Methyl methacrylate–chloroprene copolymerization: an evaluation of copolymerization models

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(Received 13 December 1982; revised 4 May 1983)

The composition and triad fraction data of Ebdon (*Polymer* 1974, **15**, 782) for the copolymerization of methyl methacrylate with chloroprene have been re-evaluated using non-linear least squares curve-fitting procedures and statistical testing of conclusions. Using the compositions and triad fractions separately, best estimates of reactivity ratios together with the joint confidence intervals for these parameters for terminal and penultimate models have been calculated. It has been shown that the terminal model cannot describe adequately the experimental compositions or triad fractions. While the allowance of a penultimate effect for methyl methacrylate chain end radicals provides a significant improvement over the fit of the terminal model to the copolymer compositions, there is only a small probability that both the triad fraction and the composition data can be described adequately by one set of penultimate reactivity ratios.

Keywords Methyl methacrylate–chloroprene; evaluation of copolymerization models

INTRODUCTION

Methyl methacrylate (MMA) and chloroprene (CP) copolymerize by a free radical mechanism in which homopropagation of CP radicals and cross-propagation of MMA radicals are favoured. Doak and Dineen[1], in early work, reported that the polymerization followed the terminal model at 60°C with reactivity ratios $r_1 = 0.080$ and $r_0 = 6.12$ (MMA is monomer 1). Ebdon[2] later re-investigated the copolymerization for thirteen comonomer compositions with MMA contents $>30\%$ in the feed by measuring copolymer compositions and MMA-centred triad fraction distributions from ^{1}H n.m.r. He rejected the terminal model on the basis of the curvature of the Finemann–Ross plot of the composition data and because of the poor agreement between the experimental triad fractions and those predicted by the reactivity ratios obtained by curve-fitting the composition data according to the procedure of Braun *et al.*[3]

Ebdon then examined the applicability of the penultimate model, calculating r_{11} and r_{01} values from the experimental triad fractions using the equations proposed by Chujo *et al.*[4] Because these two values were different ($r_{11} = 0.107, r_{01} = 0.057$) he concluded a penultimate effect for the MMA chain-end radicals. An average value of r_0 was obtained from the copolymer/comonomer compositions using the calculated values of r_{11} and r_{01}.

Motoc *et al.*[5] subsequently re-examined Ebdon's data using the Monte Carlo method to generate a typical polymer chain with the assumption of terminal model behaviour. They used the reactivity ratios obtained by Ebdon from curve fitting of the composition data. The copolymer compositions and triad fractions of the generated chains at some monomer feeds were found to be in better agreement with the corresponding experimental values than were the predictions reported by Ebdon for the penultimate model. Motoc *et al.* thus concluded that the terminal model provided an appropriate description of the copolymerization.

Despite the evidence presented by these two publications, the choice of a correct model to describe the copolymerization behaviour of chloroprene and methyl methacrylate remains inconclusive. It is necessary to re-evaluate the experimental data using non-linear least squares curve fitting procedures to obtain best values of the reactivity ratios as well as applying statistical tests to determine the 'goodness-of-fit' and the significance of improvements to the fit which result from the use of higher order models if the question of the correct model is to be answered.

Linearization methods (e.g. Fineman–Ross or Kelen–Tudos equations) have been used extensively to obtain reactivity ratios from copolymer composition data. However, the importance of non-linear least squares curve fitting procedures was noted by Tidwell and Mortimer[6] and reiterated recently by McFarlane *et al.*[7] Deviations from linearity in Fineman–Ross or Kelen–Tudos plots have been used as evidence for penultimate effects, but it has been shown that curvature in these plots may be caused by random analytical error arising because of the error structure of the transformed variables. Thus, it may not be justified to reject the terminal model in favour of a higher order model[8] on this basis. Objective tests, such as the statistical *F*-test, provide a better assessment of the suitability of copolymerization models.

The aim of this paper is to re-examine both the composition and triad fraction data using these statistical techniques to determine which model may provide an appropriate description for the MMA–CP

0032-3861/84/040569-05$03.00

copolymerization system, and the degree of confidence with which that model can be applied.

RESULTS AND DISCUSSION

Terminal model

Compositions. To calculate reactivity ratios from composition data, Ebdon used an iterative curve-fitting procedure devised by Braun *et al.*[3] which is based on the sum of the deviations of the experimental data from the calculated compositions. Although this technique is an improvement over linearization methods in this case, it does not lead to values of the reactivity ratios which provide the closest agreement with the experimental values (see *Figure 1*).

