

## Free-Radical Copolymerization I. Reactivity Ratios in Bulk-Copolymerization of *p*-Chlorostyrene and Methyl Acrylate

Takeshi FUKUDA, Yung-Dae MA, and Hiroshi INAGAKI

*Institute for Chemical Research, Kyoto University,  
Uji, Kyoto 611, Japan*

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**ABSTRACT:** In order to establish the composition equation for the bulk-copolymerization of *p*-chlorostyrene (monomer 1) and methyl acrylate (monomer 2) at 40°C, an extraordinarily large number of careful polymerization runs were carried out covering a wide range of feed composition. The samples were analyzed for composition by both potentiometric titration for chlorine and combustion analysis for carbon. The optimum set of terminal-model parameters evaluated by a least-squares curve-fitting procedure are  $r_1=1.21$  and  $r_2=0.144$ , quite at variance with the literature values, but conform to the  $Q-e$  scheme. However, the chlorine and carbon sets of data consistently indicate failure of the terminal model to accurately represent this system. The penultimate model parameters  $r_1=0.92$ ,  $r_1'=2.3$ , and  $r_2(=r_2')=0.18$  represent the system almost perfectly. This indicates the presence of significant penultimate effects on type-1 radicals. The question as to the penultimate effects on type-2 radicals remains to be answered.

**KEY WORDS** Reactivity Ratios / *p*-Chlorostyrene / Methyl Acrylate / Terminal Model / Penultimate Model / Least-Squares Curve-Fitting /  $Q-e$  Scheme /

Of the great number of papers in the literature on free-radical copolymerization, the overwhelming majority are concerned with reactivity ratios.<sup>1-3</sup> Recently, some of the original reactivity ratio values compiled by Young<sup>4</sup> have been recalculated by Greenley<sup>5</sup> according to the method of Kelen and Tüdös.<sup>6</sup> In many cases, this recalculation showed significant differences with the original values. Since the method of Kelen and Tüdös is statistically superior<sup>6,7</sup> to earlier methods such as that of Fineman and Ross,<sup>8</sup> new values should generally be closer to the true values. This, of course, is not necessarily the case with individual copolymers. One should rather regard a set of experimental data as poor, if it gives largely different results when evaluated in different ways. As a general rule, a set of data of sufficient quality and quantity should provide the same results regardless of the method of evaluation. It seems that poor sets of data are rather numerous in the literature.

Except for some limited systems,<sup>9</sup> *e.g.*, those in which one monomer hardly polymerizes by itself,

reactivity ratio values seem to have been established without full justification of the assumed physical model, *i.e.*, the terminal model. The propriety of the model can be, in principle, evaluated by a comparison of experimental and calculative composition.<sup>10</sup> In practice, this requires extremely accurate and elaborate experiments, since the differences between terminal and higher-order models, *e.g.*, the penultimate model,<sup>11</sup> are usually very small even when the model parameters are very different.<sup>12,13</sup> Most of the reported experiments do not seem to have been designed to provide data accurate enough in this respect, nor do they take the alternative approach of examining the sequential distributions of comonomers in a chain.<sup>14</sup> One may argue that the problem of model propriety may not be too serious since most data can be, at least to good approximations, represented by the terminal model. This may be true, as far as copolymer compositions are concerned. The problem is crucial, however, when one deals with rate equations of copolymerization, as will be discussed in detail in a forth-

coming paper of this series.<sup>15</sup>

In this paper, we examine the composition equation of the bulk-copolymerization of *p*-chlorostyrene (pCS) and methyl acrylate (MA).<sup>16</sup> Originally, we were interested in the composition distribution of the copolymers produced in a continuous stirred tank reactor (CSTR), as a measure for fluid mixing in the reactor.<sup>17-19</sup> To this end, the pCS-MA system appeared to be beneficial in several technical aspects. However, at the beginning of the work, we became aware of the general shortage of accumulated knowledge on incipient copolymerization kinetics, and this has been a major incentive for the present study.

In each experiment, an attempt was made to carry out as many independent runs as possible. Even in the most careful work, experimental errors originating from various sources were unavoidable, but insofar as they were "random" errors, their influence upon final results may be considered minimal, provided a sufficient number of statistics are available.

