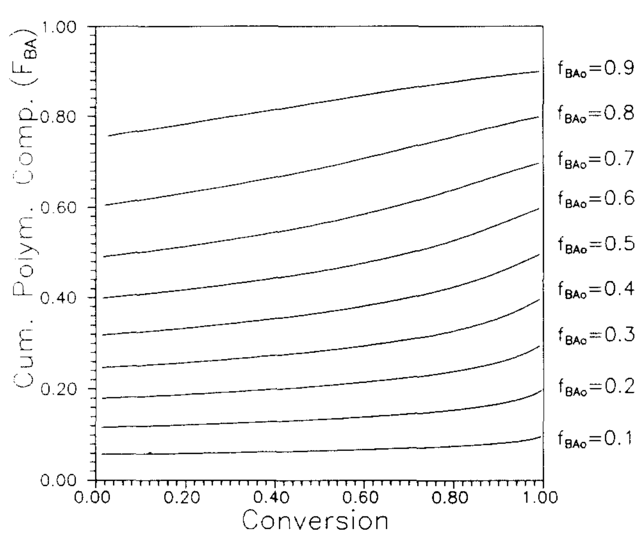

Figure 2 BA/MMA, cumulative polymer composition curves at various monomer feed concentrations

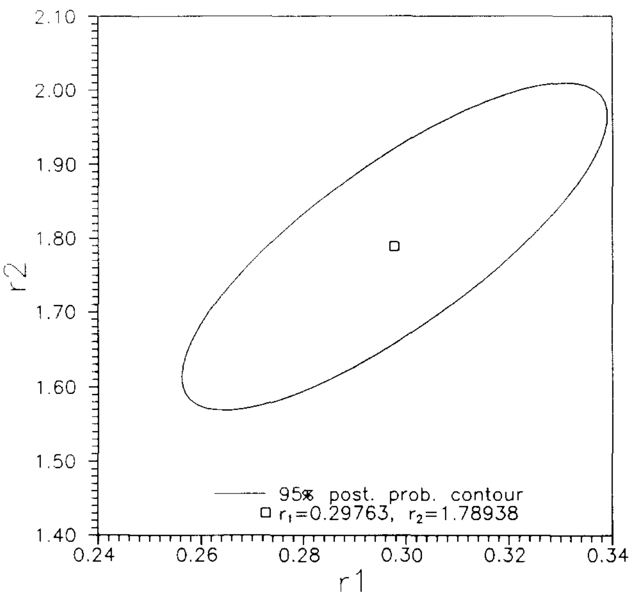

Figure 3 BA/MMA, reactivity ratios: 95% posterior probability contour

The Tidwell–Mortimer experimental design is considered to be an iterative procedure. In order to test this design procedure, an additional set of reactivity ratio experiments were performed for this copolymer system. The iterative sequence of reactivity ratio experiments for the BA/MMA system started with the re-estimation of reactivity ratios based on the data of ref. 18 using RREVM. These re-estimated reactivity ratios were then used as the initial guesses for the Tidwell–Mortimer criterion (see equations (1) and (2)). The resulting feed compositions were the design levels for the experiments of the first step of this work (see *Table 2*). The experiments from step 1 were subsequently analysed using RREVM (see *Table 5*). The reactivity ratio estimates from step 1 were used as initial guesses for the Tidwell–Mortimer criterion and new feed compositions were obtained for

Table 6 Literature values of reactivity ratios: BA/MMA copolymers

Source	r_1	r_2	Conditions
Ref. 23	0.20	1.74	60°C, bulk
Ref. 24	0.105	2.75	55°C, solution
ibid. RREVM	0.128	2.552	
Ref. 25	0.23	2.3	
Ref. 18	0.37	1.8	60°C, bulk
ibid. RREVM	0.507	2.375	

Table 7 Experimental results: BA/MMA copolymerization (step 2)

f_{10}	F_1	Conversion (%)
0.472	0.290	2.850
0.472	0.282	1.999
0.472	0.277	3.325
0.472	0.281	2.933
0.870	0.761	10.538
0.870	0.775	9.756
0.870	0.765	10.490
0.870	0.772	10.102

Table 8 Reactivity ratios: BA/MMA copolymerizations

Analysis	Data source	r_1	r_2
RREVM	Ref. 18	0.507	2.375
RREVM	Step 1: this work	0.298	1.789
RREVM	Step 2: this work	0.523	2.44
Meyer–Lowry	This work: all data	0.355	1.979

step 2 (step 2 of the reactivity ratio estimation for the BA/MMA system was part of an undergraduate design project[26]). The results of these experiments (step 2) are shown in *Table 7*. As mentioned above, the composition drift for this system is negligible for conversions below 40% and hence the higher conversion levels for four of the samples in *Table 7* are not expected to affect the results. The results were then analysed using RREVM. A summary of all of the reactivity ratio experiments and analyses for the BA/MMA system from this study is reported in *Table 8*. Step 2 yielded reactivity ratios similar to the re-estimated values of ref. 18 (i.e. compare rows 1 and 3 of *Table 8*). This, in effect, brought the experimental design levels back to those of the first step! The final entry in *Table 8* is the estimation of the reactivity ratios using all of the data generated in this work. These data include data from the two steps in the reactivity ratio estimation described earlier and all of the high-conversion data shown below. The final estimates of the reactivity ratios fall between the values estimated in the two iterative steps. A sensitivity analysis has revealed that, for the BA/MMA case, even at high conversion levels, the prediction of composition is not compromised severely with the use of either of the reactivity ratios shown in *Table 8*. The cycling behaviour of the design levels for the reactivity ratio estimation is currently under further scrutiny.