A non-linear search procedure[9] based on finding the minimum value of the sum of the squares of the deviations of the calculated from the experimental data has been used to obtain the reactivity ratios given in *Table 1*. These values provide much better agreement with the experimental data than those of Ebdon.

The quality of the fit is shown by the estimated standard errors in the fitted mol fractions, $S_y = 0.021$. This value yields a 95% confidence interval of 0.038 which is considerably larger than Ebdon's estimate of the experimental error in the mol fractions of ≈ 0.02 (this is taken to correspond to at least a 95% confidence interval), thus indicating an inadequate representation of the experimental data. Moreover, an examination of the 'goodness-of-fit' across the monomer feed range (*Figure 1*) shows that the calculated curve is less than the experimental points at the ends of the range and greater than the experimental points near the centre. This structure in the deviations is further evidence that the terminal model cannot adequately describe the data.

Sequence distributions. Sequence distributions can be expected to be more sensitive to copolymerization behaviour than composition data. The triad fractions calculated from the best fit reactivity ratio $r_1 = 0.078$ do not provide good agreement with the experimental values (*Figure 2*). This is shown especially in the case of the triad $F_{011+110}$ where it can be demonstrated that the experimental data is not consistent with terminal model behaviour. Variation of the value of r_1 within a wide range can improve the agreement with experimental values at one end of the monomer feed range only, while simultaneously worsening the agreement at the other end of the range.

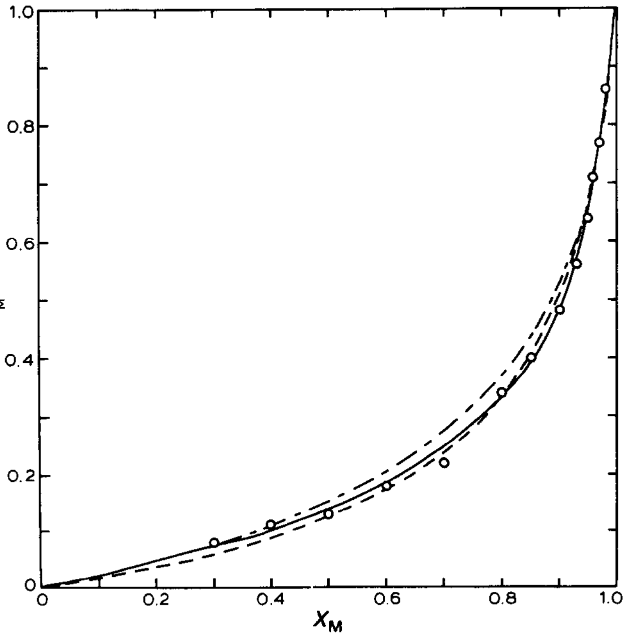

Figure 1 Variation in the polymer composition (Y_M) with the feed composition (X_M) (Y_M, X_M are mol fractions of methyl methacrylate) showing the 'goodness-of-fit' (a) for the terminal model reactivity ratios of Ebdon[2] $r_1 = 0.08$, $r_0 = 5.1$ (– - – - –); present work $r_1 = 0.078$, $r_0 = 6.81$ (– – –); and (b) for the penultimate model present work, $r_{11} = 0.173$, $r_{01} = 0.022$, $r_0 = 5.5$ (——)

Table 1 Calculated reactivity ratios for the methyl methacrylate (1)–chloroprene (0) copolymerization at 60°C in benzene solution

Terminal model	r_1	r_0	s_y[a]
Ebdon[2,b]	0.08	5.1	0.036
This paper[c]	0.078	6.81	0.021

Penultimate model	r_{11}	r_{01}	r_0	s_y[a]
Ebdon[2,b]	0.107 ± 0.008	0.057 ± 0.004	6.7 ± 0.5	0.020
This paper[d]	0.102 ± 0.015	0.058 ± 0.010	6.13 ± 0.9	0.019
This paper[c]	0.173	0.022	5.5	0.012

[a] Calculated according to $s_y = [\Sigma(Y_{exp} - Y_{calc})^2/(n-p)]^{1/2}$ where Y_{exp} and Y_{calc} are the experimental and calculated polymer compositions, n is the number of data points and p is the number of fitted parameters in the copolymer equation

[b] By the procedure of Braun *et al.*[3]

[c] By curve fitting procedures applied to Ebdon's[2] copolymer compositions

[d] r_{11} and r_{01} calculated by the procedure of Chujo *et al.*[4] from the triad fractions

This point can be further demonstrated by calculating the MMA reactivity ratio directly from the triad fractions. It is possible to calculate r_1 from each triad fraction value. While in general the values display a large variation, for $F_{011+110}$ there is an obvious decreasing trend in the calculated r_1 as the mol fraction of MMA in the feed decreases.