## EXPERIMENTAL

### Materials

The pCS monomer was synthesized from *p*-dichlorobenzene (pDCB) by a standard procedure.<sup>20,21</sup> The yield, weight ratio of pCS to pDCB, was about 40%. The raw pCS was distilled under a reduced nitrogen atmosphere, dried over blue silicagel, and kept in a refrigerator ( $-20^{\circ}\text{C}$ ) until required. It was redistilled just prior to use. Analysis by gas chromatography, combustion, and infrared spectroscopy showed that the pCS was pure to a sufficient degree (*cf.* Table I and Figure 1).

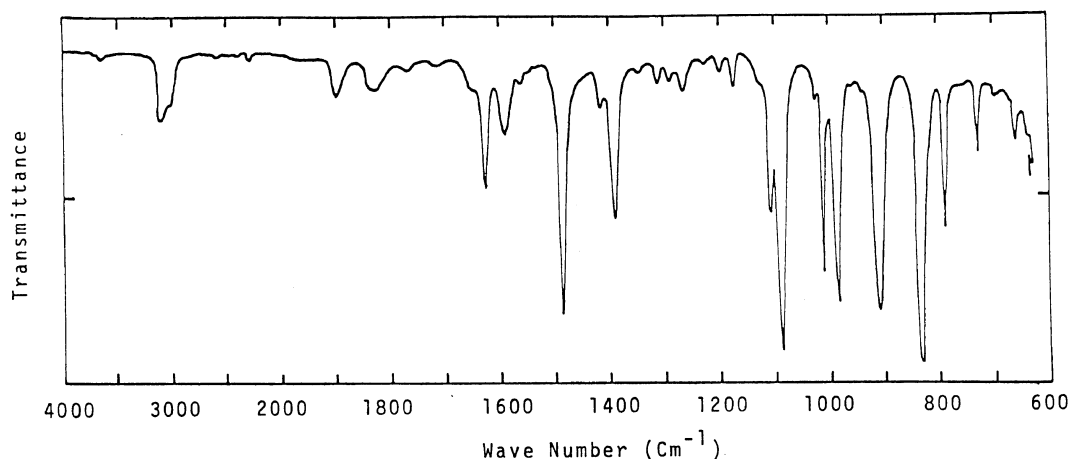
The MA monomer (Nakarai Chemicals Ltd.) was washed from two to three times with a 10%-aqueous solution of sodium hydroxide and then five to seven times with distilled water, dried over blue silicagel at  $-20^{\circ}\text{C}$  for one day, and distilled twice under a reduced nitrogen atmosphere. Prior to use, it was dried over calcium hydride for several hours and distilled again.

Azobisisobutyronitrile (AIBN) purchased from

**Table I.** Characteristics of *p*-chlorostyrene

	Combustion analysis		Chlorine assay <sup>a</sup>	Gas chromatography
	C/%	H/%	Cl/%	Purity/%
Found	69.8	5.11	25.7	99.8
Theoretical	69.3	5.05	25.6	—

<sup>a</sup> Values for the polymer.



**Figure 1.** Infrared spectrum of the pCS synthesized in this study. A commercial sample (Nakarai Chemicals Ltd.) gave a spectrum essentially the same as this.

Nakarai Chemicals Ltd. was recrystallized twice from an ethanol solution, dried in a vacuum oven, and kept in a refrigerator until required.

#### Sample Preparation and Characterization

A known amount of the initiator, AIBN, was charged in a pyrex tube equipped with a three-way tap, through which pCS and then MA were syringed in under a nitrogen atmosphere, the tube plus fittings being weighed at each stage to determine the monomer weights charged. The tube was then connected by a rubber tube to a vacuum line, and degassed with freezing-and-thawing cycles repeated (usually six to eight cycles) until no bubbles were formed in the mixture. Finally, the tube was sealed off under vacuum or in an extrapure nitrogen atmosphere. The mixture ampoule thus prepared was weighed again. In some cases, the weight loss caused by degassing was not negligible. Since no weight loss was detectable in the case of pure pCS, the loss could be ascribed totally to that of the more volatile MA.

