This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Strategies in Improving the Accuracy of Reactivity Ratios Estimation

Cornel Hagiopol[a]; Octavian Frangu[b]
[a] Georgia-Pacific Resins Inc., Decatur, Georgia, USA [b] ICECHIM, 202 Spl. Independentei, Bucharest, Romania

Online publication date: 28 April 2003

To cite this Article Hagiopol, Cornel and Frangu, Octavian(2003) 'Strategies in Improving the Accuracy of Reactivity Ratios Estimation', Journal of Macromolecular Science, Part A, 40: 6, 571 — 584
To link to this Article: DOI: 10.1081/MA-120020857
URL: http://dx.doi.org/10.1081/MA-120020857

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. A40, No. 6, pp. 571–584, 2003

Strategies in Improving the Accuracy of Reactivity Ratios Estimation

Cornel Hagiopol[1],* and Octavian Frangu[2]

[1]Georgia-Pacific Resins Inc., Decatur, Georgia, USA
[2]ICECHIM, 202 Spl. Independentei, Bucharest, Romania

ABSTRACT

Recently published experimental data concerning more than ten copolymerization systems were re-analyzed. Newer, more accurate, reactivity ratios were calculated using a non-linear method (PROCOP) which involves all the experimental data including conversion values. The differences between the reactivity ratios provided in the original articles and the recalculated values are discussed in terms of experimental errors, analytical methods, conversion values and solvent effect. The present paper shows what is routine, what needs to be changed and what can be realistically hoped for as far as accuracy in reactivity ratios estimation is concerned.

Key Words: Copolymerization; Reactivity ratios; Estimation method; ProCop computer program; Solvent effect; Conversion effect; Analytical method.

INTRODUCTION

Copolymerization-related articles are currently published on a regular basis in most macromolecular chemistry journals. The way reactivity ratios are estimated has seemingly become a matter of sheer routine. One could assume that advance on the path of knowledge is thus ensured and scientific information gets richer with each such article.

---

*Correspondence: Cornel Hagiopol, Georgia-Pacific Resins Inc., 2883 Miller Road, Decatur, GA 30035, USA; E-mail: CHAGIOPO@GAPAC.com.

DOI: 10.1081/MA-120020857
1060-1325 (Print); 1520-5738 (Online)

www.dekker.com

However, we are bound to note that reactivity ratio values are mostly reached through unreliable linear estimation methods, which only add up to those determined during the last 50 years through less than accurate estimation methods. As many as 75% of the 68 articles published after 1990 and reviewed[1] in 1998, used the Fineman-Ross (FR) and/or the Kelen-Tudos (KT) methods. The FR and KT methods are still being used[2,3] and so is even the oldest intersection method.[4] These methods may provide acceptable results but quite often the values obtained for reactivity ratios are far from those calculated via nonlinear methods. The scientific perspective brought about by articles involving miscalculated data is fraught with the risk of creating a rather chaotic image of this research field.

The paradox we are confronted with is that on the one hand an exceptionally useful amount of experimental data has been gathered so far, such as the copolymer compositions obtained via certain comonomer feed compositions at various conversion values. On the other hand, that huge amount of experimental data often gets misinterpreted which results in coming up with unreliable reactivity ratios.

In an attempt at stopping erroneous information from further spreading, efforts were made to point out the shortcomings of linear methods. Standard-setting works in copolymerization literature[5–10] mentioned that methods such as FR or KT are not always appropriate. These works also suggest that, since new and more reliable methods have been developed, a reevaluation of experimental data became imperative. Furthermore, when the experimental data are captioned only[11] or mentioned for too small a number of experiments,[12] the recalculation and recasting cannot be performed. However, even with rich experimental data, several sources of errors can be found.

The present paper attempts to identify the main sources for statistic and systematic errors in recently published articles. The experimental data will be analyzed using a non-linear method for the estimation of reactivity ratios (with a computer program (ProCop)[13]) that considers all data (conversion values included).

RESULTS AND DISCUSSIONS

The Calculation Method

The ProCop computer program uses a non-linear calculation method[13,14] able to minimize the F (1) value:

$$F = \sqrt{\frac{\sum_{i=1}^{n} \left(m_i^{\exp} - m_i^{cal} \right)^2}{n-2}} \tag{1}$$

where: $m_i^{\exp}$ is the copolymer composition experimentally determined for the i point, m_i^{cal} is the copolymer composition calculated for the *i* experiment with a pair of reactivity ratios and n is the overall number of experiments. Based on a Simplex algorithm, the computer program is searching for the reactivity ratio pair able to minimize the F value. The Simplex algorithm provides a step-by-step optimization by selectively taking over the results of the previous step. More specifically, the modified algorithm of Nelder and Mead[15] was developed to improve the convergence rate. With experimental data involving conversion values for each experiment, the calculated copolymer composition is obtained after the integration of the May-Lewis equation up to the declared conversion. Thus, no information provided by experimental data is left aside by the ProCop computer program, which increases the reliability of final reactivity ratio values.