Butyl acrylate/vinyl acetate (*BA/VAc*). As in the case of the BA/MMA system, a family of cumulative polymer composition curves was generated and are plotted in *Figure 4*. There is little composition drift at high BA monomer feeds, but the drift becomes significant even at low conversions when the VAc content is high in the feed. From *Tables 1* and *3*, one notices that there may be significant composition drift for the last four experiments of *Table 3* owing to their high VAc content. While the conversion levels did not go above 5%, there may still be cause for concern owing to the steep nature of the composition drift curve in *Figure 4* for initial mole fractions of BA around or below 0.1.

The parameter estimation results for the BA/VAc copolymerizations are shown in *Table 5*. The analysis performed with the integrated copolymer composition equation did not alter the estimation for r_1 to any significant degree but that for r_2 differs from the RREVM result. While one may attribute this discrepancy to composition drift, it is unwise to draw any hard conclusions in this case owing to the fact that r_1 and r_2 differ by three orders of magnitude and are highly correlated.

The 95% posterior probability contour for the estimates obtained using RREVM is plotted in *Figure 5*. Various

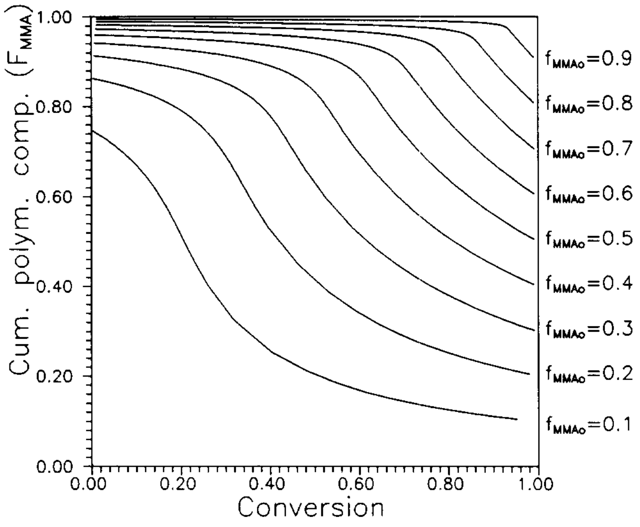

Figure 4 BA/VAc, cumulative polymer composition curves at various monomer feed concentrations

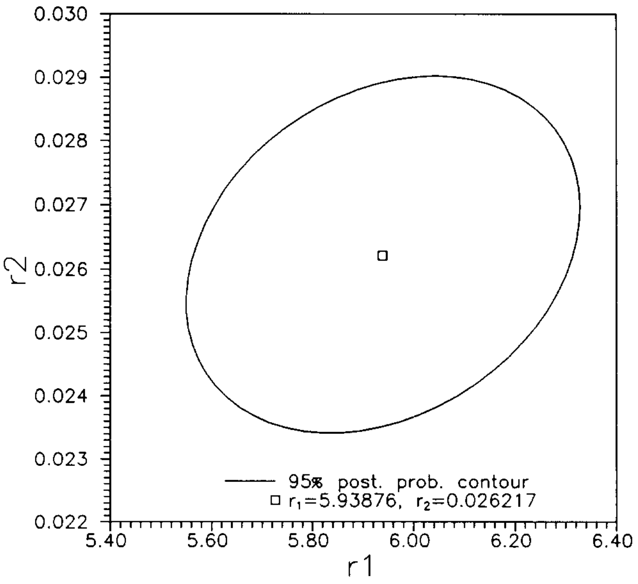

Figure 5 BA/VAc, reactivity ratios: 95% posterior probability contour

Table 9 Literature values of reactivity ratios: BA/VAc copolymers

Source	r_1	r_2	Conditions
Ref. 27	10.67	0.024	60°C, emulsion
ibid. RREVM	8.777	0.0265	
Ref. 28	2.92	0.02	70°C, ^{13}C n.m.r.
Ref. 29	8	0	68.4°C, emulsion
Ref. 19	3.07	0.06	70°C, bulk
ibid. RREVM	3.393	0.0565	
Ref. 30	5.50	0.040	60°C, emulsion
ibid. RREVM	7.330	0.247	

Table 10 Literature values of reactivity ratios: MMA/VAc copolymers

Source	r_1	r_2	Conditions
Ref. 31	28.6	0.035	30°C, bulk
Ref. 32	29.9	0.0445	60°C, bulk
Ref. 33	26	0.03	60°C, solution
Ref. 20	24	0.029	49°C, bulk
ibid. RREVM	17.340	0.0253	
Ref. 34	22	0.04	
Ref. 35	21.2	0.016	60°C, bulk
Ref. 36	2.710	−0.200	60°C, bulk
ibid. RREVM	2.577	−0.2254	
Ref. 37	22.21	0.072	60°C
Ref. 38	2.77	0.11	80°C
Ref. 39	181		30°C
ibid.	127		60°C
Ref. 40	27.8	0.014	

reactivity ratio estimates from the literature are shown in *Table 9*. For the cases where the data were published, the results were reanalysed using RREVM and the reactivity ratios are included in the table. For the BA/VAc system, there is a wide range of reactivity ratio estimates. This variation can be attributed to the use of emulsion polymerization data to calculate reactivity ratios without taking into account the partitioning of the monomers in the different phases. As well, improper statistical techniques have persisted in the literature and this system is no exception. The estimates from the present study fall within the range of the literature values (see *Tables 5* and *9*).

Methyl methacrylate/vinyl acetate (MMA/VAc). The cumulative polymer composition curves for the MMA/VAc system in *Figure 6* show an even more significant composition drift than the BA/VAc system at low acrylic monomer feed levels (compare with *Figure 4*). In this case, all eight experiments need to be carefully scrutinized as their MMA feed levels are such that these runs are susceptible to large drifts in composition (see *Table 4*). As in the case of the BA/VAc experiments, the conversion levels are low (see *Table 4*), but the steepness of the composition curves still indicates the possibility of drift (see *Figure 6*).