The mixture was allowed to polymerize at 40°C in a water bath equipped with a shaker. Polymerization was terminated by quenching in liquid nitrogen. The precipitate from a 30-fold excess of methanol was dried to a constant weight, and weighed to determine the conversion. The polymer thus obtained was further purified by precipitation from a benzene solution into methanol, and subjected to molecular characterization.

More than forty such runs were carried out over feed compositions from  $f_1=0.05$  to 0.87 (henceforth, we designate pCS as monomer 1 and MA as monomer 2), keeping the initiator concentrations at the same level, and conversions at low values (see below).

The copolymer compositions were determined by both combustion analysis for carbon and potentiometric titration with silver nitrate for chlorine.

Several samples were analyzed by gel permeation chromatography (GPC) for their approximate molecular weights. All runs were carried out at an ambient temperature using reagent grade tetrahydrofuran as a carrier solvent. The column system was calibrated with seven Pressure Chemical Standard Polystyrenes with molecular weights from  $4.0 \times 10^3$  to  $2.0 \times 10^6$ .

## RESULTS AND DISCUSSION

Table II summarizes the polymerization conditions and composition of the copolymers obtained with conversions not exceeding 2.5% by weight. This upper limit of conversion was low enough so that the composition drifts with conversion could be neglected.

Figure 2 shows the number-average molecular weights  $M_n$  and the ratios,  $M_w/M_n$ , of the weight- to number-average molecular weights, which were approximately evaluated by the polystyrene-calibrated GPC. To our knowledge, the approximations involved were reasonable for our particular system. The figure suggests that the values of  $M_n$  of our samples are of the order  $10^5$ , apparently large enough for "long-chain approximations"<sup>1-3</sup> to be applicable. Incidentally, the  $M_w/M_n$  ratios seem to range between 1.5 and 2.0, as is typical of polymers produced by "normal" mechanisms of free-radical polymerization.<sup>22</sup> The figure interestingly suggests the presence of a minimum in  $M_w/M_n$  at an intermediate feed composition, but this should be discussed on a more quantitative basis.

#### Analysis Based on the Terminal Model

We analyze the composition data based on the terminal model equation<sup>23</sup>:

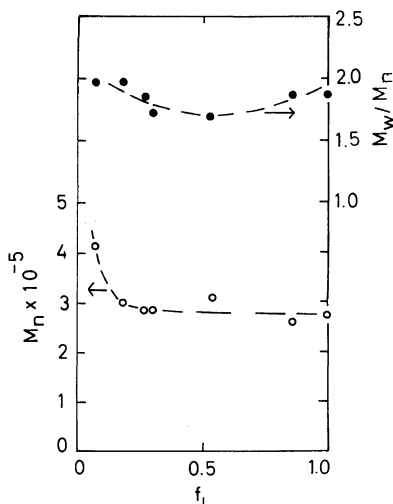


Figure 2. Values of  $M_n$  and  $M_w/M_n$  of several samples plotted against pCS feed composition. Sample codes for the data points are, from left to right, 2, 7, 10, 12, 20, 29, and 31, respectively (cf. Table II).

Table II. pCS-MA bulk-copolymerization data (40°C)