Estimating Reactivity Ratios

The fact that for one and the same copolymerization system, many authors indicate (and publish) several pairs of reactivity ratio values could be explained either by an improper experimental design or by the use of inaccurate analytical or estimation methods.[16]

The number of experimental points required by an accurate determination of reactivity ratios was at the core of an extensive debate. It certainly involves the optimal experiment as well. However, when few points are considered[12,17] which are not located within the optimum range, the reactivity ratios are poorly estimated. In such cases, errors (of variable amplitude) associated with each experimental point will alter the final results to an unacceptable degree.

The identification of the source of error needs to become the aim of any approach at critically evaluating the experimental data. The effort to obtain reliable reactivity ratios goes, therefore, beyond the answer to the question "What is the best calculation method?" The answer to that question is just one element among those that need to be carefully considered. Special attention must also be paid to the number of experimental points, to the conversion values, to the experimental errors, to the solvent effect or to the appropriate kinetic model for each binary copolymerization.

Strange as it may seem, articles published very recently include calculation errors due to obviously careless mistakes.

Other errors may be traced down to the calculation involved by the simplest methods (as FR or KT).

For the 4-chlorophenyl acrylate (M_1)–methyl acrylate copolymerization[18] the authors determined the reactivity ratios via the FR and KT methods (for the five experimental points). When plotting the KT graph they deliberately left aside two experimental points, which allowed them to draw a straight-line through the three points left. No wonder that the curve calculated (Fig. 1) with the reactivity ratio estimated by the authors is far from fitting the experimental data.

When the experimental data for 4-chlorophenyl acrylate (M_1)–methyl acrylate copolymerization[18] were used in ProCop program, resulted in a different value for the reactivity ratios which, this time, do fit better the experimental data (Fig. 1).

Large calculation errors can occur when using any method. With the copolymerization of vinyl-trimethylsilane (M_1) with N-vinyl-2-pyrrolidone,[19] the authors indicate $r_1 = 0.0$ and $r_2 = 1.391$, while mentioning that their product is $r_1 \cdot r_2 = 1.391$ (!). That value clearly and unjustifiably contradicts the Q-e scheme. Consequently, it is no wonder that, after re-indexing, the RREVM method (actually, an excellent calculation method) is regarded as inaccurate by the authors, who indicate an entirely inadequate confidence region.

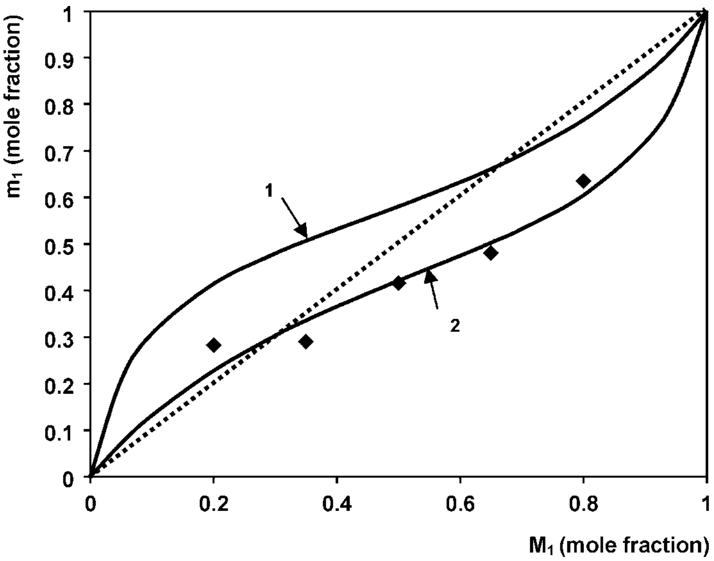

Figure 1. The dependence of the copolymer composition on the feed comonomer composition for 4-chlorophenyl acrylate (M_1)–methyl acrylate: 1-curve calculated by using the reactivity ratios indicated by the authors[18]: $r_1 = 0.64$, $r_2 = 0.13$; 2-curve calculated by using the best fitted reactivity ratios: $r_1 = 0.1926$, $r_2 = 0.6385$ (◆-experimental points).

When using different calculation methods that lead to different results for the same experimental data, any attempt at averaging them should be avoided. Both the averaging and the arbitrary choice of one or another set of results are equally un-recommendable options in the absence of sound comparison criteria. Performing an arbitrary choice may result in ignoring a better result, while the averaging might level off good and not so good results.

Discrepancies are often noted between the values obtained via the different methods used to determine reactivity ratios. Various researchers have shown that the precision of experimentally determined reactivity ratios depends on such factors as the experimental design, the analytical method and the data processing techniques.[6,9,10]

For the reactivity ratio estimation in the copolymerization of styrene (M_1) with N-cyclohexylacrylamide[20] (conversion values of 6–8%) the authors used the FR and KT method to obtain very similar results: $r_1 = 2.8$ and $r_2 = 0.68$. Obviously, the product is much higher than 1.0 ($r_1 \cdot r_2 \gg 1.0$) which means that an error occurred. Their own FR method graph shows that the line defining the r_{ij} does not pass through the points: the first three consecutive points are located beneath it, while the others are above it. The graphic analysis may be inaccurate. A correct use of the FR and KT methods would result in getting negative values for the N-cyclohexylacrylamide reactivity ratio. That can be seen in the graph published by the authors.

If the ProCop program is used, reactivity ratios that best check the experimental data are $r_1 = 2.24$ and $r_2 = 0.0001$.