The results of the parameter estimation are shown in *Table 5*. From this table, it appears that composition drift may have affected the reactivity ratio estimations, although the extent of this effect may be considered negligible by some. The prediction of composition to high conversion levels using these estimates will bring their validity to bear.

The 95% posterior probability contour for the estimates obtained using RREVM is plotted in *Figure 7*. Various reactivity ratio estimates from the literature are shown in *Table 10*. For the cases where the data were published, the results were reanalysed using RREVM and the reactivity ratios are included in the table. The literature values and those estimated in this study compare favourably (see *Tables 5* and *10*). Worthy of note are the estimates by ref. 35, as they also used the Tidwell–Mortimer criterion to obtain their values. Their results are quite close to those of the present study. Also, there is a remarkable agreement between our estimates and those used by Ma *et al.*[40].

Full conversion range experiments

Butyl acrylate/methyl methacrylate (BA/MMA). The feed compositions for the BA/MMA full conversion range experiments were chosen based on a number of criteria. The first composition, $f_{10} = 0.439$, corresponded to a 1:1 weight ratio of the two monomers. This ratio of the acrylic monomers is identical to that in the terpolymerization

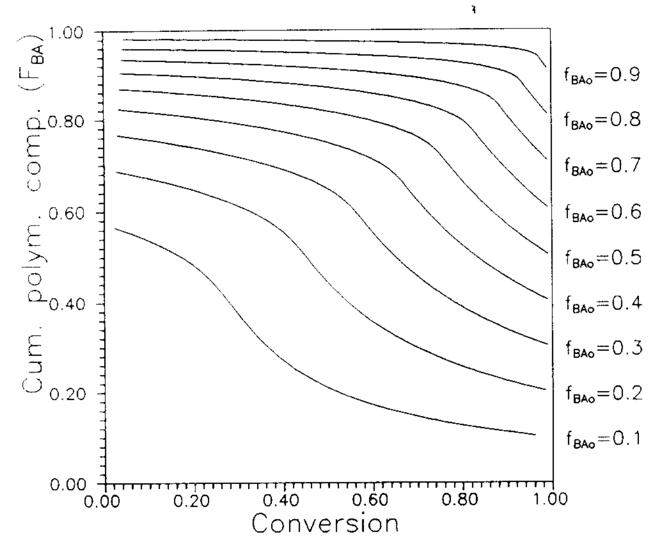

Figure 6 MMA/VAc, cumulative polymer composition curves at various monomer feed concentrations

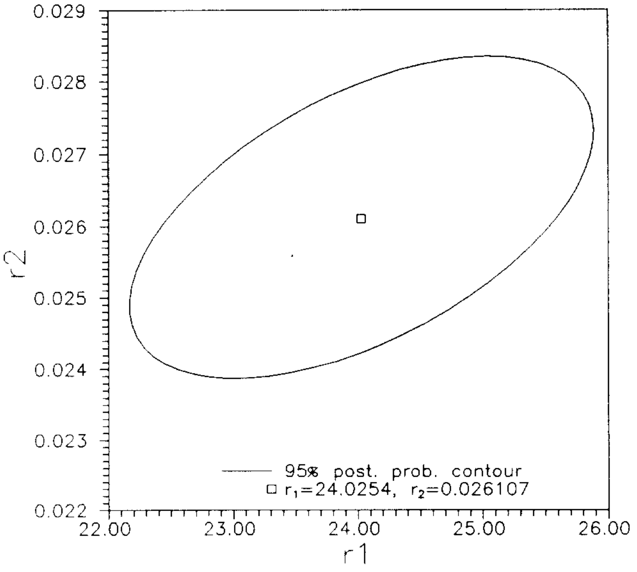

Figure 7 MMA/VAc, reactivity ratios: 95% posterior probability contour

experiments that are to be performed. The second composition, $f_{10} = 0.163$, was chosen in order to minimize the composition drift. This was done in order to simplify the molecular-weight analyses.

Results of the BA/MMA full conversion range experiments are reported in *Tables 11* and *12*. The experiments were run as part of an undergraduate design project[26]. Conversion vs. time plots for this system are shown in *Figures 8* and *9*. These figures reveal the typical S-shaped curve encountered during diffusion-controlled polymerization reactions. As an example, *Figure 9* indicates that, for the higher initiator concentration, during the first 30% of conversion, the reaction proceeds as a chemically controlled reaction (note the nearly linear behaviour). As conversion increases, the reaction becomes translational diffusion-controlled and the resultant decrease in the termination rate causes the autoacceleration or gel effect. Visual observations during the experiments confirmed that there was a marked increase in the viscosity of the reaction medium. Comparing *Figures 8* and *9*, it is also evident that the more BA there is in the system, the slower the reaction rate (this is in agreement with the reactivity ratio estimates of *Table 5*). Finally, these figures also reveal the expected trend that an increase in initiator concentration results in higher polymerization rates.

Figure 10 is a plot of the composition data for all of the BA/MMA experiments. The terminal model predictions of the data are quite good. The predictions employ the reactivity ratios estimated in this work (see *Table 5*) and thus support their validity. The composition drift for the conditions used for this system is low.

