

Supporting Information for "Atom Transfer Radical Polymerization of Styrene and *n*-Butyl Acrylate"

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Introduction

The material is broken up into the following sections. Section 1 details a single propagation-of-error calculation starting with the observed %CV measured by GC and propagating that through to the final estimates of conversion and composition using standard analytical formulas. Section 2 presents kinetic, molecular weight and composition data for every copolymerization presented in the manuscript. Each experiment is named "experiment #" in reference to the parent manuscript. Section 3 outlines how we implemented the SS-space approach in Excel, taking advantage of the macro function. The results of the calculations and the visual basic code used to calculate the reactivity ratios are shown. Section 4 shows polymerizations of *n*-butyl acrylate under conditions which are comparable to some copolymerizations in the manuscript, and the kinetic data used to estimate equilibrium constants.

Section 1: Calculating Error in GC Parameters

As mentioned in the Statistical Considerations portion of the experimental section in the parent manuscript, conversion in this manuscript was measured by gas chromatography using an internal standard. Therefore, for each monomer, equation (1) can be written:

$$\text{conversion} = \frac{A_0 - A_t}{A_0} \quad (1)$$

Where A_o and A_t are ratios of areas of monomer to internal standard at the beginning of the polymerization (A_o) and at some time during the polymerization (A_t). Accordingly, measurement error in conversion and composition calculated from residual feed analysis comes from the imprecision of the GC in measuring these ratios. According to Table 1 in the parent manuscript, the $\%CV_A$ for measuring these response ratios did not depend systematically on either the initial feed condition or on conversion for a given feed condition. In order to have a number to use for calculations, all the $\%CV_A$'s listed in Table 1 of the parent manuscript were averaged together and this average value was used for all error propagation calculations. The formulas used to compute the error are standard error propagation formulas for sums/differences and products/quotients in a standard analytical chemistry textbook.¹

Consider sample 1 of Experiment 1 in Section 2. The detector response ratio A_t (the detector area from styrene divided by the detector area from 1,4-dimethoxybenzene, the internal standard) measured by GC for styrene is 2.801. The initial detector response ratio, A_o for styrene was 4.639. Conversion, as calculated from equation (1) is 0.396 for styrene. The error in this can be calculated using equation (2):

$$s_{\text{conv,st}} = \text{conv}^* \sqrt{\left(\frac{s_{(A_o-A_t)}}{(A_o-A_t)} \right)^2 + \left(\frac{s_{(A_o)}}{A_o} \right)^2} \quad (2)$$

where $s_{(A_o-A_t)}$ is the standard deviation of the difference between A_o and A_t (this difference is in the numerator of equation (1)) and $s_{(A_o)}$ is the standard deviation of the initial ratio A_o . The mean of $\%CV_A$ values listed in Table 1 of the parent manuscript is $\langle \%CV_A \rangle = 2.4$, meaning that s_A can be calculated by $s_A = A * CV_A = A * 0.02$ for all A in all experiments (where $CV_A = \%CV_A / 100$ - this puts the value into a useful fractional form). Thus, the quantities $s_{(A_o-A_t)}$ and $s_{(A_o)}$ can be easily calculated by equations (3a) and (3b):

$$\begin{aligned}
 S_{(A_0-A_t)} &= \sqrt{S_{(A_t)}^2 + S_{(A_0)}^2} = \sqrt{(A_t * CV_A)^2 + (A_0 * CV_A)^2} \\
 &= \sqrt{(2.801 * 0.02)^2 + (4.639 * 0.02)^2} \\
 &= 0.108
 \end{aligned} \tag{3a}$$

$$S_{(A_0)} = A_0 * CV_A = 4.639 * 0.02 = 0.093 \tag{3b}$$

Thus at 300 seconds, styrene has reached a conversion of 0.396 ± 0.025 or 0.39 ± 0.03 . Similar analyses can be done for the acrylates. At this time, A_t for *n*-butyl acrylate is 21.708, $A_0 = 25.636$. Following the analysis above, *n*-butyl acrylate has reached a conversion of 0.15 ± 0.03 . For the total monomer, $A_0 = 25.636 + 4.639 = 30.725$; $A_t = 21.708 + 2.801 = 24.509$. Following the analysis above, at 300 seconds, 0.19 ± 0.03 monomer has been converted to copolymer.

Table 1 below shows the calculated values for the quantities A_0 , A_t , $S_{(A_0-A_t)}$, $S_{(A_0)}$ conversion, and S_{conv} for each data point for the two monomers for this polymerization.

Table 1. Statistical Quantities for Experiment 1.

A_t^*	$S_{(A_0-A_t)}$	styrene		<i>n</i> -butyl acrylate			
		conv,st	$S_{\text{conv},st}$	A_t^*	$S_{(A_0-A_t)}$	conv, ba	$S_{\text{conv},ba}$
4.639	0.093			25.636	0.513		
2.801	0.108	0.396	0.025	21.708	0.672	0.153	0.026
1.561	0.098	0.663	0.025	16.628	0.611	0.351	0.025
1.358	0.097	0.707	0.025	18.667	0.634	0.272	0.025
0.829	0.094	0.821	0.026	14.587	0.590	0.431	0.025
0.375	0.093	0.919	0.027	11.571	0.563	0.549	0.025
0.011	0.093	0.998	0.028	6.284	0.528	0.755	0.026
0.013	0.093	0.997	0.028	5.922	0.526	0.769	0.026
0.014	0.093	0.997	0.028	3.360	0.517	0.869	0.027
0.022	0.093	0.995	0.028	3.625	0.518	0.859	0.027
0.013	0.093	0.997	0.028	3.780	0.518	0.853	0.026

* the first value in this column is A_0 .

To construct first order kinetic plots, $-\ln(1-\text{conv})$ (shown as $\ln \frac{[M]_0}{[M]}$ in the parent manuscript) is plotted against time. Accordingly, errors in this calculated quantity come from the errors in the measured conversion. For a natural log value, the error term is the standard deviation of the

mantissa divided by the estimated mean value. For these reactions, the error in “-ln(1-conv)” can be calculated from equation (4):

$$S_{-\ln(1\text{-conv})} = \frac{S_{1\text{-conv}}}{(1\text{-conv})} \quad (4)$$

where $s_{1\text{-conv}}$ is the estimated standard deviation of the value of (1-conversion) in the denominator. Since there is no error in the constant unity, $s_{1\text{-conv}} = s_{\text{conv}}$ and $s_{-\ln(1\text{-conv})}$ can be calculated for each value of conversion. The results of these calculations for this experiment are shown in Table 2.

Table 2. More statistical quantities for Experiment 1.

styrene			<i>n</i> -butyl acrylate		
conv,st	-ln(1-conv)	S _{-ln(1-conv)}	conv,ba	-ln(1-conv)	S _{-ln(1-conv)}
0.396	0.505	0.041	0.153	0.166	0.031
0.663	1.089	0.074	0.351	0.433	0.038
0.707	1.228	0.086	0.272	0.317	0.035
0.821	1.722	0.146	0.431	0.564	0.043
0.919	2.514	0.336	0.549	0.795	0.054
0.998	6.079	12.333	0.755	1.406	0.104
0.997	5.858	9.886	0.769	1.465	0.111
0.997	5.815	9.466	0.869	2.032	0.203
0.995	5.343	5.904	0.859	1.956	0.187
0.997	5.874	10.050	0.853	1.914	0.179

As described in the parent manuscript, cumulative copolymer composition can be calculated from conversion using equation (5):

$$F_{\text{cum}, M1} = \frac{\Delta[M_1]}{\Delta\{[M_1] + [M_2]\}} \quad (5)$$

$$= \frac{[M_1]_0 * (M_1 \text{ conversion})}{\{[M_1]_0 * (M_1 \text{ conversion})\} + \{[M_2]_0 * (M_2 \text{ conversion})\}}$$

Therefore, error in F_{cum} also arises from the error in measuring the initial moles of monomer in the feed and the conversion. In this analysis, we have assumed that the error in measuring the initial moles of monomer in the reaction is small compared to the error in conversion, since the former quantity was measured with an analytical balance. Equation (6) can be used to express the error in composition:

$$S_{\text{Fcum, styrene}} = F_{\text{cum, styrene}} * \sqrt{\left(\frac{s_{\text{mol st}}}{\text{mol st}}\right)^2 + \left(\frac{s_{\text{total mol}}}{\text{total mol}}\right)^2} \quad (6)$$

where mol styrene and total mol are the moles of remaining styrene and total remaining moles of monomer at a given conversion (for instance, mol styrene at some conversion is the product of $(\text{mol styrene})_0 * \text{conversion of styrene}$). $s_{\text{mol st}}$ and $s_{\text{total mol}}$ can be calculated from equations (7a) and (7b):

$$s_{\text{mol st}} = (\text{mol styrene})_0 * (\text{styrene conversion}) * \sqrt{\left(\frac{s_{\text{conv st}}}{(\text{conv st})}\right)^2} \quad (7a)$$

$$s_{\text{total mol}} = (\text{total mol})_0 * (\text{total conversion}) * \sqrt{\left(\frac{s_{\text{conv total}}}{(\text{conv total})}\right)^2} \quad (7b)$$

At 300 seconds for this reaction, styrene conversion = 0.396 ± 0.025 and *n*-butyl acrylate conversion = 0.153 ± 0.026 . The total conversion is 0.190 ± 0.026 . The initial moles of styrene in the feed $(\text{mol styrene})_0 = 0.004899$ and the initial total moles of monomer $(\text{total mol})_0 = 0.03711$. From equation (7a), $s_{\text{mol styrene}} = 0.000121$ and from equation (7b) $s_{\text{total mol}} = 0.000965$. Calculating composition based on equation (5) gives $(0.004899 * 0.396) / ((0.004899 * 0.396) + ((0.03711 - 0.004899) * (0.153))) = 0.282$. (Calculating composition by $(0.004899 * 0.396) / (0.03711) * (0.190) = 0.275$. Differences like this will occur since the *measured* total conversion may not be the *exact* conversion which satisfies the mass balance relation. In any case, the error in composition is larger than small differences due to calculation methods.) Using $F_{\text{cum, styrene}} = 0.282$ (cf. Experiment 1 in Section 2) and the relations above for calculating error gives $F_{\text{cum, styrene}} = 0.282 \pm 0.04$.

Table 3 shows the calculated values of styrene and *n*-butyl acrylate composition for every measured value of total monomer conversion, along with the estimated standard deviation of these values. As conversion increases, the %CV for the composition for each monomer

decreases, suggesting that composition calculated from low conversion have more error* than composition calculated from higher conversions.