Those values, determined via the FR or KT methods, and showing reactivity ratios equal to zero ($r_i = 0.0$) are rather suspicious. It is the case, among others, of the hydroxyalkyl methacrylates copolymerization with acrylamide or methacrylamide.[21] The correct use of the FR and/or KT methods leads to negative values for acrylamide or methacrylamide, respectively. These values are not trustworthy, since they lack physical meaning. On the one hand the calculation methods are not accurate enough, on the other hand experimental errors can lead to groundless conclusions. If calculation (or transcription) errors as well as the option for more convenient calculation methods are left aside, two types of errors should be further discussed: the statistical error (due to the analytical method especially) and the systematic error (due to the ruling out of conversion values or of the solvent effect).

The Analytical Method

The composition of copolymers obtained by the copolymerization[22] of acrylonitrile (M_1) with pentyl acrylate was determined by nitrogen analysis and by ^{13}C-NMR. If the ProCop programs are used, the two analytic methods lead to different values of the reactivity ratios (by elemental analysis $r_{AN} = 0.8489$ and $r_{PA} = 0.48$, by ^{13}C-NMR analysis $r_{AN} = 0.7897$ and $r_{PA} = 0.4571$), but the confidence regions (Fig. 2) are largely overlapping. Accordingly, the results of these types of analyses can be regarded as being in agreement (considering the experimental error).

Results obtained via different analytical methods may check one another,[23,24] however, certain small discrepancies can exceed the limits of the Q-e scheme ($r_1 \cdot r_2 > 1.0$).[25] With the copolymerization of tetrafluoroethylene (M_1) and 2,3,3-trifluoroallyl alcohol, the use of various methods cannot prevent the formation of a large area within the confidence region where the product $r_1 \cdot r_2 > 1.0$, which definitely goes beyond the limits of the Q-e scheme. The consistency of the Q-e scheme can be debatable, but it certainly is a good starting point in this discussion.

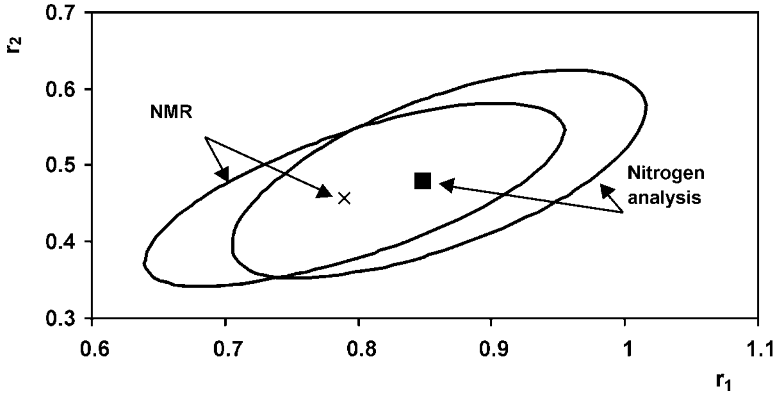

Figure 2. The approximate 95% confidence regions for the reactivity ratios of acrylonitrile (M_1)–pentyl acrylate copolymerization.

Even when a more reliable analytical method is used, the radioactivity assay technique[26] for styrene (M_1)–p-isopropylstyrene copolymerization, the product $r_1 \cdot r_2$ exceeds 1.0 ($r_1 = 1.22$ and $r_2 = 0.89$).

With one method or another the experimental error may push the system towards the limits of physical meaning or of the rules regarded as valid in the field of copolymerization (the Q-e scheme). The option for an analytical method cannot be made irrespective of the kinetic model, of the copolymer type and, not even, of conversion values. They all belong in one and the same picture; oversimplifying it, by superficial evaluation, would only result in jeopardizing the accuracy of the experimental data processing.

Consistency among results reached at via different analytic methods is, more often than not, accidental. Largely different results can be obtained when comparing several analytical methods. They will obviously generate different values for the reactivity ratios (Fig. 3). With the copolymerization of 4-methyl styrene with acrylonitrile[27] both the elemental analysis and the H NMR and C NMR were used.

As a general rule, when using the ProCop program to determine the best reactivity ratios, the results obtained appear to suggest that the confidence region for r_{ij} determined for an analytical method does not include results reached at via the other two methods. Mention must be made that ProCop involves the integral form of the equation, i.e., it includes the conversion values.

The fact that different analytic methods lead to different pairs of r_{ij} values needs to be associated with the errors generated by the use of other, less performing methods of estimating reactivity ratios. Thus, the authors of article,[27] who used the KT method for