In summary, the non-linear least squares search technique has provided reactivity ratios which give much better agreement with the experimental compositions than those of Ebdon. However, not only does the nature of the fit to the compositions show the inadequacy of the terminal model, but the triad fractions also provide strong evidence that the model cannot apply, both in the calculation of r_1 directly from the triad fractions and in the poor agreement between the experimental triads and those predicted by the terminal model reactivity ratios obtained from the composition data.

The conclusion of Motoc *et al.*[5] that the terminal model provides an appropriate description of this system cannot be substantiated. Calculations using the appropriate analytical equations emphasize the discrepancies which result from working with the comparatively short chains (300 units) which were generated in the Monte Carlo simulation.

Penultimate Model

Compositions. Penultimate effects for MMA-radicals have rarely been demonstrated in the literature. Recently Jiang *et al.*[10] in an ^{1}H n.m.r. examination of a similar system, methyl methacrylate–isoprene, found it was necessary to consider penultimate effects for both

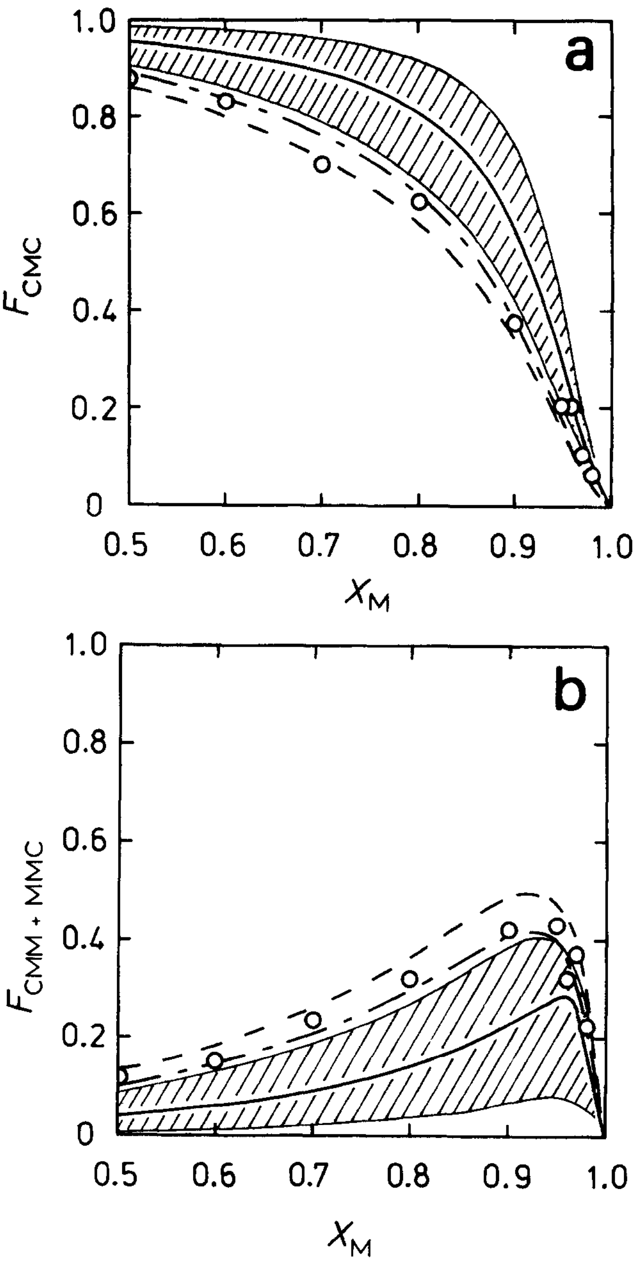

Figure 2 Variation of the triad fractions F_{CMC} or $F_{CMM+MMC}$ with initial comonomer feed. (X_M is mol fraction of methyl methacrylate). ○, experimental points; ---, calculated from fitting the terminal model to composition data, $r_1=0.078$; —-—-, calculated from fitting penultimate model to experimental triad fractions, $r_{11}=0.107$, $r_{01}=0.057$; ——, calculated from fitting penultimate model to composition data, $r_{11}=0.173$, $r_{01}=0.022$; shaded area represents range of triad fractions calculated from 95% confidence in reactivity ratios, $r_{11}=0.173$ and $r_{01}=0.022$. For most of monomer feed range F_{MMM} is close to zero and so it is not displayed

monomers, to explain the triad sequence distributions.