Table 3. Statistical Quantities for Composition For Experiment 1.

conversion	%CV _{F_{cum}, styrene}		F _{cum, n-butyl}	%CV _{F_{cum,n-butyl acrylate}}		
	F _{cum, styrene}	S _{F_{cum, styrene}}		styrene	acrylate	S _{F_{cum, acrylate}}
0.190	0.282	0.042	15.0	0.718	0.158	22.0
0.399	0.223	0.016	7.2	0.777	0.073	9.4
0.339	0.283	0.023	8.2	0.717	0.085	11.9
0.491	0.225	0.013	5.9	0.775	0.059	7.6
0.605	0.203	0.010	5.0	0.797	0.048	6.1
0.792	0.167	0.007	4.3	0.833	0.039	4.7
0.804	0.165	0.007	4.3	0.835	0.039	4.6
0.889	0.149	0.006	4.1	0.851	0.037	4.3
0.880	0.150	0.006	4.2	0.850	0.037	4.3
0.875	0.151	0.006	4.2	0.849	0.037	4.4

Section 2**Experiment 1****Table 4a. Kinetic Parameters (Molecular Weight Data Unavailable)**

time (s)	Conversion			ln [M] ₀ /[M]		
	<i>n</i> -butyl acrylate		total	<i>n</i> -butyl acrylate		total
	styrene	acrylate		styrene	acrylate	
0	0.000	0.000	0.000	0.000	0.000	0.000
300	0.396	0.153	0.190	0.505	0.166	0.211
600	0.663	0.351	0.399	1.089	0.433	0.509
1320	0.707	0.272	0.339	1.228	0.317	0.413
1860	0.821	0.431	0.491	1.722	0.564	0.675
3900	0.919	0.549	0.605	2.514	0.795	0.930
5640	0.998	0.755	0.792	6.079	1.406	1.571
7200	0.997	0.769	0.804	5.858	1.465	1.629
12900	0.997	0.869	0.889	5.815	2.032	2.194
31080	0.995	0.859	0.880	5.343	1.956	2.116
86520	0.997	0.853	0.875	5.874	1.914	2.077

Table 4b. Kinetic Parameter Error Terms

styrene error	Conversion			ln [M] ₀ /[M]		
	<i>n</i> -butyl acrylate error	total error	styrene error	<i>n</i> -butyl acrylate error	total error	
0.025	0.026	0.026	0.041	0.031	0.032	
0.025	0.025	0.025	0.074	0.038	0.041	
0.025	0.025	0.025	0.086	0.035	0.038	
0.026	0.025	0.024	0.146	0.043	0.048	
0.027	0.025	0.025	0.336	0.054	0.063	
0.028	0.026	0.026	12.333	0.104	0.124	
0.028	0.026	0.026	9.886	0.111	0.132	
0.028	0.027	0.027	9.466	0.203	0.241	
0.028	0.027	0.027	5.904	0.187	0.222	
0.028	0.026	0.027	10.050	0.179	0.213	

Table 4c. Composition Parameters and Error Terms

conversion	F _{cum, styrene}	S _{Fcum, styrene}	%CV _{Fcum, styrene}	F _{cum, n- butyl acrylate}	S _{Fcum,n-butyl acrylate}	%CV _{Fcum,n- butyl acrylate}
0.190	0.282	0.042	15.0	0.718	0.158	22.0
0.399	0.223	0.016	7.2	0.777	0.073	9.4
0.339	0.283	0.023	8.2	0.717	0.085	11.9
0.491	0.225	0.013	5.9	0.775	0.059	7.6
0.605	0.203	0.010	5.0	0.797	0.048	6.1
0.792	0.167	0.007	4.3	0.833	0.039	4.7
0.804	0.165	0.007	4.3	0.835	0.039	4.6
0.889	0.149	0.006	4.1	0.851	0.037	4.3
0.880	0.150	0.006	4.2	0.850	0.037	4.3
0.875	0.151	0.006	4.2	0.849	0.037	4.4

Experiment 2**Table 5a. Kinetic Parameters**

time (s)	Conversion			ln [M]₀/[M]			$M_n \times 10^{-4}$	M_w/M_n		
	<i>n</i> -butyl			<i>n</i> -butyl						
	styrene	acrylate	total	styrene	acrylate	total				
300	0.544	0.232	0.275	0.786	0.264	0.322				
600	0.649	0.263	0.317	1.047	0.306	0.381				
1320	0.793	0.355	0.416	1.576	0.439	0.538	0.347	1.39		
1860	0.883	0.519	0.570	2.142	0.733	0.843	0.700	1.14		
3900	0.964	0.635	0.681	3.322	1.009	1.142	0.805	1.10		
5640	0.983	0.701	0.740	4.055	1.209	1.348	0.996	1.14		
7200	0.965	0.774	0.801	3.343	1.488	1.612	1.21	1.10		
12900	0.971	0.828	0.848	3.536	1.761	1.883	1.37	1.11		
31080	0.981	0.947	0.952	3.957	2.943	3.035	1.44	1.13		
86520	0.999	0.939	0.948	7.107	2.802	2.948	1.53	1.30		

Table 5b. Kinetic Parameter Error Terms

styrene error	Conversion			ln [M]₀/[M]		
	styrene	<i>n</i> -butyl	total error	styrene	<i>n</i> -butyl	total error
	error	acrylate error		error	acrylate error	
0.025	0.026	0.025	0.054	0.033	0.035	
0.025	0.025	0.025	0.071	0.034	0.037	
0.026	0.025	0.025	0.125	0.039	0.042	
0.027	0.025	0.025	0.228	0.051	0.057	
0.028	0.025	0.025	0.770	0.068	0.078	
0.028	0.025	0.025	1.617	0.084	0.098	
0.028	0.026	0.026	0.787	0.114	0.130	
0.028	0.026	0.026	0.957	0.152	0.173	
0.028	0.028	0.028	1.466	0.523	0.575	
0.028	0.027	0.028	34.503	0.452	0.526	

Table 5c. Composition Parameters and Error Terms

conversion	$F_{cum, styrene}$	$S_{Fcum, styrene}$	%CV_{Fcum, styrene}		$F_{cum, n\text{-}butyl}$	$S_{Fcum,n\text{-}butyl}$	%CV_{Fcum,n\text{-}butyl}	
			styrene	acrylate			butyl	acrylate
0.275	0.263	0.027	10.2		0.737	0.106		14.4
0.317	0.273	0.024	8.8		0.727	0.091		12.5
0.416	0.253	0.017	6.8		0.747	0.068		9.2
0.570	0.205	0.011	5.3		0.795	0.051		6.4
0.681	0.187	0.009	4.7		0.813	0.044		5.4
0.740	0.176	0.008	4.5		0.824	0.041		5.0
0.801	0.159	0.007	4.3		0.841	0.039		4.6
0.848	0.151	0.006	4.2		0.849	0.038		4.4
0.952	0.136	0.006	4.1		0.864	0.036		4.1
0.948	0.139	0.006	4.1		0.861	0.036		4.1

Experiment 3**Table 6a. Kinetic Parameters**

time (s)	styrene	Conversion		ln [M] ₀ /[M]			M _n × 10 ⁻⁴	M _w /M _n		
		<i>n</i> -butyl acrylate		styrene	<i>n</i> -butyl acrylate					
		total	styrene		total	acrylate				
300	0.436	0.172	0.209	0.572	0.189	0.235	0.271	1.36		
600	0.564	0.231	0.277	0.831	0.262	0.325	0.410	1.29		
1560	0.795	0.372	0.432	1.583	0.466	0.565	0.565	1.33		
2160	0.859	0.403	0.467	1.959	0.516	0.629	0.865	1.36		
3840	0.946	0.558	0.612	2.915	0.816	0.947	1.10	1.08		
5400	0.975	0.630	0.679	3.694	0.995	1.135	1.24	1.08		
7320	0.977	0.699	0.738	3.781	1.200	1.339	1.29	1.10		
12000	0.984	0.800	0.826	4.144	1.608	1.746	1.34	1.15		
23400	0.990	0.949	0.951	4.605	2.969	3.012				
67800	0.990	0.933	0.931	4.605	2.696	2.679	1.80	1.17		

Table 6b. Kinetic Parameter Error Terms

styrene error	Conversion		ln [M] ₀ /[M]		
	<i>n</i> -butyl acrylate error	total error	styrene error	<i>n</i> -butyl acrylate error	total error
0.025	0.026	0.026	0.044	0.032	0.033
0.025	0.026	0.025	0.056	0.033	0.035
0.026	0.025	0.025	0.126	0.039	0.043
0.027	0.025	0.025	0.188	0.041	0.046
0.028	0.025	0.025	0.509	0.055	0.064
0.028	0.025	0.025	1.124	0.067	0.078
0.028	0.025	0.025	1.227	0.083	0.097
0.028	0.026	0.026	1.770	0.129	0.150
0.029	0.028	0.028	2.854	0.537	0.562
0.029	0.027	0.027	2.922	0.406	0.399

Table 6c. Composition Parameters and Error Terms

conversion	F _{cum, styrene}	S _{Fcum, styrene}	%CV _{Fcum, styrene}	F _{cum, n-butyl acrylate}	S _{Fcum, n-butyl acrylate}	%CV _{Fcum, n-butyl acrylate}
0.209	0.278	0.038	13.6	0.722	0.142	19.6
0.277	0.271	0.027	10.1	0.729	0.105	14.4
0.432	0.245	0.016	6.6	0.755	0.066	8.8
0.467	0.245	0.015	6.1	0.755	0.061	8.1
0.612	0.205	0.010	5.0	0.795	0.047	6.0
0.679	0.190	0.009	4.7	0.810	0.044	5.4
0.738	0.175	0.008	4.5	0.825	0.041	5.0
0.826	0.158	0.007	4.3	0.842	0.038	4.5
0.951	0.137	0.006	4.1	0.863	0.035	4.1
0.931	0.139	0.006	4.2	0.861	0.036	4.2

Experiment 4**Table 7a. Kinetic Parameters**

time (s)	Conversion			ln [M] ₀ /[M]				M _n × 10 ⁻⁴	M _w /M _n		
	<i>n</i> -butyl acrylate			<i>n</i> -butyl acrylate		total					
	styrene	<i>n</i> -butyl acrylate	total	styrene	<i>n</i> -butyl acrylate						
900	0.181	0.151	0.168	0.199	0.164	0.184	0.295	1.48			
1320	0.318	0.241	0.285	0.383	0.276	0.335	0.514	1.27			
1920	0.337	0.232	0.292	0.411	0.264	0.345					
3720	0.505	0.369	0.447	0.704	0.461	0.592	0.602	1.16			
5400	0.544	0.397	0.481	0.786	0.506	0.655	0.707	1.15			
7200	0.603	0.445	0.534	0.923	0.588	0.764	0.797	1.16			
11400	0.729	0.565	0.658	1.307	0.831	1.073	0.921	1.18			
23400	0.840	0.680	0.771	1.834	1.140	1.474	1.12	1.15			
67800	0.921	0.818	0.876	2.540	1.702	2.091	1.20	1.22			

Table 7b. Kinetic Parameter Error Terms

styrene error	Conversion			ln [M] ₀ /[M]		
	<i>n</i> -butyl acrylate error	total error	styrene error	<i>n</i> -butyl acrylate error	total error	
0.026	0.026	0.026	0.032	0.031	0.032	
0.025	0.026	0.025	0.037	0.034	0.035	
0.025	0.026	0.025	0.038	0.033	0.036	
0.024	0.025	0.025	0.050	0.039	0.044	
0.025	0.025	0.025	0.054	0.041	0.047	
0.025	0.025	0.025	0.062	0.044	0.053	
0.025	0.025	0.025	0.094	0.056	0.073	
0.026	0.025	0.026	0.165	0.078	0.112	
0.027	0.026	0.027	0.345	0.143	0.216	