Run	$f_1^a$	$M_T^b$ mol l <sup>-1</sup>	$10^2 I^c$ mol l <sup>-1</sup>	$t^d$ min	$Y^e$ wt%	$F_{1,c}^f$	$F_{1,c}^g$
1	0.049	10.54	3.146	—	0.544	0.222	0.207
2	0.073	10.44	2.938	54	1.346	0.283	0.251
3	0.085	10.39	2.887	25	0.544	0.277	0.265
4	0.179	10.04	3.960	120	2.416	0.429	—
5	0.181	10.03	2.809	—	0.500	0.444	0.431
6	0.184	10.02	3.094	120	2.262	0.442	0.473
7	0.184	10.02	3.393	59	1.042	0.445	0.419
8	0.239	9.821	4.141	120	2.363	0.471	0.561
9	0.241	9.815	2.695	—	0.617	0.486	—
10	0.272	9.705	3.706	59	1.080	0.511	0.501
11	0.293	9.634	2.919	—	0.702	0.539	0.546
12	0.301	9.606	4.347	59	1.178	0.563	0.534
13 <sup>h</sup>	0.336	9.488	2.620	—	0.542	0.548	0.542
14	0.390	9.314	3.042	—	0.731	0.617	0.632
15	0.414	9.239	3.799	60	1.127	0.616	0.605
16	0.421	9.216	3.029	—	0.735	0.628	0.641
17	0.443	9.149	4.431	120	2.431	0.638	0.638
18	0.462	9.029	4.920	60	1.322	0.632	0.625
19	0.525	8.904	2.718	46	~1	0.672	—
20	0.532	8.885	4.239	60	1.203	0.679	0.666
21	0.635	8.597	2.806	45	~1	0.730	—
22	0.638	8.587	4.293	60	1.191	0.746	0.757
23	0.639	8.584	3.311	—	0.783	0.731	0.753
24	0.709	8.400	4.705	60	1.315	—	0.806
25	0.714	8.387	4.056	120	2.273	0.766	0.785
26	0.756	8.279	2.853	50	~1	0.806	—
27	0.757	8.277	3.007	50	0.867	0.807	0.805
28	0.858	8.032	4.318	59	1.234	—	0.843
29	0.861	8.024	3.675	60	1.158	0.866	0.888
30	0.868	8.008	3.262	60	1.075	0.855	0.898
31 <sup>i</sup>	1.000	7.710	4.452	120	2.595	1.004	1.002

<sup>a</sup> Mole fraction of pCS in feed.

<sup>b</sup> Total monomer concentration.

<sup>c</sup> AIBN concentration.

<sup>d</sup> Reaction time.

<sup>e</sup> Conversion.

<sup>f</sup> Mole fraction of pCS in copolymer (chlorine assay).

<sup>g</sup> Mole fraction of pCS in copolymer (carbon analysis).

<sup>h</sup> Run with a commercially obtained pCS.

<sup>i</sup> pCS homopolymerization.

$$F_1 = 1 - F_2 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (1)$$

where  $F$  and  $f$  are the compositions of copolymer and feed, respectively, and  $r_1$  and  $r_2$  are the reactivity ratios,

$$r_i = k_{ii}/k_{ij} \quad (i \neq j) \quad (2)$$

with  $k_{mn}$  being the rate constant for the terminal radical  $m$  to add monomer  $n$  ( $m, n = 1$  or  $2$ ).

The  $r_1, r_2$  values were so determined that the sum  $E$  of the squared residuals was minimum:

$$E = \sum_s (F_{\text{obs}} - F_{\text{term}})^2 \quad (3)$$

where  $F_{\text{obs}}$  and  $F_{\text{term}}$  are the observed and calcu-

**Table III.** Reactivity ratios in bulk-copolymerization of pCS and MA at 40°C<sup>a</sup>

	Terminal-model parameters			<i>s</i>	$(E/s)^{1/2}$
	$r_1$	$r_2$			
Chlorine	1.16	0.138		28	0.0159
Carbon	1.28	0.150		25	0.0253
Chlorine + Carbon	1.21	0.144		53	0.0212
	Penultimate-model parameters			<i>s</i>	$(E/s)^{1/2}$
	$r_1$	$r_1'$	$r_2=r_2'$		
Chlorine	0.87	2.1	0.17	28	0.0118
Carbon	0.96	2.6	0.19	25	0.0223
Chlorine + Carbon	0.92	2.3	0.18	53	0.0181

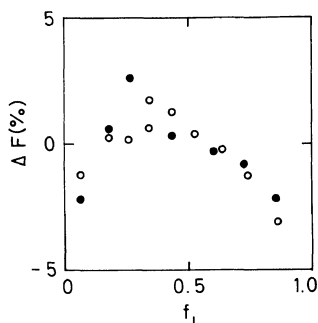
<sup>a</sup> *s* = number of samples; *E* = sum of squared residuals.

relative compositions, and the summation extends over *s* independent runs. [As stated previously, the amount of the charged monomers was determined by the gravimetric method which should generally be more reliable than the volumetric method, and the conversions were kept at strictly low values. Thus, we may expect that our values of *f* are correct to an extent no greater than 0.3%. This figure being much smaller than the errors associated with the values of  $F_{\text{obs}}$  (see below), it will suffice to consider errors in  $F_{\text{obs}}$  only.] In the calculations, use of a digital computer, Facom 230-48, Fujitsu Ltd., was made. The results are reported in Table III.