Table 11 Experimental results: BA/MMA copolymerizations

Time (min)	Conversion (wt%)	F_1	$\bar{M}_n(10^3)$	$\bar{M}_w(10^3)$
$f_{10} = 0.439$, [AIBN] = 0.005 M				
75	8.9	0.261	435	1020
150	22.0	0.281	489	1113
180	29.2	0.305	596	1208
210	33.6	0.288	728	1429
240	67.0	0.354	251	1327
285	79.1	0.349	655	2055
360	94.1	0.426	922	2447
435	96.6	0.411	–	–
$f_{10} = 0.439$, [AIBN] = 0.005 M, replicate				
60	9.3	0.258	516	900
120	19.3	0.258	481	979
180	36.5	0.317	649	1374
220	60.3	0.295	323	1440
230	65.2	0.326	290	1460
260	84.3	0.374	550	1982
320	95.9	0.407	935	2475
480	98.7	0.426	–	–
$f_{10} = 0.439$, [AIBN] = 0.01 M				
60	13.8	0.344	316	943
120	26.5	0.316	237	804
150	41.3	0.341	346	852
180	53.1	0.324	477	1185
210	87.9	0.347	491	1543
270	97.1	0.390	694	2156
360	102.8	0.415	–	–

Table 12 Experimental results: BA/MMA copolymerizations

Time (min)	Conversion (wt%)	F_1	$\bar{M}_n(10^3)$	$\bar{M}_w(10^3)$
$f_{10} = 0.163$, [AIBN] = 0.005 M				
70	10.5	0.078	435	809
140	21.1	0.087	340	897
145	24.1	0.065	352	847
170	29.2	0.097	502	1031
200	36.5	0.092	352	1230
215	94.1	0.110	440	1836
230	83.0	0.096	398	1813
260	101.3	0.115	1021	2719
280	101.6	0.160	1092	2717
350	101.5	0.146	914	2724
$f_{10} = 0.163$, [AIBN] = 0.01 M				
60	12.3	0.099	216	583
105	22.2	0.098	310	614
125	28.5	0.114	222	620
165	73.5	0.123	225	980
195	102.8	0.115	753	2236
200	100.8	0.202	678	1924
240	106.8	0.135	803	2572
270	106.5	0.151	794	2358