Table 7c. Composition Parameters and Error Terms

conversion	F _{cum} , styrene	S _{Fcum} , styrene	%CV _{Fcum,} styrene	F _{cum, n} -butyl acrylate	S _{Fcum,n} -butyl acrylate	%CV _{Fcum,n} - butyl acrylate
0.168	0.555	0.118	21.3	0.445	0.105	23.5
0.285	0.578	0.069	11.9	0.422	0.058	13.8
0.292	0.602	0.068	11.4	0.398	0.056	14.0
0.447	0.587	0.043	7.3	0.413	0.036	8.7
0.481	0.588	0.040	6.8	0.412	0.033	8.0
0.534	0.585	0.036	6.1	0.415	0.030	7.2
0.658	0.574	0.029	5.1	0.426	0.025	5.8
0.771	0.562	0.026	4.6	0.438	0.022	5.0
0.876	0.540	0.023	4.2	0.460	0.020	4.4

Experiment 5**Table 8a. Kinetic Parameters (Molecular Weight Data Unavailable)**

time (s)	Conversion			ln [M] _o /[M]		
	<i>n</i> -butyl acrylate		total	<i>n</i> -butyl acrylate		total
	styrene	acrylate		styrene	acrylate	
360	0.071	0.045	0.060	0.073	0.046	0.061
900	0.226	0.142	0.190	0.256	0.154	0.210
1380	0.249	0.175	0.217	0.286	0.192	0.244
1920	0.309	0.207	0.265	0.370	0.231	0.308
3780	0.452	0.339	0.403	0.601	0.414	0.516
5460	0.502	0.364	0.442	0.697	0.453	0.584
7260	0.607	0.464	0.546	0.935	0.625	0.789
11220	0.704	0.567	0.645	1.219	0.837	1.036
29880	0.836	0.720	0.786	1.808	1.273	1.541
86820	0.913	0.830	0.877	2.445	1.772	2.099

Table 8b. Kinetic Parameter Error Terms

styrene error	Conversion			ln [M] _o /[M]		
	<i>n</i> -butyl acrylate error		total error	<i>n</i> -butyl acrylate error		total error
	styrene	<i>n</i> -butyl acrylate		styrene	acrylate	
0.027	0.028	0.027	0.029	0.029	0.029	0.029
0.026	0.027	0.026	0.033	0.031	0.032	0.032
0.026	0.026	0.026	0.034	0.032	0.033	0.033
0.025	0.026	0.025	0.036	0.033	0.035	0.035
0.025	0.025	0.025	0.045	0.038	0.041	0.041
0.024	0.025	0.025	0.049	0.039	0.044	0.044
0.025	0.025	0.025	0.063	0.046	0.054	0.054
0.025	0.025	0.025	0.085	0.057	0.070	0.070
0.026	0.025	0.026	0.160	0.090	0.120	0.120
0.027	0.026	0.027	0.313	0.154	0.218	0.218

Table 8c. Composition Parameters and Error Terms

conversion	F _{cum, styrene}	S _{Fcum, styrene}	%CV _{Fcum, styrene}	F _{cum, n-butyl acrylate}	S _{Fcum,n-butyl acrylate}	%CV _{Fcum,n-butyl acrylate}
0.060	0.619	0.373	60.2	0.381	0.292	76.6
0.190	0.622	0.111	17.8	0.378	0.087	23.1
0.217	0.597	0.094	15.7	0.403	0.077	19.1
0.265	0.609	0.076	12.6	0.391	0.062	15.8
0.403	0.581	0.048	8.2	0.419	0.040	9.6
0.442	0.589	0.044	7.4	0.411	0.036	8.8
0.546	0.576	0.035	6.1	0.424	0.029	6.9
0.645	0.564	0.030	5.3	0.436	0.025	5.8
0.786	0.547	0.025	4.5	0.453	0.022	4.8
0.877	0.534	0.023	4.3	0.466	0.020	4.4

Experiment 6**Table 9a. Kinetic Parameters**

time (s)	styrene	Conversion			ln [M] ₀ /[M]			$M_n \times 10^{-4}$	M_w/M_n
		n-butyl acrylate	total	styrene	n-butyl acrylate	total			
360	0.115	0.090	0.104	0.122	0.094	0.110	0.0849	1.95	
900	0.200	0.136	0.173	0.223	0.146	0.190	0.274	1.20	
1188	0.205	0.148	0.181	0.229	0.160	0.199	0.328	1.19	
1908	0.329	0.227	0.286	0.399	0.257	0.337	0.453	1.14	
3600	0.449	0.345	0.405	0.597	0.423	0.520	0.652	1.12	
5400	0.569	0.441	0.515	0.843	0.581	0.724	0.793	1.11	
7200	0.618	0.469	0.555	0.961	0.633	0.809	0.881	1.13	
11520	0.734	0.583	0.670	1.323	0.875	1.109	1.00	1.14	
86400	0.925	0.851	0.894	2.594	1.901	2.242	1.31	1.18	

Table 9b. Kinetic Parameter Error Terms

styrene error	Conversion			ln [M] ₀ /[M]		
	n-butyl acrylate error	total error	styrene error	n-butyl acrylate error	total error	
0.027	0.027	0.027	0.030	0.030	0.030	
0.026	0.027	0.026	0.032	0.031	0.032	
0.026	0.026	0.026	0.033	0.031	0.032	
0.025	0.026	0.025	0.037	0.033	0.035	
0.025	0.025	0.025	0.045	0.038	0.041	
0.025	0.025	0.024	0.057	0.044	0.051	
0.025	0.025	0.025	0.065	0.046	0.055	
0.025	0.025	0.025	0.095	0.059	0.076	
0.027	0.026	0.027	0.365	0.177	0.253	

Table 9c. Composition Parameters and Error Terms

conversion	F _{cum, styrene}	S _{Fcum, styrene}	%CV _{Fcum,}		F _{cum, n- butyl acrylate}	S _{Fcum,n-butyl acrylate}	%CV _{Fcum,n-}
			styrene	acrylate			
0.104	0.572	0.199	34.8	0.428	0.170	39.8	
0.173	0.605	0.121	19.9	0.395	0.098	24.7	
0.181	0.590	0.113	19.2	0.410	0.094	22.9	
0.286	0.602	0.070	11.6	0.398	0.057	14.4	
0.405	0.576	0.047	8.2	0.424	0.040	9.4	
0.515	0.574	0.037	6.4	0.426	0.031	7.3	
0.555	0.578	0.035	6.0	0.422	0.029	6.8	
0.670	0.567	0.029	5.1	0.433	0.024	5.6	
0.894	0.531	0.022	4.2	0.469	0.020	4.3	

Experiment 7**Table 10a. Kinetic Parameters**

time (s)	styrene	Conversion		ln [M] ₀ /[M]		M _n × 10 ⁻⁴	M _w /M _n
		n	n-butyl acrylate	total	styrene		
300	0.024	0.039	0.025	0.024	0.040	0.025	0.046 1.53
600	0.099	0.096	0.099	0.105	0.101	0.104	0.063 1.61
1320	0.126	0.131	0.127	0.135	0.140	0.136	0.170 1.21
1800	0.133	0.131	0.132	0.142	0.140	0.142	0.200 1.19
3840	0.323	0.319	0.323	0.390	0.385	0.390	0.336 1.13
5400	0.359	0.209	0.345	0.445	0.234	0.423	0.405 1.12
7680	0.462	0.459	0.462	0.620	0.613	0.619	0.517 1.10
13740	0.593	0.606	0.594	0.899	0.931	0.902	0.697 1.10
64800	0.899	0.916	0.900	2.291	2.479	2.307	1.20 1.12

Table 10b. Kinetic Parameter Error Terms

styrene error	Conversion			ln [M] ₀ /[M]			
	n-butyl acrylate error	styrene	n-butyl acrylate error	styrene	n-butyl acrylate error	total error	
		total error	error	error	acrylate error		
0.028	0.028	0.028	0.029	0.029	0.029	0.029	
0.027	0.027	0.027	0.030	0.030	0.030	0.030	
0.027	0.027	0.027	0.031	0.031	0.031	0.031	
0.027	0.027	0.027	0.031	0.031	0.031	0.031	
0.025	0.025	0.025	0.037	0.037	0.037	0.037	
0.025	0.026	0.025	0.039	0.033	0.038		
0.025	0.025	0.025	0.046	0.045	0.046		
0.025	0.025	0.025	0.061	0.063	0.061		
0.027	0.027	0.027	0.266	0.324	0.271		

Table 10c. Composition Parameters and Error Terms

conversion	F _{cum, styrene}	S _{Fcum, styrene}	%CV _{Fcum,}		F _{cum, n-butyl acrylate}	S _{Fcum,n-butyl acrylate}	%CV _{Fcum,n-butyl acrylate}
			styrene	acrylate			
0.025	0.792	1.291	163.0	0.208	0.275	132.1	
0.099	0.868	0.334	38.5	0.132	0.052	39.2	
0.127	0.860	0.256	29.8	0.140	0.041	29.3	
0.132	0.866	0.246	28.4	0.134	0.038	28.6	
0.323	0.865	0.095	11.0	0.135	0.015	11.0	
0.345	0.916	0.092	10.0	0.084	0.012	14.3	
0.462	0.865	0.065	7.5	0.135	0.010	7.5	
0.594	0.861	0.051	5.9	0.139	0.008	5.8	
0.900	0.862	0.037	4.2	0.138	0.006	4.2	

Experiment 8**Table 11a. Kinetic Parameters**

time (s)	Conversion			ln [M] ₀ /[M]			M _n × 10 ⁻⁴	M _w /M _n		
	<i>n</i> -butyl acrylate			<i>n</i> -butyl acrylate						
	styrene	total	styrene	acrylate	total					
300	0.167	0.134	0.164	0.183	0.144	0.179	0.034	2.08		
600	0.153	0.139	0.152	0.166	0.150	0.164	0.061	2.01		
1320	0.180	0.118	0.173	0.198	0.125	0.190	0.164	1.20		
1860	0.218	0.201	0.216	0.246	0.225	0.244	0.202	1.19		
3840	0.278	0.286	0.279	0.326	0.337	0.327	0.350	1.13		
5640	0.401	0.406	0.401	0.512	0.521	0.513	0.482	1.12		
7440	0.489	0.489	0.489	0.672	0.672	0.672	0.553	1.12		
12120	0.571	0.652	0.579	0.846	1.055	0.866	0.708	1.12		

Table 11b. Kinetic Parameter Error Terms

styrene error	Conversion			ln [M] ₀ /[M]		
	<i>n</i> -butyl acrylate error	total error	styrene error	<i>n</i> -butyl acrylate error	total error	
0.026	0.027	0.026	0.032	0.031	0.031	
0.026	0.027	0.026	0.031	0.031	0.031	
0.026	0.027	0.026	0.032	0.030	0.032	
0.026	0.026	0.026	0.033	0.032	0.033	
0.025	0.025	0.025	0.035	0.035	0.035	
0.025	0.025	0.025	0.041	0.041	0.041	
0.024	0.024	0.024	0.048	0.048	0.048	
0.025	0.025	0.025	0.057	0.071	0.058	

Table 11c. Composition Parameters and Error Terms

conversion	F _{cum, styrene}	S _{Fcum, styrene}	%CV _{Fcum, styrene}		F _{cum, n-butyl acrylate}	S _{Fcum,n-butyl acrylate}	%CV _{Fcum,n-butyl acrylate}	
			styrene	acrylate			butyl acrylate	
0.164	0.888	0.199	22.4	0.112	0.029	25.5		
0.152	0.875	0.214	24.5	0.125	0.032	25.8		
0.173	0.907	0.190	21.0	0.093	0.026	27.3		
0.216	0.873	0.147	16.8	0.127	0.022	17.5		
0.279	0.861	0.110	12.8	0.139	0.018	12.6		
0.401	0.862	0.075	8.7	0.138	0.012	8.6		
0.489	0.864	0.061	7.1	0.136	0.010	7.1		
0.579	0.848	0.051	6.0	0.152	0.009	5.7		