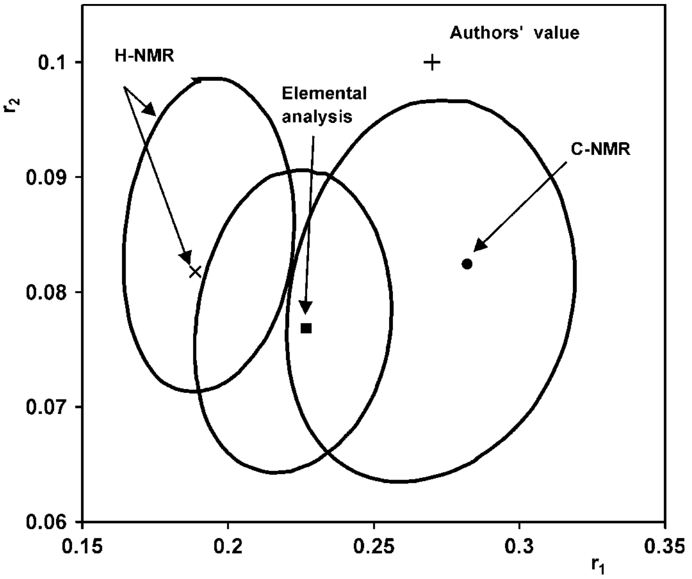

Figure 3. The approximate 95% confidence regions for the re-calculated reactivity ratios for 4-Methyl Styrene (M_1)–Acrylonitrile copolymerization using different analytical methods for copolymer characterization (x—reactivity ratios estimated by the authors of the original paper.[27]

the average copolymer compositions, obtained a reactivity ratio pair located outside all the confidence regions shown in Fig. 3. In other words, the summing up of errors generated by the analytical and the estimation methods can lead to completely unreliable data.

An interesting and particularly topical discussion concerned the error associated with each experimental point.[8,10] As of now, it is practically impossible to define the error induced by a method before determining it experimentally for the case under study. A research team used the same analytical method (^{1}H NMR) to characterize both 4-acetyl phenylacrylate (APA), methyl methacrylate and 4-acetyl phenylacrylate (APA), butyl methacrylate copolymers.[28] The same estimation method (ProCop) for reactivity ratios came up with confidence domains of largely variable size (Fig. 4). The area within the joint confidence limits includes[6] the correct values of the reactivity ratios with a probability of 95%. In the two cases, very different experimental errors are noted. Accordingly, the value of the experimental error (for the same analytical method) cannot be taken over from one system to another and not even from one composition to another.

In the case of styrene (M_1)–hydroxyethyl acrylate[29] copolymerization, if the copolymer composition is analyzed via the ^{1}H NMR, the experimental error exceeds 20% when the copolymer composition is poor in styrene, and is less than 2% when the copolymer is rich in styrene. Consequently, the setting of an average error of 5%, when EVM is used, does not seem to be the right choice, particularly since the authors indicate an error of 0.0055% only for the feed composition. That is a perfect illustration of the current situation in copolymerization studies: the experimental error for the feed composition is more than 100 times smaller than the experimental error in the determination of the copolymer composition. In cases where the error in feed composition is much smaller than that recorded for the copolymer composition, the EVM and the non-linear least squares methods (such as the ProCop program) are equivalent.[1] Moreover the ProCop program can use the conversion data as well.

Increasingly, accurate lab equipment can limit statistical errors induced by analytic methods. The choice of methods to calculate reactivity ratios that minimize function (1) is of major importance in estimating experimental errors.

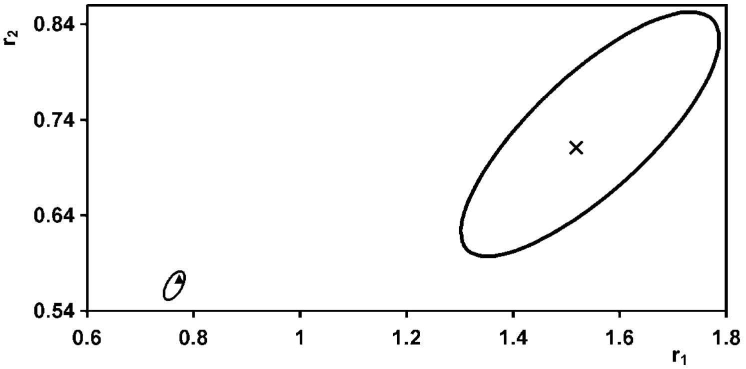

Figure 4. The approximate 95% confidence regions for the reactivity ratios for APA (M1)–methyl methacrylate (▲) − $r_1 = 0.77$ and $r_2 = 0.57$, and APA(M1)–butyl methacrylate (**x**) − $r_1 = 1.52$ and $r_2 = 0.71$ − copolymerization.

The Effect of the Conversion Values

The conversion effect may be a function of the feed composition and of the comonomer pair to undergo copolymerization. If r_i and $r_j < 1.0$ the effect of conversion is relatively unimportant. With the copolymerization of styrene with butyl acrylate (maximum conversion was 9.6%),[17] the differential methods (either linear—KT, or non-linear—TM) lead to results that are fairly close to those reached at via a non-linear method (ProCop) involving conversion. Although the differential methods (FR and KT) cannot be used at conversions above 10%, they are used even with conversions of over 80%.[30]

When large differences occur in the reactivity of the comonomers ($r_i \gg 1.0$, $r_j \ll 1.0$), a strong conversion effect is noted even at very low values. It is the case, for instance, of the copolymerization of N-(4-bromophenyl) maleimide (M_1) with ethyl methacrylate[31] in benzene at 60° (conversion values ranging between 6.26% and 12.4%). Figure 5 shows the reactivity ratios estimated by differential methods (FR, KT, TM and RREVM) and by a method (ProCop) able to exploit the integral form of the copolymerization equation.[13,14]

All the reactivity ratio values calculated via differential methods are located outside the 95% confidence domain for the reactivity ratios estimated by an integral method. That is why the conversion values should be considered for the reactivity ratio estimation.