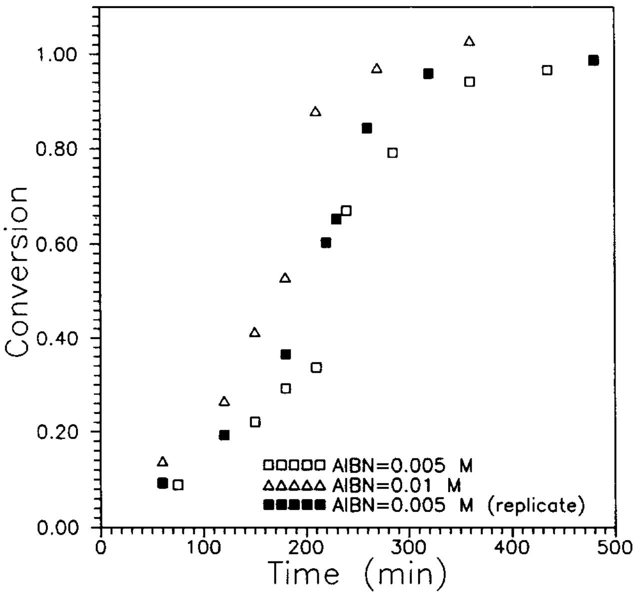

Figure 8 BA/MMA, $f_{10} = 0.439$, 60°C, conversion vs. time

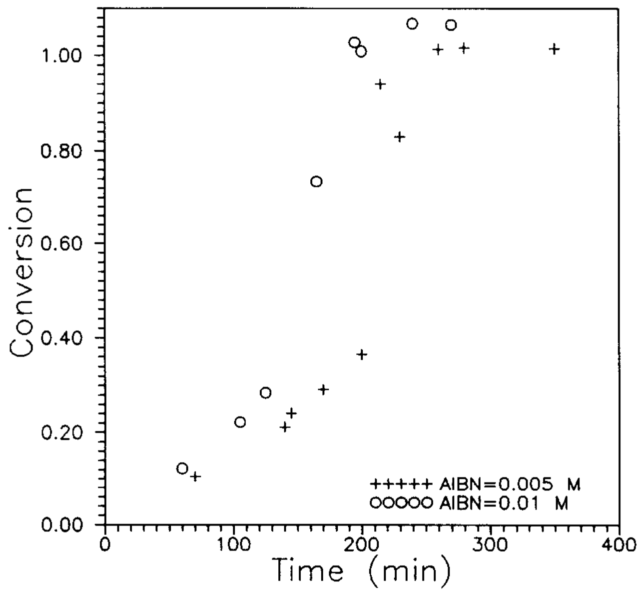

Figure 9 BA/MMA, $f_{10} = 0.163$, 60°C, conversion vs. time

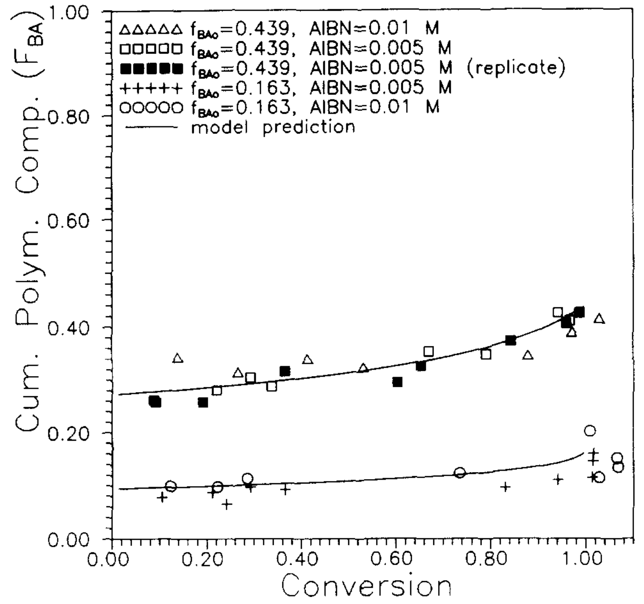

Figure 10 BA/MMA, 60°C, cumulative polymer composition vs. conversion

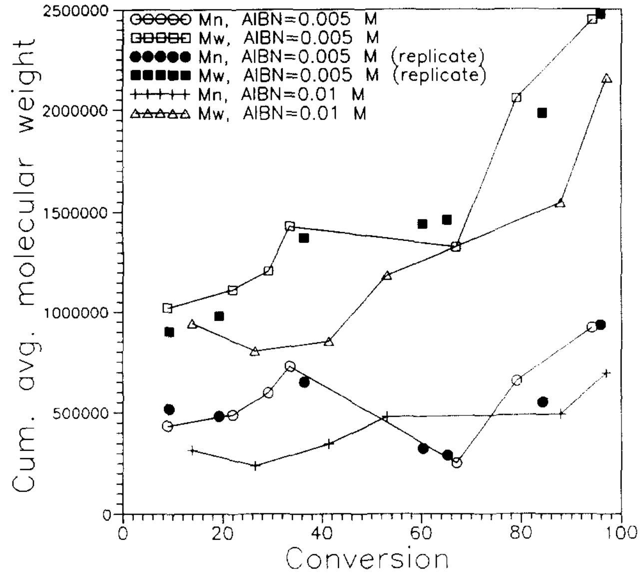

Figure 11 BA/MMA, f_{10} = 0.439, 60°C, cumulative average molecular weights vs. conversion

Molecular-weight results are plotted in *Figures 11* and *12*. (Note that the fall lines in the plots are not model predictions but only serve to make the graphs more readable.) The trends of the molecular-weight results are in line with theory: higher initiator concentrations resulted in lower molecular-weight averages. The cumulative weight-average molecular weights for the BA/MMA copolymers ranged from 0.58×10^6 to 2.7×10^6. These high values attest to the branching reactions associated with the butyl acrylate monomer.

The reproducibility of these experiments was confirmed with the replicate experiment (see *Figures 8*, *10* and *11*).

Butyl acrylate/vinyl acetate (*BA/VAc*). As was the case for BA/MMA, there are no comprehensive kinetic studies for the BA/VAc system in the literature. It was therefore decided, in the interest of minimizing composition drift in order to simplify the molecular-weight analyses, that the BA/VAc run be performed at a feed composition of $f_{10} = 0.8$.

The results from the BA/VAc run are cited in *Table 13*. In *Figure 13* are plotted the conversion vs. time results. The BA/VAc copolymerization exhibited the phenomenon that we refer to as the 'double gel effect'. That is, during the first period of the reaction, the copolymerization proceeded virtually as a BA 'homopolymerization' and exhibited the characteristics of a 'solution' polymerization with the VAc acting as the 'solvent'. At the point where the acrylic monomer concentration had gone to almost zero (see *Figure 13* at about 240 min), the remaining vinyl acetate monomer polymerized and exhibited its own characteristic gel effect. The 'double gel effect' phenomenon is attributed to the widely differing monomer and radical reactivities. As shown earlier in

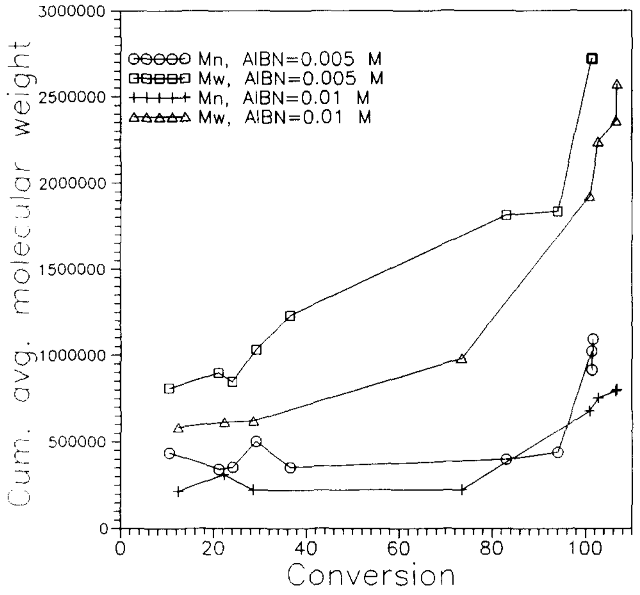

Figure 12 BA/MMA, f_{10} = 0.163, 60°C, cumulative average molecular weights vs. conversion

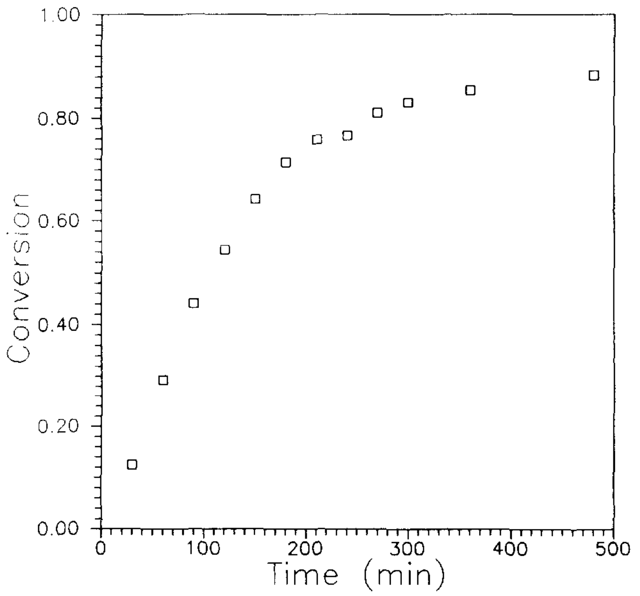

Figure 13 BA/VAc, f_{10} = 0.8, 60°C, [AIBN] = 0.00054 M, conversion vs. time

Table 13 Experimental results: BA/VAc copolymerizations

Time (min)	Conversion (wt%)	F_1	$\bar{M}_n(10^3)$	$\bar{M}_w(10^3)$
30	12.5	0.939	2061	3808
60	29.3	0.932	2490	3886
90	44.1	0.916	2082	3752
120	54.5	0.949	–	–
150	64.3	0.944	–	–
180	71.4	0.907	–	–
210	75.8	–	–	–
240	76.6	0.934	–	–
270	81.1	–	–	–
300	83.1	–	–	–
360	85.5	0.956	–	–
480	88.4	0.930	–	–