Experiment 9**Table 12a. Kinetic Parameters**

time (s)	Conversion			ln [M] ₀ /[M]			M _n × 10 ⁻⁴	M _w /M _n		
	<i>n</i> -butyl acrylate			<i>n</i> -butyl acrylate						
	styrene	total	styrene	total	M _n × 10 ⁻⁴					
300	0.074	0.052	0.072	0.077	0.053	0.074				
1320	0.157	0.121	0.153	0.171	0.129	0.166				
1800	0.199	0.204	0.199	0.221	0.228	0.222	0.153	1.19		
3720	0.199	0.211	0.201	0.222	0.237	0.224	0.246	1.29		
5880	0.326	0.350	0.329	0.394	0.431	0.399	0.289	1.26		
7740	0.499	0.521	0.502	0.692	0.735	0.697	0.473	1.13		
13320	0.685	0.702	0.687	1.154	1.211	1.161				
87240	0.881	0.917	0.885	2.125	2.487	2.161	0.836	1.16		

Table 12b. Kinetic Parameter Error Terms

styrene error	Conversion			ln [M] ₀ /[M]		
	<i>n</i> -butyl acrylate error	total error	styrene error	<i>n</i> -butyl acrylate error	total error	
0.027	0.028	0.027	0.029	0.029	0.029	
0.026	0.027	0.026	0.031	0.030	0.031	
0.026	0.026	0.026	0.032	0.033	0.032	
0.026	0.026	0.026	0.032	0.033	0.032	
0.025	0.025	0.025	0.037	0.038	0.037	
0.024	0.025	0.024	0.049	0.051	0.049	
0.025	0.025	0.025	0.079	0.084	0.080	
0.027	0.027	0.027	0.224	0.327	0.233	

Table 12c. Composition Parameters and Error Terms

conversion	F _{cum, styrene}	S _{Fcum, styrene}	%CV _{Fcum,}		F _{cum, n-butyl}	S _{Fcum,n-butyl}	%CV _{Fcum,n-}
			styrene	acrylate			
0.072	0.901	0.477	52.9	0.099	0.065		65.5
0.153	0.892	0.215	24.0	0.108	0.030		28.1
0.199	0.861	0.159	18.4	0.139	0.025		18.2
0.201	0.857	0.157	18.3	0.143	0.025		17.8
0.329	0.855	0.092	10.8	0.145	0.015		10.4
0.502	0.859	0.059	6.9	0.141	0.010		6.8
0.687	0.861	0.044	5.2	0.139	0.007		5.1
0.885	0.859	0.037	4.3	0.141	0.006		4.2

Experiment 10**Table 13a. Kinetic Parameters**

time (s)	Conversion			ln [M] ₀ /[M]				$M_w \times 10^{-4}$	M_w/M_n
	<i>n</i> -butyl acrylate		total	styrene	<i>n</i> -butyl acrylate		total		
	styrene	<i>n</i> -butyl acrylate	styrene	<i>n</i> -butyl acrylate	styrene	<i>n</i> -butyl acrylate	styrene		
360	0.121	0.108	0.118	0.128	0.114	0.125	0.088	1.67	
612	0.175	0.150	0.170	0.193	0.163	0.187	0.110	1.76	
1260	0.240	0.209	0.234	0.275	0.234	0.266	0.289	1.18	
1908	0.327	0.295	0.320	0.396	0.350	0.386	0.379	1.15	
3600	0.401	0.367	0.394	0.512	0.458	0.500	0.502	1.10	
5400	0.456	0.426	0.450	0.609	0.556	0.598	0.613	1.08	
7920	0.546	0.511	0.539	0.790	0.716	0.774	0.708	1.09	
11520	0.624	0.588	0.617	0.978	0.886	0.958	0.780	1.09	
14760	0.649	0.610	0.641	1.047	0.943	1.025	0.858	1.07	
21600	0.787	0.737	0.776	1.545	1.337	1.498	0.933	1.08	
86400	0.918	0.909	0.916	2.507	2.393	2.482	1.14	1.10	

Table 13b. Kinetic Parameter Error Terms

styrene error	Conversion			ln [M] ₀ /[M]		
	<i>n</i> -butyl acrylate error	total error	styrene error	<i>n</i> -butyl acrylate error	total error	
0.027	0.027	0.027	0.030	0.030	0.030	
0.026	0.026	0.026	0.032	0.031	0.032	
0.026	0.026	0.026	0.034	0.033	0.033	
0.025	0.025	0.025	0.037	0.036	0.037	
0.025	0.025	0.025	0.041	0.039	0.041	
0.025	0.025	0.025	0.045	0.043	0.045	
0.025	0.024	0.025	0.054	0.050	0.053	
0.025	0.025	0.025	0.066	0.060	0.064	
0.025	0.025	0.025	0.071	0.063	0.069	
0.026	0.025	0.026	0.121	0.097	0.115	
0.027	0.027	0.027	0.334	0.297	0.325	

Table 13c. Composition Parameters and Error Terms

conversion	F _{cum} , styrene	S _{Fcum} , styrene	%CV _{Fcum,}		F _{cum, n} -butyl acrylate	S _{Fcum,n} -butyl acrylate	%CV _{Fcum,n} - butyl acrylate
			styrene	acrylate			
0.118	0.762	0.242	31.7	0.238	0.080	33.7	
0.170	0.769	0.165	21.4	0.231	0.054	23.4	
0.234	0.767	0.117	15.3	0.233	0.039	16.5	
0.320	0.760	0.083	10.9	0.240	0.028	11.6	
0.394	0.757	0.067	8.8	0.243	0.022	9.2	
0.450	0.754	0.058	7.7	0.246	0.020	7.9	
0.539	0.753	0.048	6.4	0.247	0.016	6.6	
0.617	0.752	0.042	5.6	0.248	0.014	5.8	
0.641	0.753	0.041	5.4	0.247	0.014	5.6	
0.776	0.753	0.035	4.7	0.247	0.012	4.8	
0.916	0.743	0.031	4.2	0.257	0.011	4.2	

Experiment 11**Table 14a. Kinetic Parameters**

time (s)	Conversion			ln [M] ₀ /[M]				M _n × 10 ⁻⁴	M _w /M _n
	<i>n</i> -butyl acrylate		total	styrene	<i>n</i> -butyl acrylate		total		
	styrene	<i>n</i> -butyl acrylate			styrene	<i>n</i> -butyl acrylate			
299	0.262	0.161	0.193	0.304	0.175	0.214	0.234	0.234	1.29
612	0.314	0.152	0.204	0.377	0.165	0.228	0.309	0.309	1.25
1440	0.519	0.279	0.355	0.732	0.327	0.438	0.505	0.505	1.16
2412	0.615	0.331	0.421	0.954	0.402	0.546	0.644	0.644	1.09
3600	0.699	0.397	0.492	1.201	0.506	0.678	0.746	0.746	1.07
6120	0.788	0.473	0.573	1.552	0.641	0.850	0.839	0.839	1.08
7200	0.841	0.551	0.643	1.842	0.801	1.029	0.889	0.889	1.07
10800	0.872	0.570	0.665	2.054	0.843	1.094	0.949	0.949	1.08
14760	0.902	0.619	0.708	2.319	0.965	1.231	0.963	0.963	1.10
22680	0.921	0.659	0.741	2.536	1.075	1.353	0.960	0.960	1.13
86400	0.959	0.758	0.821	3.192	1.417	1.721	0.975	0.975	1.12

Table 14b. Kinetic Parameter Error Terms

styrene error	Conversion			ln [M] ₀ /[M]		
	<i>n</i> -butyl acrylate error	total error	styrene error	<i>n</i> -butyl acrylate error	total error	
0.025	0.026	0.026	0.034	0.031	0.032	
0.025	0.026	0.026	0.037	0.031	0.033	
0.025	0.025	0.025	0.051	0.035	0.038	
0.025	0.025	0.025	0.064	0.037	0.042	
0.025	0.025	0.024	0.084	0.041	0.048	
0.026	0.025	0.025	0.122	0.047	0.058	
0.026	0.025	0.025	0.166	0.055	0.069	
0.027	0.025	0.025	0.208	0.057	0.074	
0.027	0.025	0.025	0.274	0.065	0.086	
0.027	0.025	0.025	0.344	0.073	0.098	
0.028	0.026	0.026	0.675	0.105	0.146	

Table 14c. Composition Parameters and Error Terms

conversion	F _{cum, styrene}	S _{Fcum, styrene}	%CV _{Fcum, styrene}		F _{cum, n-butyl acrylate}	S _{Fcum,n-butyl acrylate}	%CV _{Fcum,n-butyl acrylate}	
			styrene	acrylate			butyl acrylate	acrylate
0.193	0.352	0.059	16.6	0.648	0.138	21.2		
0.204	0.407	0.061	15.0	0.593	0.127	21.5		
0.355	0.383	0.032	8.4	0.617	0.071	11.5		
0.421	0.382	0.027	7.1	0.618	0.059	9.5		
0.492	0.370	0.023	6.1	0.630	0.050	8.0		
0.573	0.357	0.019	5.4	0.643	0.043	6.7		
0.643	0.337	0.017	5.0	0.663	0.039	5.9		
0.665	0.338	0.016	4.8	0.662	0.038	5.7		
0.708	0.327	0.015	4.7	0.673	0.036	5.3		
0.741	0.318	0.014	4.5	0.682	0.035	5.1		
0.821	0.297	0.013	4.3	0.703	0.033	4.6		

Experiment 12**Table 15a. Kinetic Parameters**

time (s)	styrene	Conversion		ln [M] ₀ /[M]			M _n × 10 ⁻⁴	M _w /M _n
		<i>n</i> -butyl acrylate	total	styrene	<i>n</i> -butyl acrylate	total		
2220	0.164	0.122	0.146	0.179	0.130	0.157	0.062	1.77
3960	0.156	0.118	0.139	0.170	0.125	0.150	0.163	1.26
6660	0.159	0.111	0.138	0.174	0.118	0.149	0.197	1.25
10560	0.246	0.163	0.210	0.282	0.178	0.235	0.261	1.22
13260	0.280	0.201	0.246	0.329	0.225	0.282	0.299	1.21
17820	0.305	0.225	0.270	0.364	0.254	0.315	0.377	1.17
86460	0.693	0.535	0.624	1.180	0.766	0.978	0.911	1.10
107220	0.746	0.591	0.679	1.371	0.894	1.135	0.939	1.11
164820	0.854	0.715	0.794	1.927	1.255	1.578	1.08	1.11
241500	0.916	0.819	0.874	2.478	1.707	2.068		