The examination of the residuals $[m_i^{\exp} - m_i^{cal}]$ (the difference between the experimental value determined for the copolymer composition and the value calculated via the differential form of the Mayo-Lewis equation and the reactivity ratios estimated by the authors) showed no systematic deviation (acrylamide–vinyl acetate copolymerization[32]) when a differential method was used. Different estimation methods (TM, EVM and Alex van Herk-NLLS-method[8]) led to very close results.

The use of an integral method (ProCop) resulted in getting new reactivity ratios: $r_{AA} = 9.34$ and $r_V = 0.0751$. Although conversion was ranging between 2.5% and only

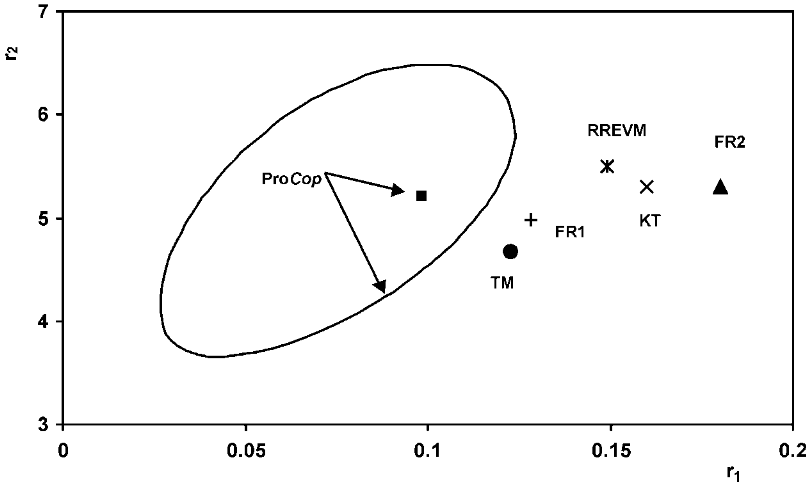

Figure 5. The approximate 95% confidence regions for the reactivity ratios with the copolymerization of N-(4-bromophenyl) maleimide (M_1) with ethyl methacrylate.

5.1%, the former reactivity ratios calculated by Mukherjee et al.[32] are now located outside the 95% confidence domain of the new reactivity ratios (Fig. 6).

The residuals now show a systematic deviation (the diamonds in Fig. 7). At a low acrylamide content in the feed, all the residuals showed a positive value. A theoretical curve plotted for residuals calculated at an average conversion (conv. = 3.9%) shows a systematic deviation as well. It fits quite well the residuals calculated for each pair feed composition—conversion value indicated by the authors.[32]

We can conclude that the often ignored conversion values might play a very important role in the poor reactivity ratio estimation especially in the cases when $r_i \gg 1.0$ and $r_j \ll 1.0$.

The Solvent Effect

Precipitating polymerization[33] is a special case and, therefore, special attention must be paid to the estimation of reactivity ratios. The styrene–N-cyclohexyl acrylamide copolymerization was performed in methanol.[34] During polymerization the copolymer precipitated and was filtered. As the copolymer precipitated, a different comonomer composition was punctually recorded.[35] If the reactivity ratio estimation takes into account the overall comonomer feed composition, the source of errors can be easily identified.

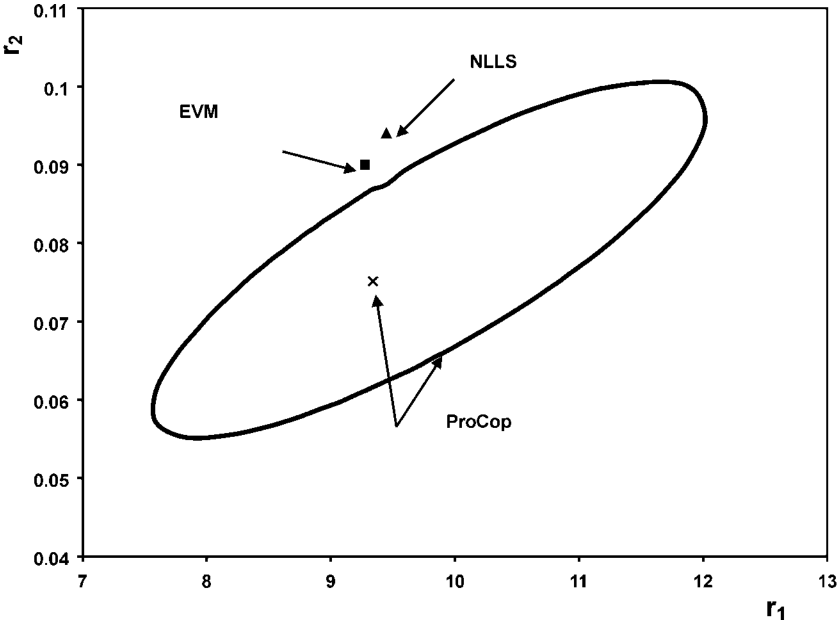

Figure 6. The approximate 95% confidence regions for the reactivity ratios (calculated using all the experimental data including the conversion values) with the acrylamide–vinyl acetate copolymerization.