Table 14 Experimental results: MMA/VAc copolymerizations

Time (min)	Conversion (wt%)	F_1	$\bar{M}_n(10^3)$	$\bar{M}_w(10^3)$
30	1.5	0.906	117	207
60	3.4	0.887	114	198
90	5.1	0.884	103	180
120	6.7	0.910	118	190
180	9.7	0.882	97	169
240	12.7	0.877	87	175
300	15.3	0.898	101	174
390	19.0	0.840	98	176
510	26.4	0.859	98	188
630	30.3	0.831	85	156
693	28.8	0.894	84	161
810.5	32.3	0.813	84	160
930	33.7	0.850	85	160
1058	37.7	0.822	86	159
1161	41.1	0.854	102	172
1282	56.4	0.522	136	579
1365	95.1	0.338	–	–
1440	96.2	0.322	–	–

Table 5, the reactivity ratios for this system are different by at least two orders of magnitude. It is noted that VAc is being incorporated into the copolymer chains throughout the reaction, but during the early part of the reaction it is only reacting in small quantities relative to the acrylic monomer.

The cumulative polymer composition is plotted in *Figure 14*. For the reaction conditions used in this study, the BA/VAc cumulative polymer composition did not drift significantly until the reaction was well above 90% conversion. The model prediction confirms the accuracy of the reactivity ratios estimated earlier (see *Table 5*).

In *Table 13*, molecular-weight analyses for only three samples are reported. This is due to the fact that extremely high-molecular-weight material was being produced and the higher-conversion samples would not completely dissolve in the g.p.c. solvent, THF. Weight-average molecular weights of 3.5×10^6 were found for the BA/VAc copolymerization at low conversion levels. These high molecular weights are indicative of the branching reactions such as transfer to polymer and terminal double-bond reactions, which are common to both butyl acrylate and vinyl acetate.

Methyl methacrylate/vinyl acetate (MMA/VAc). MMA/VAc has been studied in solution at $f_{10}=0.5$ and $f_{10}=0.09$[13]. Composition and molecular-weight results were reported, but the reactions were only conducted to conversion levels of about 50%. It was therefore decided that a run should be performed at different conditions, viz. $f_{10}=0.3$, in order to complement the other study.

The gravimetric, composition and molecular-weight results are shown in *Table 14*. As in the case of the BA/VAc system, the MMA/VAc copolymerization exhibits a (much more pronounced) 'double gel effect' (see *Figure 15*). This is due to the large difference in reactivity ratios for this system, viz. $r_1=24.0254$, $r_2=0.02611$ (see *Table 5*). As in the BA/VAc case, the acrylic monomer (MMA) polymerization dominates the reaction until it is nearly depleted. In *Figure 15*, at about the 1000 min mark, one sees that a mass conversion of about 30% has been achieved. This corresponds to the mole fraction of 30% MMA in the feed. The MMA reacts as a virtual solution MMA homopolymerization with its characteristic gel

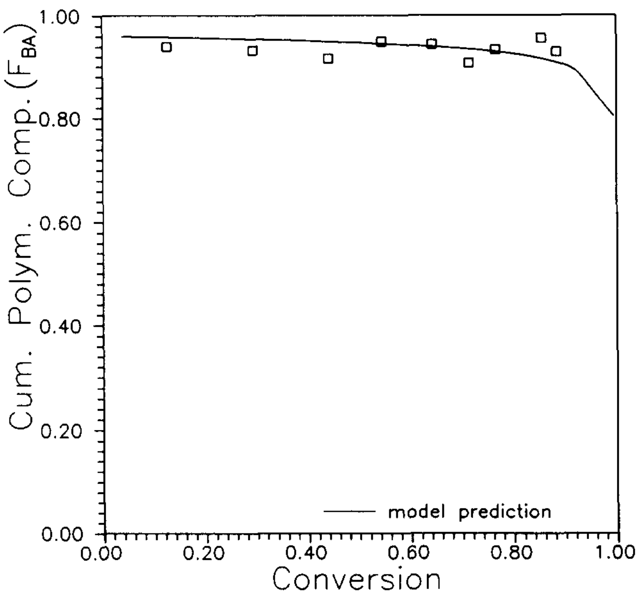

Figure 14 BA/VAc, $f_{10}=0.8$, 60°C, [AIBN] = 0.00054 M, cumulative polymer composition vs. conversion