Table 15b. Kinetic Parameter Error Terms

styrene error	Conversion		ln [M] ₀ /[M]		
	<i>n</i> -butyl acrylate error	total error	styrene error	<i>n</i> -butyl acrylate error	total error
0.026	0.027	0.026	0.031	0.030	0.031
0.026	0.027	0.027	0.031	0.030	0.031
0.026	0.027	0.027	0.031	0.030	0.031
0.026	0.026	0.026	0.034	0.031	0.033
0.025	0.026	0.026	0.035	0.032	0.034
0.025	0.026	0.025	0.036	0.033	0.035
0.025	0.025	0.025	0.082	0.053	0.066
0.025	0.025	0.025	0.100	0.060	0.078
0.026	0.025	0.026	0.182	0.089	0.125
0.027	0.026	0.027	0.324	0.144	0.211

Table 15c. Composition Parameters and Error Terms

conversion	F _{cum} , styrene	S _{Fcum} , styrene	%CV _{Fcum} , styrene	F _{cum, n} -butyl acrylate	S _{Fcum,n} -butyl acrylate	%CV _{Fcum,n} - butyl acrylate
0.146	0.582	0.141	24.3	0.418	0.119	28.4
0.139	0.580	0.148	25.4	0.420	0.125	29.7
0.138	0.599	0.151	25.3	0.401	0.124	30.8
0.210	0.611	0.099	16.1	0.389	0.079	20.3
0.246	0.592	0.081	13.7	0.408	0.067	16.5
0.270	0.586	0.073	12.5	0.414	0.061	14.8
0.624	0.574	0.031	5.4	0.426	0.026	6.1
0.679	0.568	0.029	5.0	0.432	0.024	5.6
0.794	0.554	0.025	4.5	0.446	0.021	4.8
0.874	0.538	0.023	4.3	0.462	0.020	4.4

Experiment 13**Table 16a. Kinetic Parameters**

time (s)	Conversion			ln [M] ₀ /[M]			M _n × 10 ⁻⁴	M _w /M _n
	<i>n</i> -butyl acrylate		total	styrene	<i>n</i> -butyl acrylate			
	styrene	<i>n</i> -butyl acrylate			styrene	<i>n</i> -butyl acrylate		
360	0.113	0.062	0.092	0.120	0.064	0.096		
828	0.151	0.087	0.124	0.164	0.091	0.133	0.181	1.15
1188	0.171	0.099	0.141	0.188	0.104	0.152	0.191	1.25
1980	0.235	0.144	0.197	0.268	0.155	0.219	0.238	1.22
3600	0.311	0.211	0.269	0.373	0.237	0.313	0.337	1.19
5400	0.368	0.245	0.316	0.459	0.281	0.380	0.456	1.15
7560	0.457	0.322	0.400	0.610	0.389	0.511	0.556	1.13
12240	0.587	0.436	0.523	0.884	0.572	0.741	0.716	1.12
22680	0.708	0.551	0.642	1.230	0.802	1.027	0.920	1.14
86400	0.907	0.801	0.862	2.376	1.613	1.983	1.28	1.11

Table 16b. Kinetic Parameter Error Terms

styrene error	Conversion			ln [M] ₀ /[M]		
	styrene	<i>n</i> -butyl acrylate error	total error	styrene	<i>n</i> -butyl acrylate error	total error
0.027	0.027	0.027	0.027	0.030	0.029	0.030
0.026	0.027	0.027	0.027	0.031	0.030	0.030
0.026	0.027	0.027	0.027	0.032	0.030	0.031
0.026	0.026	0.026	0.026	0.034	0.031	0.032
0.025	0.026	0.025	0.025	0.036	0.033	0.035
0.025	0.026	0.025	0.025	0.039	0.034	0.037
0.025	0.025	0.025	0.025	0.045	0.037	0.041
0.025	0.025	0.025	0.025	0.060	0.044	0.051
0.025	0.025	0.025	0.025	0.086	0.055	0.069
0.027	0.026	0.027	0.291	0.130	0.193	

Table 16c. Composition Parameters and Error Terms

conversion	F _{cum} , styrene	S _{Fcum} , styrene	%CV _{Fcum} , styrene		F _{cum, n} -butyl acrylate	S _{Fcum,n} -butyl acrylate	%CV _{Fcum,n} - butyl acrylate
			styrene	acrylate			
0.092	0.653	0.248	38.0	0.347	0.184		53.1
0.124	0.644	0.178	27.7	0.356	0.135		37.9
0.141	0.643	0.156	24.3	0.357	0.118		33.1
0.197	0.630	0.108	17.1	0.370	0.084		22.6
0.269	0.606	0.075	12.4	0.394	0.061		15.4
0.316	0.610	0.063	10.4	0.390	0.051		13.1
0.400	0.596	0.049	8.2	0.404	0.040		9.9
0.523	0.584	0.037	6.3	0.416	0.030		7.3
0.642	0.572	0.030	5.3	0.428	0.025		5.9
0.862	0.541	0.023	4.3	0.459	0.020		4.5

Experiment 14**Table 17a. Kinetic Parameters**

time (s)	styrene	Conversion			ln [M] ₀ /[M]			M _n × 10 ⁻⁴	M _w /M _n		
		<i>n</i> -butyl acrylate		total	styrene	<i>n</i> -butyl acrylate					
		acrylate	total			acrylate	total				
360	0.115	0.090	0.104	0.122	0.094	0.110	0.0849	1.20			
900	0.200	0.136	0.173	0.223	0.146	0.190	0.274	1.19			
1188	0.205	0.148	0.181	0.229	0.160	0.199	0.328	1.19			
1908	0.329	0.227	0.286	0.399	0.257	0.337	0.453	1.14			
3600	0.449	0.345	0.405	0.597	0.423	0.520	0.652	1.12			
5400	0.569	0.441	0.515	0.843	0.581	0.724	0.793	1.11			
7200	0.618	0.469	0.555	0.961	0.633	0.809	0.881	1.13			
11520	0.734	0.583	0.670	1.323	0.875	1.109	1.0	1.14			
86400	0.925	0.851	0.894	2.594	1.901	2.242	1.31	1.18			

Table 17b. Kinetic Parameter Error Terms

styrene error	Conversion			ln [M] ₀ /[M]		
	<i>n</i> -butyl acrylate error	total error	styrene error	<i>n</i> -butyl acrylate error	total error	
	0.027	0.027	0.027	0.030	0.030	0.030
0.026	0.027	0.026	0.032	0.031	0.032	
0.026	0.026	0.026	0.033	0.031	0.032	
0.025	0.026	0.025	0.037	0.033	0.035	
0.025	0.025	0.025	0.045	0.038	0.041	
0.025	0.025	0.024	0.057	0.044	0.051	
0.025	0.025	0.025	0.065	0.046	0.055	
0.025	0.025	0.025	0.095	0.059	0.076	
0.027	0.026	0.027	0.365	0.177	0.253	

Table 17c. Composition Parameters and Error Terms

conversion	F _{cum, styrene}	S _{Fcum, styrene}	%CV _{Fcum,}		F _{cum, n-butyl}	S _{Fcum,n-butyl}	%CV _{Fcum,n-}
			styrene	acrylate			
0.104	0.572	0.199	34.8	0.428	0.170	0.098	39.8
0.173	0.605	0.121	19.9	0.395	0.098	0.057	24.7
0.181	0.590	0.113	19.2	0.410	0.094	0.057	22.9
0.286	0.602	0.070	11.6	0.398	0.057	0.029	14.4
0.405	0.575	0.047	8.2	0.425	0.040	0.024	9.4
0.515	0.574	0.037	6.4	0.426	0.031	0.024	7.3
0.555	0.578	0.034	6.0	0.422	0.029	0.024	6.8
0.670	0.567	0.029	5.1	0.433	0.024	0.024	5.6
0.894	0.531	0.022	4.2	0.469	0.020	0.020	4.3

Experiment 15**Table 18a. Kinetic Parameters**

time (s)	Conversion		ln [M] ₀ /[M]				$M_n \times 10^{-4}$	M_w/M_n
	styrene	n-butyl acrylate	n	styrene	n-butyl acrylate	total		
300	0.087	0.057	0.074	0.091	0.058	0.077		
600	0.154	0.101	0.131	0.168	0.106	0.141		
1320	0.147	0.102	0.128	0.159	0.108	0.137	0.734	1.17
1800	0.211	0.124	0.174	0.238	0.132	0.191	1.04	1.10
3840	0.353	0.252	0.310	0.435	0.290	0.371	1.52	1.08
5400	0.437	0.307	0.381	0.574	0.367	0.480	2.00	1.05
7680	0.504	0.358	0.441	0.701	0.443	0.582	2.29	1.05
13740	0.628	0.463	0.557	0.988	0.623	0.815	2.68	1.06
64800	0.893	0.795	0.851	2.237	1.584	1.904		

Table 18b. Kinetic Parameter Error Terms

styrene error	Conversion			ln [M] ₀ /[M]		
	styrene		total error	n-butyl acrylate		total error
	n-butyl acrylate error	styrene error	n-butyl acrylate error	styrene	n-butyl acrylate error	total error
0.027	0.028	0.027	0.030	0.029	0.029	
0.026	0.027	0.027	0.031	0.030	0.031	
0.026	0.027	0.027	0.031	0.030	0.031	
0.026	0.027	0.026	0.033	0.030	0.032	
0.025	0.025	0.025	0.038	0.034	0.036	
0.025	0.025	0.025	0.044	0.036	0.040	
0.024	0.025	0.025	0.049	0.039	0.044	
0.025	0.025	0.025	0.066	0.046	0.055	
0.027	0.026	0.026	0.252	0.126	0.177	

Table 18c. Composition Parameters and Error Terms

conversion	F _{cum} , styrene	S _{Fcum} , styrene	%CV _{Fcum} ,		F _{cum, n-butyl} acrylate	S _{Fcum,n-butyl} acrylate	%CV F _{cum,n-} butyl acrylate
			styrene	acrylate			
0.074	0.616	0.297	48.2	0.384	0.234	61.0	
0.131	0.615	0.163	26.5	0.385	0.129	33.6	
0.128	0.600	0.165	27.5	0.400	0.134	33.6	
0.174	0.640	0.124	19.4	0.360	0.095	26.3	
0.310	0.593	0.064	10.7	0.407	0.053	13.0	
0.381	0.597	0.051	8.6	0.403	0.042	10.4	
0.441	0.594	0.044	7.4	0.406	0.036	8.9	
0.557	0.585	0.035	5.9	0.415	0.029	6.9	
0.851	0.539	0.023	4.3	0.461	0.021	4.5	

Experiment 16**Table 19a. Kinetic Parameters**

time (s)	styrene	Conversion		ln [M] ₀ /[M]				M _n × 10 ⁻⁴	M _w /M _n
		n	n-butyl acrylate	total	styrene	n-butyl acrylate	total		
300	0.034	0.022	0.029	0.035	0.023	0.030			
600	0.152	0.114	0.136	0.165	0.121	0.146			
1320	0.118	0.097	0.109	0.125	0.102	0.116	0.410	1.28	
1800	0.153	0.102	0.132	0.166	0.108	0.142	0.502	1.19	
3840	0.195	0.141	0.173	0.217	0.152	0.189	0.635	1.16	
5400	0.288	0.217	0.259	0.340	0.244	0.299	0.963	1.09	
7680	0.336	0.234	0.294	0.410	0.267	0.348	1.17	1.12	
13740	0.406	0.295	0.360	0.520	0.349	0.446	1.34	1.12	
64800	0.658	0.510	0.597	1.072	0.714	0.908	1.77	1.09	