The penultimate model is a higher order analogue of the terminal model. Its use is justified if it provides a significant improvement in the agreement between the calculated and experimental data over that provided by the terminal model. This improvement can be measured by the statistical *F* test, based on the ratio, *F*, of the residual sums of squares (SS) of two models A and B, where model B is a special case of model A, according to the formula

$$F=\frac{(\mathrm{SS_B}-\mathrm{SS_A})/(p_A-p_B)}{\mathrm{SS_A}/(n-p_A)}$$

where p_A and p_B are the number of parameters for each model and *n* is the number of experimental observations. The ratio *F* is compared with critical values of $F(\alpha)$ for selected probability levels, α, which are available in tables.

The 'best' set of reactivity ratios determined from the composition data by the non-linear least squares procedure for the penultimate model, with penultimate effects for MMA chain end radicals only, provides a significant improvement in the agreement with experimental data over the terminal model reactivity ratios with a level of significance of 99.5% (see *Figure 1*). The extension to the full penultimate model of four variables by allowing a penultimate effect for chloroprene end radicals provides no better agreement (based upon statistical tests) with the experimental data than the three-variable model.

The reactivity ratios for the model allowing a penultimate effect for MMA end radicals are given in *Table 1*. The quality of the fit is indicated by the 95% confidence interval for the fitted mol fractions of 0.022 which compares favourably with the estimated experimental error within compositions (≈ 0.02). Examination of the agreement across the monomer feed range (*Figure 1*) shows that the regions of poor fit by the terminal model have been significantly improved and that there is no observable trend in the deviations about the experimental points. On the basis of the composition data alone, the penultimate model provides a good description of the system.

Estimates of the reactivity ratios are not statistically independent and, therefore, rather than appending an error range to each reactivity ratio, it is necessary to specify joint confidence limits within which the set of correct values is believed to occur with a given certainty. The general procedures for doing this have been discussed extensively by Tidwell and Mortimer[6] and Behnken[11] and references therein. Here the more precise procedure is used which involves searching the parameter space in the region of the 'best estimate' for sets of parameter values which yield residual sums of squares less than or equal to a value which depends on the level of certainty required.*

For the three-dimensions of the simplified form of the penultimate model used here, the 95% confidence surface for the parameter (r_{11}, r_{01}, r_0) sets can be represented as a series of two-dimensional closed curves each being 95% joint confidence intervals for two of the parameters, at various values of the third parameter. This is depicted in *Figure 3* for each pair of parameters in turn. An examination of the shapes of these curves clearly indicates the inadequacy of attaching simple ± error ranges to the best values of the reactivity ratios. The cross-section of the 95% confidence surface in the plane of r_{11}–r_{01} is distorted from the usual shape, probably indicating a high correlation between these two parameters.

Sequences. The triad fractions predicted by the penultimate model reactivity ratios calculated from the

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* Calculated using the formula

$$S(\theta)\leqslant S(\hat{\theta})+ps^2F_\alpha(p, n-p)$$

where $S(\theta)$ is the residual sum of squares, $\sum_n (Y_{\mathrm{exp}}-Y_{\mathrm{calc}})^2$, for a given parameter set, $S(\hat{\theta})$ is the residual sum of squares for the best estimate of the parameters, *p* is the number of parameters, s^2 is an estimate of the variance in the experimental error (put equal to $S(\theta)/(n-p)$ where *n* is the number of experimental points) and $F_\alpha(p, n-p)$ is the α percentage point of the tabulated *F* distribution with *p* and $n-p$ degrees of freedom