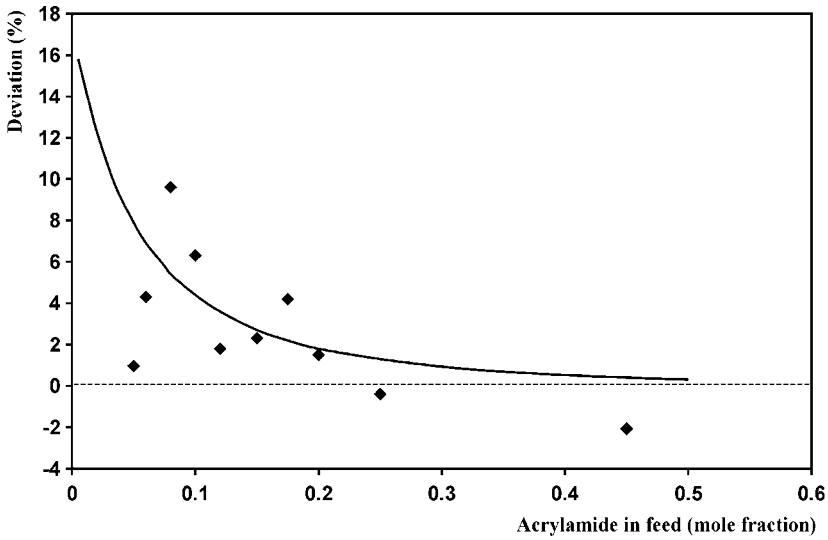

Figure 7. Theoretical residuals ($m^{3.9\%} - m^{0.1\%}$, solid curve) and experimental residuals (◆) for the acrylamide (M_1)−vinyl acetate copolymerization.

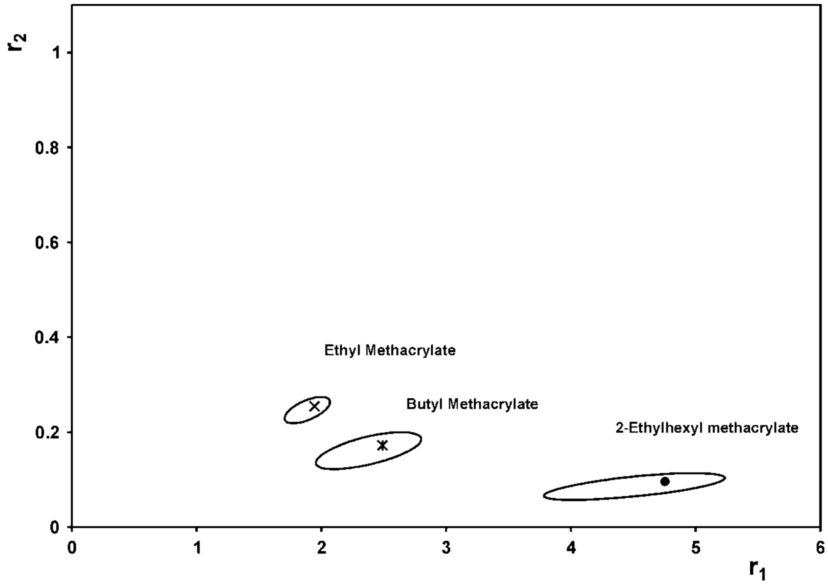

Figure 8. The approximate 95% confidence regions for the reactivity ratios for 2-hydroxypropyl methacrylate (M_1) copolymerization with ethyl methacrylate, butyl methacrylate and 2-ethylhexyl methacrylate.

The solvent effect varies with different copolymer compositions, resulting from the different comonomer feed compositions, meaning that a systematic deviation occurs. If the real local concentration of the comonomer is ignored, erroneous reactivity ratios will be obtained.

A special case is noted even in bulk copolymerization where surprising results may be recorded.[36] Several methacrylic esters show quite similar reactivities[37]: methyl methacrylate(M_1) copolymerization with furfuryl methacrylate ($r_1 = 0.75,\ r_2 = 1.19$), with n-butyl methacrylate[38] ($r_1 = 0.91,\ r_2 = 1.09$) and with iso-butyl methacrylate ($r_1 = 0.91,\ r_2 = 1.09$). However, when the methacrylic ester has a very polar structure (2-hydroxypropyl methacrylate)[36] different results are recorded (Fig. 8). The results either show a more reactive 2-hydroxypropyl methacrylate, or indicate that in the vicinity of the growing free radical the concentration of the alkyl methacrylates is lower than the overall feed composition. The local concentration concept[35,39] can successfully explain that behavior.

The copolymerization of methyl methacrylate with dodecyl methacrylate[40] can be understood in a very similar way. It results in reactivity ratios which both exceed 1.0 ($r_{MMA} = 1.71,\ r_{DMA} = 1.95$ according to the RREVM method),[8] a very rare case in free radical copolymerization.

CONCLUSION

In a copolymerization study, any results should be regarded as preliminary. When $r_i < 0.0$, or $r_i{\cdot}r_j > 1.0$ (especially when $r_i > 1.0$ simultaneously with $r_j > 1.0$) the experimental program needs to be revised particularly in terms of reproducibility, analytic method and, possibly, with regard to the solvent used.