Table 19b. Kinetic Parameter Error Terms

styrene error	Conversion			ln [M] ₀ /[M]		
	n-butyl acrylate error	total error	styrene error	n-butyl acrylate error	total error	
0.028	0.028	0.028	0.029	0.029	0.029	
0.026	0.027	0.027	0.031	0.030	0.031	
0.027	0.027	0.027	0.030	0.030	0.030	
0.026	0.027	0.027	0.031	0.030	0.031	
0.026	0.027	0.026	0.032	0.031	0.032	
0.025	0.026	0.025	0.035	0.033	0.034	
0.025	0.026	0.025	0.038	0.033	0.036	
0.025	0.025	0.025	0.041	0.036	0.039	
0.025	0.024	0.025	0.073	0.050	0.061	

Table 19c. Composition Parameters and Error Terms

conversion	F _{cum} , styrene	S _{Fcum} , styrene	%CV _{Fcum, styrene}		F _{cum, n-butyl} acrylate	S _{Fcum,n-butyl} acrylate	%CV _{Fcum,n-butyl} butyl acrylate
			styrene	acrylate			
0.029	0.615	0.767	124.6	0.385	0.603	156.9	
0.136	0.580	0.152	26.1	0.420	0.128	30.5	
0.109	0.558	0.187	33.5	0.442	0.164	37.2	
0.132	0.609	0.161	26.5	0.391	0.130	33.1	
0.173	0.590	0.119	20.2	0.410	0.099	24.2	
0.259	0.581	0.076	13.2	0.419	0.065	15.4	
0.294	0.599	0.068	11.3	0.401	0.056	13.9	
0.360	0.589	0.054	9.2	0.411	0.045	11.0	
0.597	0.573	0.032	5.6	0.427	0.027	6.3	

Experiment 17**Table 20a. Kinetic Parameters**

time (s)	styrene	Conversion			ln [M] _o /[M]			$M_n \times 10^{-4}$	M_w/M_n
		<i>n</i> -butyl acrylate	total	styrene	<i>n</i> -butyl acrylate	total			
432	0.073	0.054	0.065	0.076	0.055	0.067	0.488	1.27	
972	0.110	0.064	0.090	0.166	0.066	0.095	0.761	1.16	
1188	0.122	0.075	0.102	0.130	0.078	0.108	0.842	1.20	
1908	0.144	0.099	0.124	0.155	0.104	0.133	1.20	1.10	
3600	0.202	0.132	0.172	0.226	0.141	0.189	1.67	1.09	
5400	0.243	0.162	0.209	0.279	0.177	0.234	2.05	1.07	
7200	0.310	0.225	0.274	0.371	0.255	0.320	2.44	1.06	
12240	0.404	0.288	0.354	0.517	0.339	0.437	0.320	1.09	
23400	0.530	0.384	0.468	0.756	0.485	0.632	3.70	1.09	
86400	0.788	0.636	0.724	1.55	1.01	1.29	5.62	1.11	

Table 20b. Kinetic Parameter Error Terms

These are unavailable for this experiment.

Table 20c. Composition Parameters

conversion	$F_{cum, styrene}$	$F_{cum, n\text{-}butyl acrylate}$
0.065	0.587	0.413
0.090	0.641	0.359
0.102	0.628	0.372
0.124	0.602	0.398
0.172	0.615	0.385
0.209	0.610	0.390
0.274	0.589	0.411
0.354	0.594	0.406
0.468	0.589	0.411
0.724	0.563	0.437

Experiment 18**Table 21a. Kinetic Parameters (Molecular Weight Data Unavailable)**

time (s)	Conversion			$\ln [M]_0/[M]$		
	styrene	<i>n</i> -butyl acrylate	total	styrene	<i>n</i> -butyl acrylate	total
360	0.137	0.088	0.116	0.147	0.192	0.123
900	0.249	0.175	0.218	0.286	0.164	0.246
1200	0.231	0.151	0.197	0.263	0.190	0.219
1920	0.268	0.173	0.228	0.312	0.393	0.259
3840	0.437	0.325	0.390	0.574	0.445	0.494
5520	0.496	0.359	0.438	0.685	0.592	0.576
7380	0.589	0.447	0.529	0.889	0.828	0.753
11220	0.726	0.563	0.657	1.295	1.321	1.070
26700	0.859	0.733	0.806	1.959	1.845	1.640
86400	0.912	0.842	0.883	2.430	0.000	2.146

Table 21b. Kinetic Parameter Error Terms

These are unavailable for this experiment.

Table 21c. Composition Parameters

conversion	$F_{cum, \text{styrene}}$	$F_{cum, n\text{-butyl acrylate}}$
0.116	0.619	0.381
0.218	0.597	0.403
0.197	0.614	0.386
0.228	0.617	0.383
0.390	0.583	0.417
0.438	0.590	0.410
0.529	0.578	0.422
0.657	0.573	0.427
0.806	0.550	0.450
0.883	0.530	0.470

Experiment 19**Table 22a. Kinetic Parameters**

time (s)	total conversion	total ln [M] ₀ /[M]
360	0.146	0.158
960	0.139	0.150
1200	0.138	0.149
1500	0.210	0.236
1920	0.246	0.282
4320	0.270	0.315
6060	0.624	0.978
7320	0.679	1.136
10500	0.794	1.580
86400	0.874	2.071

Table 22b. Kinetic Parameter Error Terms

These are unavailable for this experiment.

Table 22c. Composition Parameters

conversion	F _{cum, styrene}	F _{cum, n-butyl acrylate}
0.146	0.582	0.418
0.139	0.580	0.420
0.138	0.599	0.401
0.210	0.611	0.389
0.246	0.592	0.408
0.270	0.586	0.414
0.624	0.574	0.426
0.679	0.568	0.432
0.794	0.554	0.446
0.874	0.538	0.462

Section 3

Monomer Reactivity Ratio Calculations We estimated monomer reactivity ratios from kinetic data using a non-linear least squares fit to the integrated form of the terminal model composition equation (equation (8)):

$$1 - \frac{[M]}{[M]_0} = 1 - \left(\frac{f_1}{(f_1)_0} \right)^\alpha \left(\frac{1-f_1}{1-(f_1)_0} \right)^\beta \left(\frac{(f_1)_0 - \delta}{f_1 - \delta} \right)^\gamma \quad (8)$$

where $1 - \frac{[M]}{[M]_0}$ is conversion, f_1 is the feed composition of styrene at that value of conversion, $(f_1)_0$ is the initial feed composition, $\alpha = \frac{r_2}{1-r_2}$, $\beta = \frac{r_1}{1-r_1}$, $\delta = \frac{1-r_2}{2-r_1-r_2}$ and $\gamma = \frac{1-r_1r_2}{(1-r_1)(1-r_2)}$. To use equation (8) to determine r_1 and r_2 , a non-linear least squares analysis was used where the sum of squares of residuals between measured and predicted conversion (equation (5)) are minimized by changing r_1 and r_2 :

$$SS(r_1, r_2) = \sum_{i=1}^n \frac{1}{w} \{y_i - f(r_1, r_2)_i\}^2 \quad (9)$$

where y_i is the measured value of conversion at the i th experimental data point, $f(r_1, r_2)_i$ is the value of equation (9) at the i th experimental data point calculated from measured f_1 and $(f_1)_0$, and w is a weighting factor which can be used to account for the error structure of the dependent variable. Error calculations on kinetic data (presented in Section 2) show that the standard deviation of the fitting variable (conversion) is approximately constant at 0.03. This satisfies an inference assumption of least squares analysis (the dependent variable has constant variance).

Tables 23-31 show the initial styrene feeds, measured conversions, calculated parameters of equation (8), and the conversion residuals (defined in equation (9)). These values were calculated at the point estimates for r_1 and r_2 for each experiment, listed in Table 5 of the parent

manuscript and shown in parenthesis at the end of each table title. A dark line separates experimental data with different initial feed conditions.

Table 23. Reactivity ratio calculations for experiment 1 and experiment 7 ($r_1 = 0.80$; $r_2 = 0.26$).

f_{st}	conversion	$\left(\frac{f_1}{(f_1)_o}\right)^\alpha$	$\left(\frac{1-f_1}{1-(f_1)_o}\right)^\beta$	$\left(\frac{(f_1)_o-\delta}{f_1-\delta}\right)^\gamma$	predicted conversion	residual
0.0978	0.1905	0.902058619	1.169862053	0.760590842	0.1974	4.754E-05
0.0731	0.3992	0.816136857	1.30553182	0.629297221	0.3295	4.858E-03
0.0576	0.3386	0.751883672	1.396591695	0.560543729	0.4114	5.305E-03
0.0456	0.4908	0.69360381	1.470558435	0.513229423	0.4765	2.038E-04
0.8634	0.3227	0.999757855	1.018286581	1.045757871	-0.0646	1.500E-01
0.8633	0.4616	0.999708766	1.02202323	1.055331539	-0.0783	2.915E-01
0.8678	0.5941	1.001524114	0.890339931	0.760429374	0.3219	7.407E-02

Table 24. Reactivity ratio calculations for experiment 2 and experiment 7 ($r_1 = 0.80$; $r_2 = 0.22$).

f_{st}	conversion	$\left(\frac{f_1}{(f_1)_o}\right)^\alpha$	$\left(\frac{1-f_1}{1-(f_1)_o}\right)^\beta$	$\left(\frac{(f_1)_o-\delta}{f_1-\delta}\right)^\gamma$	predicted conversion	residual
0.0828	0.2753	0.876784107	1.242434739	0.687844493	0.2507	6.063E-04
0.0676	0.3166	0.827932098	1.3257004	0.615797155	0.3241	5.640E-05
0.0465	0.4158	0.745170837	1.447588041	0.530441561	0.4278	1.434E-04
0.8634	0.3227	0.999801507	1.017718983	1.046511154	-0.0648	1.502E-01
0.8633	0.4616	0.999761266	1.02133844	1.056249182	-0.0785	2.918E-01
0.8678	0.5941	1.001249162	0.893527492	0.75740454	0.3224	7.382E-02

Table 25. Reactivity ratio calculations for experiment 3 and experiment 7 ($r_1 = 0.80$; $r_2 = 0.22$).

f_{st}	conversion	$\left(\frac{f_1}{(f_1)_o}\right)^\alpha$	$\left(\frac{1-f_1}{1-(f_1)_o}\right)^\beta$	$\left(\frac{(f_1)_o-\delta}{f_1-\delta}\right)^\gamma$	predicted conversion	residual
0.0939	0.2091	0.908540329	1.184088954	0.746911552	0.1965	1.606E-04
0.0793	0.2775	0.866146031	1.261253441	0.670399816	0.2676	9.723E-05
0.0474	0.4317	0.749254733	1.442152886	0.533827091	0.4232	7.344E-05
0.0347	0.4671	0.685980816	1.519626085	0.488685896	0.4906	5.505E-04
0.8634	0.3227	0.999801507	1.017718983	1.046511154	-0.0648	1.502E-01
0.8633	0.4616	0.999761266	1.02133844	1.056249182	-0.0785	2.918E-01
0.8678	0.5941	1.001249162	0.893527492	0.75740454	0.3224	7.382E-02

Table 26. Reactivity ratio calculations for experiment 1 and experiment 8 ($r_1 = 0.68$; $r_2 = 0.25$).