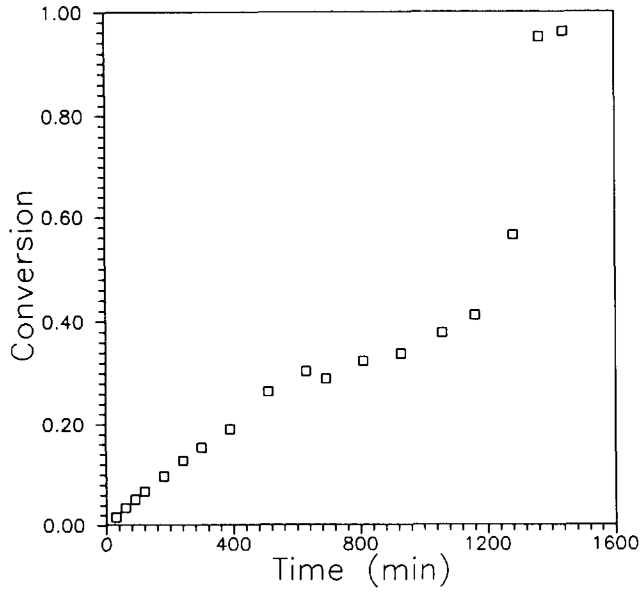

Figure 15 MMA/VAc, $f_{10}=0.3$, 60°C, [AIBN] = 0.01 M, conversion vs. time

effect dampened by the VAc, which acts more or less as a solvent. After the near-depletion of the acrylic monomer, the polymerization continues with the VAc homopolymerizing and exhibiting its own characteristic gel effect until the completion of the reaction. The VAc homopolymerization rate is very high owing to the fact that the reaction is now translational diffusion-controlled as a result of the presence of the MMA polymer, which prevents movement of the copolymer chains. As in the BA/VAc case, it is stressed that the VAc is incorporated into the copolymer at all times, but during the first part of the reaction or the acrylic virtual homopolymerization very little VAc is incorporated into the copolymer as indicated by its low reactivity ratio.

Figure 16 shows the cumulative polymer composition results. The model predictions are quite good, thus confirming the reactivity ratios estimated earlier (see *Table 5*). The MMA/VAc copolymerization exhibited significant composition drift as early as 40% conversion. The drift was visually confirmed by the cloudiness of the samples. Inhomogeneities in composition tend to alter various properties of the copolymer; in this case, optical quality (transparency) is destroyed. The conversion levels at which the composition drift occurred coincided with the 'double gel effect' phenomenon. That is, the composition drift began to occur when the acrylic monomer had been virtually depleted (see *Figure 15*).

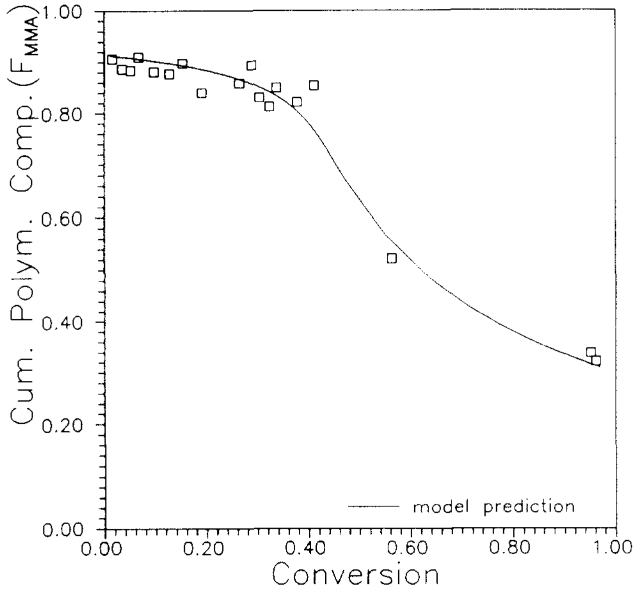

Figure 16 MMA/VAc, $f_{10}=0.3$, 60°C, [AIBN] = 0.01 M, cumulative polymer composition vs. conversion

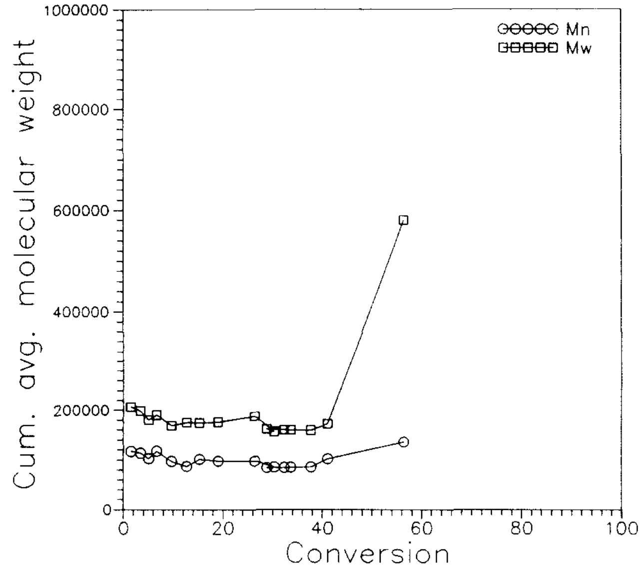

Figure 17 MMA/VAc, $f_{10}=0.3$, 60°C, [AIBN] = 0.01 M, cumulative average molecular weights vs. conversion