Statistic evaluation methods are particularly sensitive to the number of experimental points. The more experimental points are involved, the more accurate the estimation will be.

The copolymerization should be performed at as low a conversion as possible. Conversion values should be recorded and used in reactivity ratio estimation.

REFERENCES

1. Polic, A.L.; Duever, T.A.; Penlidis, A. Case studies and literature review on the estimation of copolymerization reactivity ratios. J. Polym. Sci. Polym. Chem. **1998**, *36* (5), 813–822.
2. Sideridou-Karayannidou, I.; Seretoudi, G. Copolymers of N-vinylcarbazole and ethyl iodide quaternized dimethylaminoethyl methacrylate. J. Appl. Polym. Sci. **1998**, *68* (9), 1517–1521.
3. Anand, V.; Choudhary, V. Studies on the copolymerization of methyl methacrylate with N-(O/M/P-chlorophenyl) itaconimides. J. Appl. Polym. Sci. **2001**, *82* (8), 2078–2086.
4. Wu, L.; Sheares, V.V. Polar, functionalized diene-based materials. V. Free-radical polymerization of 2-[(N-benzyl-N-methylamino)methyl]-1,3-butadiene and copolymerization with styrene. J. Polym. Sci. Part A: Polym. Chem. **2001**, *39* (19), 3227–3238.

5. Behnken, D.W. Estimation of copolymer reactivity ratios: an example of nonlinear estimation. J. Polym. Sci. **1964**, *A* (2), 645–668.
6. Tidwell, P.W.; Mortimer, G.A. An improved method of calculating copolymerization reactivity ratios. J. Polym. Sci. **1965**, *A-3* (1), 369–387.
7. O'Driscoll, K.F.; Reilly, P.M. Determination of reactivity ratios in copolymerization. Makromol. Chem. Macromol. Symp. **1987**, *10–11*, 355–374.
8. Van Herk, A.M.; Droge, T. Nonlinear least squares fitting applied to copolymerization modeling macromol. Theory Simul. **1997**, *6*, 1263–1276.
9. Van den Brink, M.; van Herk, A.M.; German, A.L. Nonlinear regression by visualization of the sum of residual space applied to the integrated copolymerization equation with errors in all variables. I. Introduction of the model, simulations and design of experiments. J. Polym. Sci. Polym. Chem. **1999**, *37* (20), 3793–3803.
10. Van den Brink, M.; Smulders, W.; van Herk, A.M.; German, A.L. Nonlinear regression by visualization of the sum of residual space applied to the integrated copolymerization equation with errors in all variables. II. Application to the system methyl methacrylate-α-methylene-γ-butyrolactone using on-line Raman spectroscopy. J. Polym. Sci. Polym. Chem. **1999**, *37* (20), 3804–3816.
11. Liaw, D.-J.; Tsai, C.-H. Radical polymerization of methacryloyl isocyanate-containing 1-adamantanol. Polym. Bull. **1999**, *42*, 373–378.
12. De, P.; Sathyanarayana, D.N. Oxidative copolymerization of indene with p-tert-butylstyrene: synthesis, characterization, thermal analysis, and reactivity ratios. J. Polym. Sci. Polym. Chem. **2002**, *40* (1), 9–18.
13. Hagiopol, C. *Copolymerization-Towards a Systematic Approach*; Kluwer-Academic/Plenum Publisher: New York, 1999.
14. Hagiopol, C.; Frangu, O.; Dumitru, L. A nonlinear method for the estimation of reactivity ratios in copolymerization processes. J. Macromol. Sci. Chem. **1989**, *A26* (10), 1363–1379.
15. Nelder, J.A.; Mead, R. A simplex method for function minimization. Comput. J. **1965**, *7*, 308–313.
16. Urzua, M.; Gatica, N.; Gargallo, L.; Radic, D. N-1-alkylitaconamic acids-co-styrene copolymers. 1. Synthesis, characterization and monomer reactivity ratios. J. Macromol. Sci. Pure Appl. Chem. **2000**, *A37* (1&2), 37–47.
17. Fernandez-Garcia, M.; Fernandez-Sanz, M.; Madruga, L.E.; Fernandez-Monreal, C. A kinetic study of free-radical copolymerization of styrene/butyl acrylate. Macromol. Chem. Phys. **1999**, *200* (1), 199–205.
18. Thamizharasi, S.; Srinivas, G.; Sulochana, N.; Reddy, B.S.R. Copolymerization of 4-chlorophenyl acrylate with methyl acrylate: synthesis, characterization, reactivity ratios, and their applications in the leather industry. J. Appl. Polym. Sci. **1999**, *73* (7), 1153–1160.
19. Gatica, N.; Diaz, F.R.; Gargallo, L.; Radic, D. Vinyltrimethylsilane-co-N-vinyl-2-pyrrolidone and vinyltrimethoxysilane-co-N-vinyl-2-pyrrolidone copolymers. Synth. React. Ratios Polym. Bull. **1998**, *40* (6), 707–713.
20. Pazhanisamy, P.; Sulochana, P.; Anwaruddin, Q.; Ariff, M. Reactivity ratios of N-cyclohexylacrylamide-styrene copolymers by ^{1}H and ^{13}CNMR spectroscopy. J. Polym. Sci. Polym. Chem. **1997**, *35* (1), 193–195.