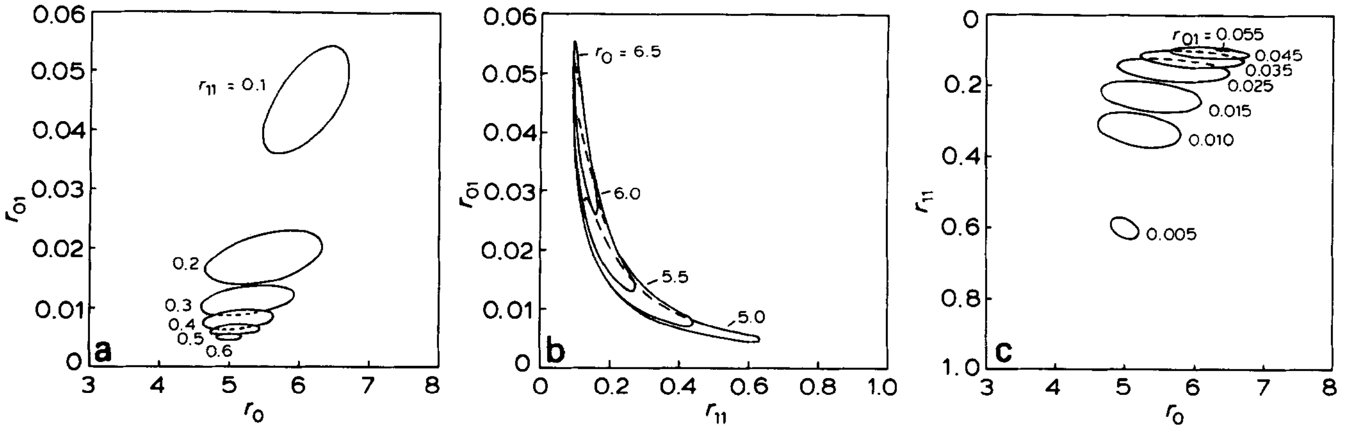

Figure 3 95% joint confidence surface for the three parameters of the simplified penultimate model. The three-dimensional surface is represented by a series of cross-sections at fixed values of one of the parameters: (a) r_{11}; (b) r_0; (c) r_{01}. By combining the different views exhibited in each of the three parts of the figure it is possible to envisage the three-dimensional banana-like structure of the confidence surface

composition data provide poor agreement with the experimental values (see *Figure 2*). In fact the experimental triad fractions for the most part are outside the range of values for the triads arising from all reactivity ratio sets within the joint 95% confidence region. Thus, there is $<5\%$ confidence that a penultimate reactivity ratio set providing reasonable agreement with the triads would be a true representation of the composition data.

As in the case of the terminal model, the reactivity ratios for the penultimate model can be calculated directly from the triad fractions. This approach was used by Ebdon who found better agreement with the experimental triads than was obtained using terminal model reactivity ratios. The triad fraction data has been re-analysed here with the added feature that the r_{11} and r_{01} values represent weighted averages of the nine experimental points. The weighting factors were calculated from Ebdon's estimates of the error in the triad fractions. The use of weights is important here because of the very wide variation in the uncertainty of the estimates of the reactivity ratios from the various experimental points. This is unlike determining reactivity ratios from the composition data where the uncertainties in the mol fraction compositions are almost identical for all experimental points.

The calculated reactivity ratios are given in *Table 1*. The value of r_0 was calculated from the copolymer composition data using the values of r_{11} and r_{01}. It also is a weighted average, the weights reflecting the uncertainties in the values of r_0 arising from the errors in the compositions and in the values of r_{11} and r_{01}.

The equations used to calculate the penultimate model reactivity ratios from the triad fractions:

$$r_{11}=\frac{[0]_0}{[1]_0}\,\frac{2F_{111}}{F_{011+110}} \qquad r_{01}=\frac{[0]_0}{[1]_0}\,\frac{F_{011+110}}{2F_{010}}$$

where $[0]_0$ and $[1]_0$ are the initial concentrations of MMA and CP in the feed and F_{010}, $F_{011+110}$ and F_{111} are the three triad fractions, would also be valid if the terminal model applied. In that case r_{11} would equal r_{01}. Thus, if r_{11} and r_{01} are different a penultimate effect is indicated. The significance of the difference between r_{11} and r_{01} with account of the error in their estimations is provided by the *t*-test analysis of the significance of the difference between two weighted means. This test applied to the reactivity ratios calculated here indicates they are different with a level of significance in excess of 99.5%, thus indicating an apparent penultimate unit effect.

However, by extending the joint confidence surface for the set of reactivity ratios calculated from the compositions, it can be shown that the set of reactivity ratios calculated directly from the triad fractions has only 1–2.5% probability of being a true representation of the penultimate model applied to the composition data. Conversely, it is possible to conclude that there is $>97.5\%$ likelihood that the experimental triad fractions are in error, or, alternatively, that the penultimate model does not describe this system.