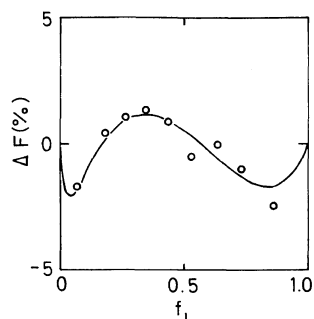
Values of  $r_1, r_2$  computed from the chlorine data are  $r_1=1.16$  and  $r_2=0.138$ , which are somewhat different from the carbon-data values,  $r_1=1.28$  and  $r_2=0.150$ . Since the difference between the carbon content of pCS and MA is relatively small (about 14%), and the analytical accuracy is around 0.3%, the values of  $F_{\text{obs}}$  from the carbon data may be in error as much as 2%. (Strictly, this figure is for copolymers of nearly equimolar composition. Provided that analytical accuracy is constant for all compositions, the error range of *mole-based* composition monotonously increases or decreases with composition, depending on which monomer has a larger molecular weight. Yamada *et al.*<sup>27</sup> propose using this composition-dependent error range as a statistical weight in least-squares calculations.) On the other hand, the chlorine  $F_{\text{obs}}$ -values are expected to be correct to 1%. The values of  $(E/s)^{1/2}$  shown in Table III in fact indicate that the carbon data

scatter more widely about the calculative curve. In this context alone, the chlorine  $r_1, r_2$  values may be more reliable. However, as has been pointed out previously,<sup>24</sup> bias in analytical methods may exist and have a powerful influence on  $r_1, r_2$  values. In this regard, we are unable to tell which of the two methods is more reliable. We thus analyzed the chlorine and carbon data altogether, giving the same statistical weight. The least-squares  $r_1, r_2$  values thus obtained are  $r_1=1.21$  and  $r_2=0.144$ . A more rigorous treatment in which analytical accuracy is taken into account would give no significantly different results.

In any case, these values are entirely different from those in the literature,  $r_1=4.8$  and  $r_2=0.002$  (or  $r_1=3.9$  and  $r_2=0.01$ ) obtained by Faber and Fowler<sup>16</sup> under the same conditions. They determined the copolymer compositions by ultraviolet (UV) absorption analysis and evaluated  $r_1, r_2$  by the Fineman and Ross method.<sup>8</sup> To our experience, the UV method did not always provide accurate results. The inadequacy of the Fineman and Ross method has been pointed out by many authors.<sup>5-7,10</sup> However, the differences between the literature and our  $r_1, r_2$  values seem too large to be explained on this basis alone, and we cannot present no adequate explanation at this time. We only wish to note the following points: Our chlorine data, if analyzed by the Fineman and Ross method, give  $r_1=1.18$  and  $r_2=0.14$ , which are almost the same as the least-squares values. We carefully checked the purity of our pCS monomer (see above). The run carried out



**Figure 3.** Residuals  $\Delta F = F_{\text{obs}} - F_{\text{term}}$  plotted against the pCS feed composition. Data points show averages of the chlorine (open circles) and carbon (filled circles) data taken at intervals of  $f_1 = 0.1$ .



**Figure 4.** Residuals  $\Delta F = F_{\text{obs}} - F_{\text{term}}$  (circles) compared to the differences  $\Delta F = F_{\text{penult}} - F_{\text{term}}$  between the penultimate- and terminal-model compositions (solid curve). Data points show averages of both chlorine and carbon data taken at intervals of  $f_1 = 0.1$ .

with the pCS monomer purchased from Nakarai Chemicals Ltd. gave data points in the  $F$  vs.  $f$  space perfectly consistent with others, as further confirmation of our results. Finally, if the  $r_1, r_2$  values are computed on the basis of the  $Q-e$  scheme<sup>25</sup> with the recently refined values of  $Q$  and  $e$ ,<sup>26</sup> i.e.,  $Q_1 = 1.33$ ,  $e_1 = -0.64$  and  $Q_2 = 0.45$ ,  $e_2 = 0.64$ , the values  $r_1 = 1.30$  and  $r_2 = 0.149$  are obtained, which are in good agreement with our values, and the claim that the  $Q-e$  theory fails to conform with the experiments<sup>16</sup> is now open to question.