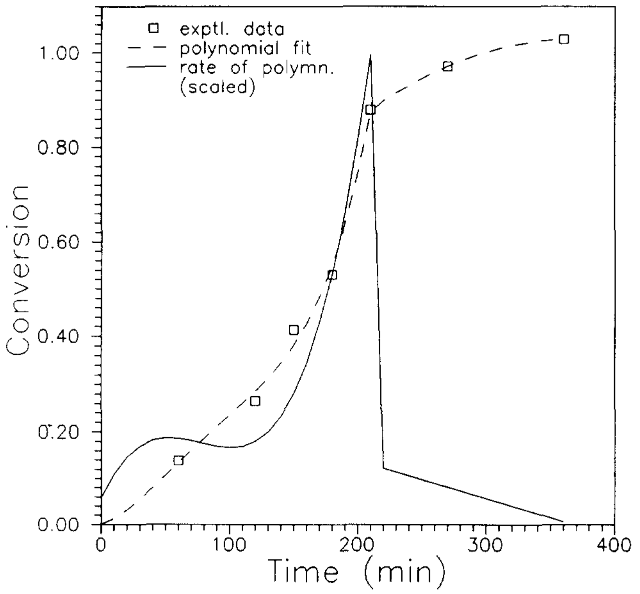

Figure 18 BA/MMA, rate of polymerization

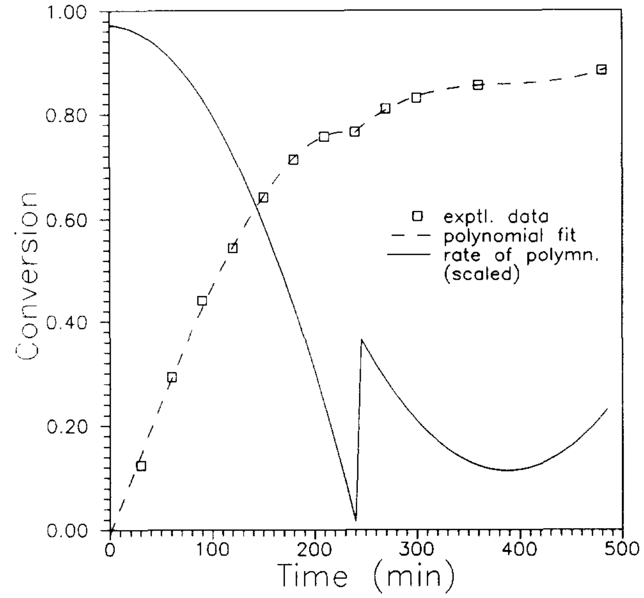

Figure 19 BA/VAc, rate of polymerization

The MMA/VAc copolymerization yielded molecular weights ranging from 1.5×10^5 to 5.8×10^5, as shown in *Table 14* and *Figure 17*. As was the case for the BA/VAc copolymerization, high-conversion samples were not soluble in THF.

Comparison of rates of polymerization

As a further clarification of the 'double gel effect' phenomenon, the rates of polymerization of the three

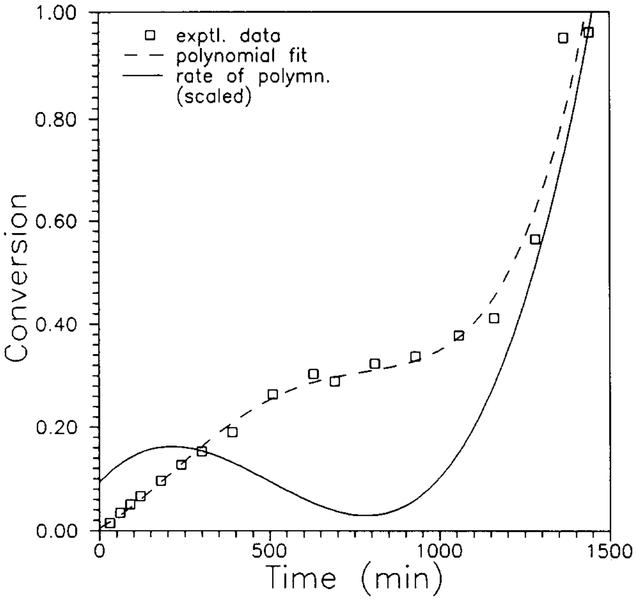

Figure 20 MMA/VAc, rate of polymerization

copolymer systems studied were compared. These rates are shown in *Figure 18* (BA/MMA), *Figure 19* (BA/VAc) and *Figure 20* (MMA/VAc). These plots were generated by fitting polynomials to the conversion data and taking the derivative of the polynomial with respect to time to get an idea about the rate of polymerization $(\mathrm{d}x/\mathrm{d}t \propto R_p)$. *Figure 18* shows a typical polymerization rate for the BA/MMA system. There is a small rate increase at the start of the reaction, then a relatively constant rate ensues. Next, a large increase in the rate occurs during the gel effect period. Finally, as the reaction nears completion and the propagation rate coefficient becomes diffusion-controlled, the rate decreases rapidly. The rate for the BA/VAc run (see *Figure 19*) shows a more or less steady decrease from the beginning of the reaction, which is typical of a solution polymerization. A sudden jump in the rate occurs when the VAc homopolymerization begins, analogous to a short gel effect period. The rate then decreases as the reaction nears completion. Finally, the MMA/VAc system (see *Figure 20*) exhibits a slow decrease in the rate at the early stages of the reaction and then a massive rate increase when the VAc 'homopolymerization' starts. From the comparison of these three figures, the occurrence of the 'double gel effect' phenomenon is well established.

CONCLUDING REMARKS

As mentioned earlier, this study is the first part of a comprehensive look at the BA/MMA/VAc terpolymer system. The value of our approach has already been demonstrated in the present bulk copolymerization study. The estimation of improved reactivity ratios has been shown. These reactivity ratios were used to predict copolymer composition successfully. The next stage of this study, the bulk and solution terpolymerization of BA/MMA/VAc, will involve the use of these copolymer reactivity ratios to predict terpolymer composition.

The estimation of the reactivity ratios and the analysis of the data through the full conversion range has also led to an explanation of the 'double gel effect' phenomenon in the vinyl acetate-containing copolymerizations. Our systematic study of the bulk polymerizations has allowed us to explain this phenomenon. In fact, the 'double gel effect' has been observed in the emulsion copolymerization of methyl acrylate/vinyl acetate[41]. In that case, however, considerable effort was needed to discount any phenomena related to emulsion polymerization such as monomer partitioning, secondary particle nucleation, etc. In this study, we have already deduced what this effect was due to, with considerably less effort.

We expect that a significant amount of branching is occurring in these copolymerizations. The analysis of the molecular weights as well as the filtration difficulties encountered during the sample preparation support this conclusion. This aspect of these copolymer systems will be considered in our future mechanistic modelling efforts as well as in the forthcoming experimental studies.

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