f_{st}	conversion	$\left(\frac{f_1}{(f_1)_0}\right)^\alpha$	$\left(\frac{1-f_1}{1-(f_1)_0}\right)^\beta$	$\left(\frac{(f_1)_0-\delta}{f_1-\delta}\right)^\gamma$	predicted conversion	residual
0.0978	0.1905	0.904002983	1.084492408	0.817705021	0.1983	6.192E-05
0.0731	0.3992	0.819607979	1.147793199	0.711985755	0.3302	4.758E-03
0.0576	0.3386	0.756376013	1.188509957	0.654505203	0.4116	5.340E-03
0.0456	0.4908	0.698924877	1.220648311	0.61393629	0.4762	2.121E-04
0.8615	0.2162	0.999028857	1.038821964	1.053535364	-0.0934	9.583E-02
0.8653	0.2792	1.000498926	0.980327935	0.973822131	0.0449	5.489E-02
0.8650	0.4015	1.000403498	0.984076216	0.978762048	0.0364	1.332E-01
0.8640	0.4894	1.000000966	0.999961726	0.99994846	0.0001	2.394E-01
0.8867	0.5792	1.008775859	0.681364661	0.642441083	0.5584	4.325E-04

Table 27. Reactivity ratio calculations for experiment 2 and experiment 8 ($r_1 = 0.67$; $r_2 = 0.22$).

f_{st}	conversion	$\left(\frac{f_1}{(f_1)_0}\right)^\alpha$	$\left(\frac{1-f_1}{1-(f_1)_0}\right)^\beta$	$\left(\frac{(f_1)_0-\delta}{f_1-\delta}\right)^\gamma$	predicted conversion	residual
0.0828	0.2753	0.880128404	1.120125015	0.760352922	0.2504	6.209E-04
0.0676	0.3166	0.832470652	1.158747516	0.701563654	0.3233	4.433E-05
0.0465	0.4158	0.75154379	1.213253549	0.629650455	0.4259	1.008E-04
0.8615	0.2162	0.999210427	1.038018606	1.054290399	-0.0935	9.591E-02
0.8653	0.2792	1.000405589	0.98072364	0.973481007	0.0449	5.488E-02
0.8650	0.4015	1.000328016	0.984397126	0.978483873	0.0365	1.332E-01
0.8640	0.4894	1.000000785	0.999962503	0.99994777	0.0001	2.394E-01
0.8867	0.5792	1.007128598	0.686695214	0.639449098	0.5578	4.603E-04

Table 28. Reactivity ratio calculations for experiment 3 and experiment 8 ($r_1 = 0.67$; $r_2 = 0.23$).

f_{st}	conversion	$\left(\frac{f_1}{(f_1)_0}\right)^\alpha$	$\left(\frac{1-f_1}{1-(f_1)_0}\right)^\beta$	$\left(\frac{(f_1)_0-\delta}{f_1-\delta}\right)^\gamma$	predicted conversion	residual
0.0939	0.2091	0.910563533	1.092539707	0.807118245	0.1971	1.462E-04
0.0793	0.2775	0.869037365	1.129271175	0.74586925	0.2680	8.980E-05
0.0474	0.4317	0.754287611	1.21139816	0.632032145	0.4225	8.580E-05
0.0347	0.4671	0.692003156	1.245059293	0.592867544	0.4892	4.875E-04
0.8615	0.2162	0.999205744	1.038106744	1.054414823	-0.0937	9.605E-02
0.8653	0.2792	1.000407996	0.980680203	0.973422712	0.0450	5.483E-02
0.8650	0.4015	1.000329962	0.984361901	0.978436448	0.0365	1.332E-01
0.8640	0.4894	1.00000079	0.999962418	0.999947653	0.0001	2.394E-01
0.8867	0.5792	1.007171041	0.686108155	0.638818111	0.5586	4.268E-04

Table 29. Reactivity ratio calculations for experiment 1 and experiment 9 ($r_1 = 0.82$; $r_2 = 0.26$).

f_{st}	conversion	$\left(\frac{f_1}{(f_1)_o}\right)^\alpha$	$\left(\frac{1-f_1}{1-(f_1)_o}\right)^\beta$	$\left(\frac{(f_1)_o-\delta}{f_1-\delta}\right)^\gamma$	predicted conversion	residual
0.0978	0.1905	0.902058619	1.196652498	0.744059273	0.1968	4.043E-05
0.0731	0.3992	0.816136857	1.356745081	0.606190446	0.3288	4.958E-03
0.0576	0.3386	0.751883672	1.465569149	0.534851463	0.4106	5.195E-03
0.0456	0.4908	0.69360381	1.554725899	0.486148886	0.4758	2.260E-04
0.8657	0.2007	1.000685852	0.942429162	0.834363266	0.2131	1.545E-04
0.8682	0.3288	1.001676938	0.863746056	0.648004776	0.4393	1.222E-02
0.8690	0.5019	1.001998431	0.839333057	0.598269831	0.4968	2.593E-05
0.8706	0.6868	1.002603127	0.794845716	0.516221159	0.5886	9.631E-03

Table 30. Reactivity ratio calculations for experiment 2 and experiment 9 ($r_1 = 0.82$; $r_2 = 0.22$).

f_{st}	conversion	$\left(\frac{f_1}{(f_1)_o}\right)^\alpha$	$\left(\frac{1-f_1}{1-(f_1)_o}\right)^\beta$	$\left(\frac{(f_1)_o-\delta}{f_1-\delta}\right)^\gamma$	predicted conversion	residual
0.0828	0.2753	0.876784107	1.280053906	0.668121648	0.2501	6.338E-04
0.0676	0.3166	0.827932098	1.378070097	0.592941059	0.3235	4.744E-05
0.0465	0.4158	0.745170837	1.523070947	0.504731005	0.4272	1.281E-04
0.8657	0.2007	1.000562166	0.944477657	0.833360928	0.2125	1.384E-04
0.8682	0.3288	1.001374397	0.868391413	0.64641654	0.4379	1.190E-02
0.8690	0.5019	1.001637842	0.844733534	0.596627154	0.4952	4.567E-05
0.8706	0.6868	1.002133313	0.801556843	0.51458593	0.5867	1.002E-02

Table 31. Reactivity ratio calculations for experiment 3 and experiment 9 ($r_1 = 0.82$; $r_2 = 0.23$).

f_{st}	conversion	$\left(\frac{f_1}{(f_1)_o}\right)^\alpha$	$\left(\frac{1-f_1}{1-(f_1)_o}\right)^\beta$	$\left(\frac{(f_1)_o-\delta}{f_1-\delta}\right)^\gamma$	predicted conversion	residual
0.0939	0.2091	0.908540329	1.211904758	0.730199151	0.1960	1.728E-04
0.0793	0.2775	0.866146031	1.302129548	0.649861951	0.2671	1.088E-04
0.0474	0.4317	0.749254733	1.516568241	0.508210454	0.4225	8.511E-05
0.0347	0.4671	0.685980816	1.609571323	0.461958623	0.4899	5.208E-04
0.8657	0.2007	1.000562166	0.944477657	0.833360928	0.2125	1.384E-04
0.8682	0.3288	1.001374397	0.868391413	0.64641654	0.4379	1.190E-02
0.8690	0.5019	1.001637842	0.844733534	0.596627154	0.4952	4.567E-05
0.8706	0.6868	1.002133313	0.801556843	0.51458593	0.5867	1.002E-02

Tables 23- 31 originated in Excel, where the conversion and f_{st} values could be entered from the experimental data. Each successive column represents an element of the integrated composition equation (it was easier to troubleshoot the calculation by breaking it up into elements). Standard formula syntax for Excel 7.0 was used to calculate the final predicted value of conversion from

the integrated form of the composition equation based on the experimental conversion and composition data.

Since the conversion values predicted from the integrated equation depend on the reactivity ratios, two cells were designated as r_1 and r_2 . The sum of the squares of the differences between the predicted and measured total conversion was calculated in a new cell. This sum of squares value can be manipulated by changing the r_1 and r_2 values and it is possible to find the minimum by hand or by using Solver in Excel, where the minimum condition for the sum of squares is set and Excel changes r_1 and r_2 until the minimum condition is satisfied.

Alternatively, it is possible to evaluate the sum of squares parameter for a large range of r_1 and r_2 and then find the minimum by inspecting this grid of numbers. We opted to write a short macro which did this automatically for a grid of r_1 and r_2 values, speeding up the time needed to generate a detailed surface. The grid was designed by placing r_1 values in a single column (occupying several rows) and the r_2 values in a single row (occupying several columns). The macro (whose commented code is shown below) was then executed.

Sub SS-space()

'The following commands place the appropriate r1 and r2 values

*'in the independent variable cells (B6 and B7)and fill the matrix with the evaluated values
'of the SS-space function (B12).*

For B = 1 To 55

Worksheets("Sheet1").Cells(7, 2).Value = Worksheets("Sheet1").Cells(7, B + 20).Value

Worksheets("Sheet1").Cells(8, B + 20).Select

For B = 1, these commands read the r₂ value in row 7, column 21 of Sheet 1 and place it in the cell designated as row 7 column 2 of Sheet 1.

For a = 1 To 255

Worksheets("Sheet1").Cells(6, 2).Value = Worksheets("Sheet1").Cells(a + 7, 20).Value

For a = 1, this line reads the r₁ value of the cell corresponding to row 8, column 20 of Sheet 1 and places that value in the cell corresponding to row 6 column 2 of Sheet 1.

Worksheets("Sheet1").Cells(a + 7, B + 20).Value = Worksheets("Sheet1").Cells(12, 2).Value

For a This line reads the sum-of-squares value in the cell corresponding to row 12, column 2 of Sheet 1 and places it in the cell corresponding to row 8, column 21.

Next a

The a index is increased by 1 and the cycle repeats. Numbers corresponding to the sum of squares space value are placed in new rows, but in the same column (column 21).

Next B

When a = 255 and the last command executed, the B index is increased by 1 and the computer returns to the beginning of the code. All new sum of squares values will be placed in column 22.

There will be as many columns of r₁ values as the largest integer of B - in this case, 55. There will be as many rows of r₁ values (for a given r₂ value) as the largest integer of a - in this case,

255. This code generates a 55x255 matrix of sum-of-squares values from which the minimum can be selected.

End Sub

Using this code, the SS-space is a grid not unlike the grid of numbers published in an early paper describing the technique.² However, it is difficult to graph the numbers corresponding to the JCI in this format since they are not arranged in a x,y-column format. Therefore, we also wrote a short macro which can convert a matrix into an x,y,z-column format. In this case, it is very easy to use a graphics routine (either one in Excel or another program) to actually visualize the surface. Additionally, Excel has very powerful sorting routines which work for data organized in columns. The code for this matrix-conversion macro is shown below:

Sub Matrixconvert()

'This algorithm converts the values of the matrix into x,y,z column format.

'This can be copied and pasted into Kaleidagraph, or graphed directly in Excel.

'Typically, plots of r2 versus r1 are shown, where values are plotted when the EVM
'is non-zero.