21. Kucharski, M.; Lubczak, R. Copolymerization of hydroxyalkyl methacrylates wit acrylamide and methacrylamide. I. Determination of reactivity ratios. J. Appl. Polym. Sci. **1997**, *64* (7), 1259–1265.
22. Brar, A.S.; Dutta, K. Microstructural characterization of acrylonitrile/pentyl acrylate copolymers by one and 2-D NMR spectroscopy. J. Polym. Sci. Polym. Chem. **1999**, *37* (5), 533–543.
23. Ameduri, B.; Bauduin, G.; Kostov, G.K.; Petrova, P.; Rousseau, A. Synthesis and polymerization of fluorinated monomers bearing a reactive lateral group. Part 7. Copolymerization of tetrafluoroethylene with ω-hydroxy trifluorovinyl monomers. J. Appl. Polym. Sci. **1999**, *73* (2), 189–202.
24. Margerison, D.; Bain, D.R.; Lindley, K.; Morgan, N.R.; Taylor, L. Reactivity ratios for the copolymerization systems styrene-p-ethoxystyrene and methyl methacrylate-p-ethoxystyrene. Polymer **1975**, *16* (4), 278–280.
25. Bune Ye, V.; Barabanova, A.I.; Bogachev Yu, S.; Gromov, V.F. Copolymerization of acrylamide with various water-soluble monomers. Eur. Polym. J. **1997**, *33* (8), 1313–1323.
26. Wiley, R.H.; Jin, J.-I. Monomer reactivity ratios for the copolymerization of P-isopropylstyrene with styrene and methyl methacrylate. J. Macromol. Sci. Chem. **1969**, *3* (5), 835–843.
27. Lin, D.J.; Petit, A.; Neel, J. Radical copolymerization of 4-methylstyrene with methyl methacrylate or acrylonitrile-determination of reactivity ratios. Makromol. Chem. **1987**, *188* (5), 1163–1175.
28. Thamizharasi, S.; Gnanasundaram, P.; Reddy, B.S.R. Copolymerization of 4-acetylphenyl acrylate with methyl methacrylate and butyl methacrylate: synthesis, characterization and reactivity ratios. Eur. Polym. J. **1997**, *33* (9), 1487–1494.
29. McManus, N.T.; Kim, J.D.; Penlidis, A. Observations on styrene-hydroxyethyl acrylate and styrene-hydroxyethyl acrylate-ethyl acrylate polymerizations. Polym. Bull. **1998**, *41* (6), 661–668.
30. Del C. Pizarro, G.; Marambio, O.G.; Rivas, B.L.; Geckeler, K.E. Synthesis, characterization, and thermal stability of poly(N-maleyl glycine-co-N-vinylpyrrolidone). Polym. Bull. **1997**, *39* (2), 165–172.
31. Ryttel, A. Copolymerization of ethyl methacrylate with N-(3-or 4-halophenyl)maleimides: the monomer reactivity ratios. J. Appl. Polym. Sci. **1999**, *74* (12), 2924–2930.
32. Mukherjee, M.; Chatterjee, S.K.; Brar, A.S.; Dutta, K. Compositional and stereochemical analysis of acrylamide/vinyl acetate copolymers by one-and two-dimensional NMR spectroscopy. Macromolecules **1998**, *31* (24), 8455–8462.
33. Cawse, J.W. *Emulsion Polymerization and Emulsion Polymers*; Lovell, P.A., El-Aasser, M.S., Eds.; John Wiley and Sons: New York, 1997; 743.
34. Pazhanisamy, P.; Sulochana, P.; Anwaruddin, Q.; Ariff, M. Reactivity ratios of N-cyclohexylacrylamide-styrene copolymers by ^{1}H and ^{13}C NMR spectroscopy. J. Polym. Sci. Polym. Chem. **1997**, *35* (1), 193–195.
35. Harwood, H.J. Structures and compositions of copolymers. Makromol. Chem. Macromol. Symp. **1987**, *10–11*, 331–354.
36. Babu, G.N.; Deshpande, A. Copolymerization of 2-hydroxypropyl methacrylate with alkyl methacrylates. J. Macromol. Sci. Chem. **1982**, *A17* (5), 717–726.

37. Bevington, J.C.; Harris, D.O. Reactivities of acrylates and methacrylates. J. Polym. Sci. Polym. Lett. Ed. **1967**, *5* (9), 799–802.
38. Manders, B.G.; Smulders, W.; Aerdts, A.M.; van Herk, A.M. Determination of reactivity ratios for the system methyl methacrylate-n-butyl methacrylate. Macromolecules **1997**, *30* (2), 322–323.
39. Kaim, A.; Oracz, P. True reactivity ratios for styrene-methyl methacrylate copolymerization in bulk macromol. Theory Simul. **1998**, *7* (1), 97–103.
40. Kleinova, A.; Borsig, E.; Schulze, U.; Pionteck, J. Determination of copolymerization parameters of methyl methacrylate with dodecyl methacrylate by means of FTIR spectroscopy. Macromol. Chem. Phys. **1996**, *197* (7), 2289–2296.

Received September 2002
Revision received January 2003