CONCLUSIONS

It has been shown that the terminal model cannot provide an adequate description of Ebdon's data for the copolymer compositions or the triad fractions. There is discernable structure in the deviations of the experimental polymer compositions about the fitted curves and the values of r_1 determined from the triad fractions change in a systematic manner across the composition range.

The penultimate model provides a significant improvement over the terminal model in the fit to both the copolymer compositions and the triad fractions, but statistical tests show that there is a $<2.5\%$ likelihood that the triad fractions and compositions are both described by the same set of penultimate model reactivity ratios. The two sets of experimental data (compositions and triad fractions) may be judged, therefore, as being inconsistent within the confines of the penultimate model.

These observations could indicate that either (a) the experimental compositions, or the triad fractions or both are incorrect, or (b) factors other than terminal and penultimate effects are dominant in influencing the polymerization kinetics.

An examination of Ebdon's experimentally determined triad fractions suggests that a plausible explanation for the inconsistency between the two sets of data could be in the calculation of the triad fractions. Several assumptions have been made in their estimation, which involves the overlapping effects of tacticity and sequence distributions. Jiang *et al.*[10] investigated the methyl methacrylate triad distributions in a similar system, isoprene (I)–methyl methacrylate (M), using the α-methyl resonance in the ^{1}H n.m.r. They calculated the triad fractions taking account of tacticity using the same assumptions as Ebdon except that, whereas Ebdon assumed the CMM + MMC triad was distributed between two peaks according to the relative configuration of the M–M linkage, in the IMM + MMI triads Jiang *et al.* assumed the distribution between the two peaks was due to the different chemical environment of α-methyl protons in an IMM triad compared to an MMI triad.

Okada and coworkers have also reported[12,13] on the sequence distribution of the CP–MMA system using ^{1}H n.m.r. They calculated M-centred triad fractions from the α-methyl resonances assuming tacticity effects were unimportant, a method they acknowledged broke down when the fraction of MMM triads became significant. However, they also claimed that M-centred triad fractions could be obtained from the methoxy proton resonance under suitable conditions and that, if shift reagents were used, the three overlapping resonances could be separated into six from which pentad fractions could be measured.

^{13}C n.m.r. also offers the possibility of confirming the validity of the triad assignments. Khan and Brame[14] examined a series of CP–MMA copolymers using this technique, assigning the multitude of peaks in the olefinic region to chloroprene centred triad sequences. Unfortunately, they did not comment on any other region of the spectrum and they ignored minor peaks which may provide evidence of anomalous structures in the copolymer.

The possibility of a large percentage of head–head and tail–tail additions in the polymer as suggested by Ebdon may be an important consideration in this system. Ebdon showed that, for copolymers comparatively rich in chloroprene, it appears from the ^{1}H n.m.r. spectra that there are approximately 19% head–head and tail–tail chloroprene–chloroprene linkages, in approximate agreement with the percentage observed in polychloroprene produced under the same conditions. Jiang *et al.*[10] claimed ^{1}H n.m.r. evidence of head–head additions between an isoprene and a methyl methacrylate unit which comprised 22.4% of the comonomer linkages in these copolymers. Thus, head–head and tail–tail additions between unlike monomers as well as between like monomers may be a factor determining the copolymerization kinetics.

The likelihood of the penultimate model being unsatisfactory does not justify the use of the terminal model, as it is less than adequate in providing agreement with either the compositions or the triad fractions. The alternatives are (1) using a set of penultimate reactivity ratios which have only a small probability of describing the properties of further copolymerizations, (2) re-examining the experimental methods for possible systematic errors in triad fractions or compositions and (3) seeking new models to explain the observed behaviour.

This analysis has shown that all the experimental data should be examined for its agreement with the proposed model and that recognised statistical tests should be made to confirm the validity of conclusions. In addition, whenever different sets of reactivity ratios are compared, such as those obtained herein using the penultimate model, the comparisons should be made using joint confidence intervals for the parameters. For the higher order models, this will require a consideration of the confidence interval surface in more than two dimensions.

The procedure of calculating reactivity ratios for all copolymerization models from the copolymer compositions and then comparing the calculated and experimental sequence distributions has the advantage that incompatibility between the two sets of data may be revealed. Ebdon's method of deriving the reactivity ratios, r_{11} and r_{01}, from the MMA-centred triad fractions and thence r_0 from the copolymer compositions disguises any incompatibility of this sort.

ACKNOWLEDGEMENT

The authors wish to thank the Australian Research Grants Scheme for supporting their research.

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