Dim x As Integer

Dim y As Integer

Dim z As Integer

Dim a As Integer

'This portion of the algorithm converts the r1 value from the matrix to column format:

For z = 1 To 55

For x = 1 To 255

Worksheets("Sheet3").Cells(x + z * 255 - 254, 1).Value =

Worksheets("Sheet1").Cells(x + 7, 20).Value

Next x

Next z

'This portion of the algorithm converts the r2 value from the matrix to column format:

For z = 1 To 55

For y = 1 To 255

Worksheets("Sheet3").Cells(y + z * 255 - 254, 2).Value =

Worksheets("Sheet1").Cells(7, z + 20).Value

Next y

Next z

'This portion of the algorithm converts the EVM parameter value

'from the matrix to column format:

For z = 1 To 55

For a = 1 To 255

Worksheets("Sheet3").Cells(a + z * 255 - 254, 3).Value =

Worksheets("Sheet1").Cells(a + 7, z + 20).Value

Next a

Next z

'In order to ensure that the elements of the matrix have been properly sorted,

*'this algorithm compares the difference between a matrix element value and the corresponding
'value for this element that has been converted to column format.*

*'In both cases, it should be the same number, and the sum over the whole range of
'converted matrix elements should equal zero.*

For z = 1 To 55

For x = 1 To 255

Worksheets("sheet3").Cells(x + z * 255 - 254, 4).Value =

Worksheets("sheet3").Cells(x + z * 255 - 254, 3).Value - Worksheets("sheet1").Cells(x + 7, z + 20).Value

Next x

Next z

End Sub

Again, we have taken advantage of nested looping structures and counting indexes to construct the x,y,z column format. The JCI can be constructed from these data by using Excel's built in sorting function, and displaying the r_1 and r_2 values for which the corresponding sum-of-squares value corresponds to the joint confidence condition, calculated from equation (6) of the parent manuscript.

Section 4

In the manuscript, it was claimed that polymerization of *n*-butyl acrylate at 90 °C with catalyst concentrations comparable to the copolymerizations is controlled. There are no published studies on ATRP of *n*-butyl acrylate under these conditions so we present these limited data to show that the polymerization is controlled under these conditions.

Table 33 shows the kinetic / molecular weight parameters for two different polymerizations of *n*-butyl acrylate under similar reaction conditions. Figure 1 shows the semilogarithmic kinetic plots of these reactions. Figure 2 shows the corresponding molecular weight behavior. The reaction seems to be controlled under these conditions to relatively high conversions, though there is a short "non-stationary" period at the beginning of the polymerization. Discrepancies between measured and theoretical molecular weights are presumably due to comparing the poly(*n*-butyl acrylate) with linear polystyrene.

Table 33. Kinetic parameters for the bulk polymerization of *n*-butyl acrylate. $[M]_0:[I]_0:[CuBr]_0:[dNbpy]_0 = 100:1:1:2$; 90 °C.

Trial	time (s)	conversion	$\ln [M]_0/[M]$	$M_{n,th} \times 10^4$	$M_n \times 10^4$	M_w/M_n
1	0	0.000	0.000	0.000	0.00	
	576	0.675	1.124	0.865	0.93	1.24
	1440	0.851	1.904	1.091	1.22	1.17
	2196	0.917	2.489	1.175	1.29	1.17
	2736	0.944	2.882	1.210	1.37	1.20
	3816	0.973	3.612	1.247	1.40	1.20
2	0	0.000	0.000	0.00	0.00	0.00
	612	0.726	1.295	0.93	1.03	1.23
	1188	0.831	1.778	1.07	1.17	1.20
	1800	0.896	2.263	1.15	1.27	1.18
	2412	0.927	2.617	1.19	1.31	1.19
	2988	0.949	2.976	1.22	1.35	1.20

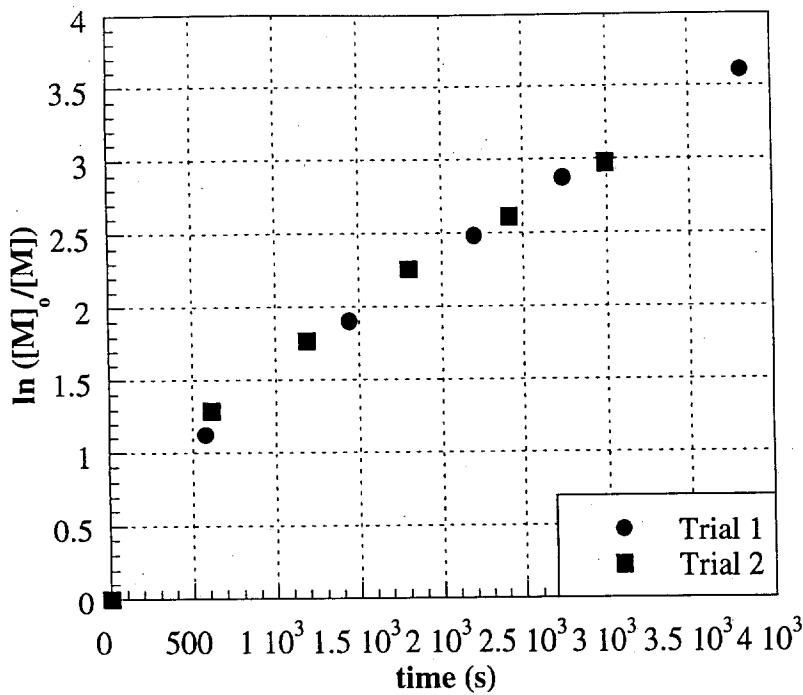


Figure 1. Semilogarithmic kinetic plots for the bulk polymerization of n-butyl acrylate at 90 °C.

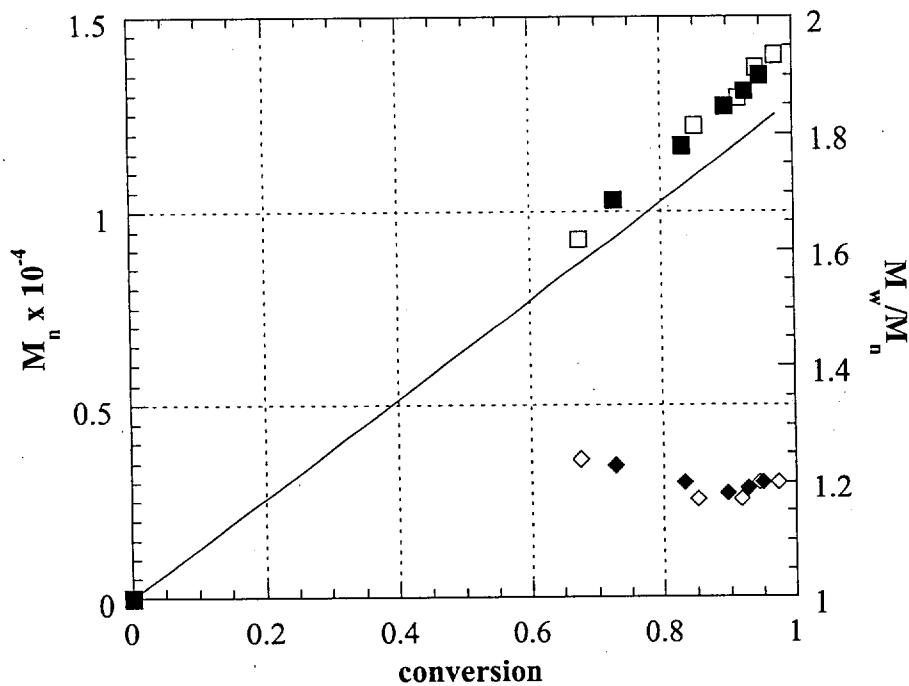


Figure 2. M_n (squares), $M_{n,\text{th}}$ (line) and M_w/M_n (diamonds) versus conversion for the bulk polymerization of n-butyl acrylate at 90 °C. Open symbols denote Trial 1; filled symbols denote Trial 2

Equilibrium Constants

According to the currently accepted mechanism of ATRP, a dynamic equilibrium between dormant and active species is established during the polymerization. Since this equilibrium position affects the rate of reaction, it is possible to estimate the equilibrium constant from kinetic data, as done previously.³ We measured the equilibrium constants of styrene and *n*-butyl acrylate under conditions similar to those reported in the parent manuscript for copolymerizations. Initially, we were trying to model the reactions to see if there were any unusual kinetic dependencies when two monomers with different equilibrium constants were simultaneously copolymerized.

Tables 34 and 35 summarize the kinetic data for the polymerization of styrene and *n*-butyl acrylate with 10 mol % copper (II) bromide. Using an excess amount of copper (II) bromide ensures that the concentration of this reagent is constant during the polymerization, simplifying the calculations.

Table 34. Reaction conditions for styrene polymerization with excess copper (II) at 100 °C.

Trial	[M] ₀	[I] ₀ × 10 ⁻²	[CuBr] ₀ × 10 ⁻²	[CuBr ₂] ₀ × 10 ⁻³	[ligand] ₀ × 10 ⁻¹	time (s)	ln [M] ₀ /[M]
1	n / a	8.26	8.37	8.06	1.67	3840	0.275
						7560	0.633
						15360	1.04
						22440	1.68
2	7.78	8.26	8.23	8.95	1.66	3540	0.422
						10800	0.815
						29160	2.28
						32640	2.43
3	7.63	8.27	8.37	8.06	1.67	3120	0.248
						9660	0.646
						16200	0.916
						23400	1.54
						27000	1.64

Table 35. Reaction conditions for *n*-butyl acrylate polymerization with excess copper (II).

Trial	[M] _o	[I] _o × 10 ⁻²	[CuBr] _o × 10 ⁻²	[CuBr ₂] _o × 10 ⁻³	[ligand] _o × 10 ⁻¹	time (s)	ln [M] _o /[M]
1	6.17	8.50	8.23	8.95	1.68	1800	0.486
						3600	1.10
						4200	1.08
						4800	1.56
						5460	1.66
2	6.15	8.50	8.23	7.16	1.66	1020	0.293
						3120	1.21
						4080	1.58
						5160	2.10
3	n/a	8.50	8.23	7.16	1.67	600	0.258
						1200	0.603
						1800	0.787
						2400	1.27
						3000	1.51
4	6.15	8.38	8.37	8.95	2.03	420	0.068
						2100	0.656
						2880	0.899
						4920	1.71
						7080	2.47
						12900	4.61

Using equation (10) with average experimental quantities from Tables 34-35 and with experimentally determined k^{app} (determined from linear regression of the kinetic data) the equilibrium constants can be estimated. Table 36 shows the results of the calculations

$$K_{eq} = \frac{k^{app}[CuBr_2]_o}{k_p[I]_o[CuBr]_o} \quad (9)$$

Table 36. Equilibrium constant measurements for styrene and *n*-butyl acrylate at 100 °C.

Monomer	k^{app} (s ⁻¹)	[I] _o	[CuBr] _o	[CuBr ₂] _o	k_p	K_{eq}
styrene	7.0×10^{-5}	8.3×10^{-2}	8.3×10^{-2}	8.3×10^{-3}	1.1×10^3	7.7×10^{-8}
<i>n</i> -butyl acrylate	3.5×10^{-4}	8.5×10^{-2}	8.2×10^{-2}	8.0×10^{-3}	6.3×10^4	6.4×10^{-9}

Cursory error analysis indicates that the equilibrium constants have a %CV = 30 %. This is due to the imprecision in measuring small amounts of copper (II) bromide in the glove box on a balance which is precise only to three decimal places.

References

- (1) Skoog, D. A.; Leary, J. J. *Principles of Instrumental Analysis*; 4th Ed. ed.; Saunders College Publishing: Forth Worth, 1992; pp. Appendix 1.
- (2) van Herk, A. M. *J. Chem. Educ.* **1995**, *72*, 138.
- (3) Qiu, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 5643.