Next, we examine the propriety of the terminal model. In Figure 3, the residual  $\Delta F = F_{\text{obs}} - F_{\text{term}}$  is plotted against  $f$ . The chlorine and carbon data are shown separately with the values of  $F_{\text{term}}$  computed for the respective least-squares  $r_1, r_2$  values. For clarity, we have averaged both  $\Delta F$  and  $f$  over several runs of similar feed composition. Actually, averages were taken at intervals of  $f = 0.1$ . For both the chlorine and carbon data, trends apparently exceeding the limit of experimental error are evident and similar. The terminal model is, thus, inadequate to describe the present system.

#### Analysis Based on the Penultimate Model

Least-squares curve-fitting calculations were made for the penultimate-model composition  $F_1 = 1 - F_2$  with<sup>11</sup>

$$\frac{F_2}{F_1} = \frac{f_2(f_2 + r_1'f_1)[f_1(f_1 + r_2'f_2) + r_2'f_2(f_1 + r_2f_2)]}{f_1(f_1 + r_2'f_2)[f_2(f_2 + r_1'f_1) + r_1'f_1(f_2 + r_1f_1)]} \quad (4)$$

and

$$r_i = k_{iii}/k_{ijj}, \quad r_i' = k_{jii}/k_{jij} \quad (i \neq j) \quad (5)$$

where  $k_{pmn}$  is the rate constant for the terminal radical  $m$  with a penultimate unit  $p$  to add monomer  $n$  ( $p, m, n = 1$  or  $2$ ).

We assumed that  $r_2 = r_2'$ , i.e., there are no penultimate effects on type-2 radicals, since nearly all the discrepancy between the observed and terminal-model compositions can be explained by assuming penultimate effects on type-1 radicals only. Indeed a slightly better curve-fit may be achieved by introducing an arbitrary difference between  $r_2$  and  $r_2'$  as well. However, it is risky to draw certain conclusions therefrom, since  $r_2$  is, whether penultimate effects exist or not, much smaller than  $r_1$ . The relative population of type-2 radicals is too small to render experimental elucidation of the details feasible. This is clear from the construction of eq 4, in which  $r_2$  appears only in a product  $r_2r_2'$ .

As before, the chlorine and carbon data were treated separately at first. Both sets of data disclose the presence of significant penultimate effects on type-1 radicals, the ratio of  $r_1'/r_1$  being 2.4 from the chlorine data, and 2.7 from carbon (Table III). If the two sets of data are treated together with the same significance, we obtain  $r_1 = 0.92$ ,  $r_1' = 2.3$  and  $r_2 = r_2' = 0.18$ . With these values for the penultimate model and the corresponding  $r_1, r_2$  values for the terminal model, we calculated the "theoretical residuals"  $\Delta F = F_{\text{penult}} - F_{\text{term}}$  and compared them with the observed residuals  $\Delta F = F_{\text{obs}} - F_{\text{term}}$ . The agreement was found to be satisfactory (Figure 4).

## CONCLUSIONS

The composition of pCS-MA copolymers prepared in bulk at 40°C may be represented only approximately by the terminal model with  $r_1 = 1.21$  and  $r_2 = 0.144$ . These values do not agree with the literature values but do conform with the  $Q-e$  scheme.

The penultimate model represents the system more perfectly, the optimum set of parameters being  $r_1 = 0.92$ ,  $r_1' = 2.3$  and  $r_2 (=r_2') = 0.18$ . The question as to penultimate effects on MA radicals still remains unanswered.

We believe that these findings could hardly have been obtained without unusually elaborate experiments. This points up the importance of such studies. At the present, we see no particular reason, e.g., phase separation,<sup>10</sup> why the terminal model fails to describe the pCS-MA system, and so we are unable to conclude that penultimate effects are particularly exceptional.

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