Use of n.m.r. data to calculate copolymer reactivity ratios

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Reactivity ratios can be determined from n.m.r. analyses of binary copolymers. Measurement of the diad or triad sequence distribution provides an estimate of the number average sequence length of each copolymer. Each average sequence length is directly related to the corresponding reactivity ratio in the terminal copolymerization model. Extension to more complicated reaction models is straightforward. A single copolymerization experiment yields values for both reactivity ratios with this procedure. When pentads or triads, centred on one monomer only, are measured the two reactivity ratios cannot normally be estimated unless the copolymer is highly alternating. It is possible, however, to combine such data with an n.m.r. or other analysis of the chemical composition of the copolymer to obtain r_1 and r_2. When the sequence distribution of runs, centred on only one of the monomers, can be analysed and the chemical composition of the copolymer is not available the procedure can yield a good value for the reactivity ratio of that monomer and a poor estimate for that of the comonomer.

INTRODUCTION

Measurement of reactivity ratios in vinyl copolymerizations continues to be a problem. The necessary experiments appear to be straightforward, provided the equation linking feed and copolymer compositions fits the data obtained by analysing copolymers formed from several different comonomer feeds. The fitting of corresponding feed and copolymer compositions is not without pitfalls, however. Many of the available reactivity ratios in the literature are deficient because of unsuspected problems which were involved in estimation procedures, use of inappropriate mathematical models to link polymer and feed compositions and experimental or analytical difficulties[1,2]. Many of the analytical difficulties can be avoided by replacing the compositional analysis of copolymers by a gas chromatographic measurement of the loss of monomers during the course of the copolymerization[3,4]. The mathematical treatment of the resulting data still requires the estimation of reactivity ratios from feed compositions and corresponding copolymer compositions which are linked through an assumed copolymerization model.

A number of procedures for extracting reactivity ratios from such data have been proposed[5-8]. Some of these are not statistically reliable however[9], and the most generally useful method, which is not practical without the use of a computer, involves direct curve fitting of copolymer–monomer compositions according to an assumed copolymerization model[2,10].

This paper focusses on a technique for deriving reactivity ratios from comonomer sequence distributions measured by n.m.r. N.m.r. methods have been used mainly to provide analytical data for conventional reactivity ratio calculation procedures. It is more efficient, however, to assume a copolymerization model and calculate the number average sequence length ($\bar{N}_i$) of each monomer in terms of this model and the measured distribution. The terminal copolymer model[5,11] is used in this article because it fits all the sequence distribution data which were available at the time of writing. Extension to more complicated copolymerization models is straightforward, in any case. Knowledge of the monomer feed composition and the corresponding $\bar{N}_i$ provides a value of the reactivity ratio, r_i. Each copolymerization experiment can produce estimates of r_1 and r_2.

Fischer, Kinsinger and Wilson[12] used diad measurements to calculate reactivity ratios in 1966 and Moritani and Iwasaki[13] have also employed the same method recently. This article considers general guidelines for the practical use of n.m.r. spectra for the estimation of reactivity ratios in vinyl copolymerizations. The use of triad and pentad sequences are illustrated and some useful expedients are introduced for cases when the characterization of the copolymer is incomplete. The limitations on the use of such expedients are explored by Monte Carlo simulations of numerous copolymerizations.

CALCULATIONS

N.m.r. senses an average composition of the copolymer molecules in a specimen. The comonomers are coded M_1 and M_2 in this context and the reactivity ratios, r_1 and r_2, have their usual meanings[14]. The mol fraction of monomer 1 units in the average chain, n_1, is given by:

$$N_{11}+1/2N_{12}=N_{212}+N_{211}+N_{111}=n_1 \qquad (1)$$

where N_{ij} is the fraction of all diads which are of type M_iM_j. The triad symbols follow by analogy. Thus N_{212} is the number of $M_2M_1M_2$ triads normalized with respect to the total number of 1-centred and 2-centred triads. Longer sequences, such as pentads are coded in a corresponding fashion. The normalization requirement implies that:

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$$N_{11}+N_{12}+N_{22}=1=N_{111}+N_{211}+N_{212}+N_{222}+N_{122}+N_{121} \quad (2)$$

(It will be noted that N_{211} includes the 112 sequences and N_{122} includes 221 sequences since the two ends of a vinyl polymer are not distinguishable.)

We define a run as a sequence of one or more like monomers terminated on either end by an unlike monomer[15]. The number of runs of monomer 1 cannot differ from the number of runs of monomer 2 by more than one. This difference is negligible for a polymer with adequately high molecular weight and a large number of sequences. Since every run of M_1 units is followed by a 1,2 linkage the total number of such linkages equals the total number of runs or twice the number of each of the M_1 runs or M_2 runs. The fraction of 1,2 diads, N_{12} in the average polymer chain is:

$$N_{12}=2N_{212}+N_{112}=N_{121}+N_{122} \quad (3)$$

The number average sequence length for monomer 1 units, $\bar{N}_1$, is obtained by dividing equation (1) by equation (3):

$$\bar{N}_1=\frac{N_{11}+\frac{N_{12}}{2}}{\frac{N_{12}}{2}}=\frac{N_{212}+N_{211}+N_{111}}{N_{212}+\frac{N_{112}}{2}} \quad (4)$$

Similarly, the number average sequence length of monomer 2 units is:

$$\bar{N}_2=\frac{N_{22}+\frac{N_{12}}{2}}{\frac{N_{12}}{2}}=\frac{N_{121}+N_{221}+N_{222}}{N_{121}+\frac{N_{221}}{2}}$$

$$=\frac{N_{121}+N_{221}+N_{222}}{N_{212}+\frac{N_{112}}{2}} \quad (5)$$

(The extra term in equation (5) is included to note that $N_{212}+\frac{N_{112}}{2}=N_{121}+\frac{N_{221}}{2}$)

The simple copolymer model [5,10] postulates a first-order Markov process in which the conditional probability of the addition of a specified monomer to the end of a growing macrospecies depends on the nature of the terminal unit in the latter entity and is unaffected by any other feature of the macrospecies. Let the probability of occurrence of an M_iM_j sequence be denoted P_{ij} (where i may $=j$). P_{ij} is of course equal to the mol fraction, N_{ij}, of the corresponding diads in the copolymer molecule. The only reactions which are taken into account in this model are four propagation reactions involving two different monomers and macrospecies with two possible different terminal units. Then[14]:

$$P_{11}=\frac{k_{11}[M_1][M_1^*]}{k_{11}[M_1][M_1^*]+k_{12}[M_2][M_1^*]}=\frac{r_1[M_1]}{r_1[M_1]+[M_2]} \quad (6)$$

since $r_1=\frac{k_{11}}{k_{12}}$. Similarly (with $r_2=\frac{k_{22}}{k_{21}}$) it follows that:

$$P_{12}=\frac{1}{r_1\frac{[M_1]}{[M_2]}+1} \quad (7)$$

and

$$P_{21}=\frac{\frac{[M_1]}{[M_2]}}{\frac{[M_1]}{[M_2]}+r_2} \quad (8)$$

It is also a straightforward matter to derive the number distribution function $n(M_i,n_i)$for M_i sequence lengths. (Here $n(M_i,n_i)$ is the fraction of all M_1 sequences which contain n_i units of this monomer.) Because this is a first order Markov process:

$$n(M_1,n_i)=P_{11}^{n_i-1}(1-P_{11})=P_{12}P_{11}^{n_i-1} \quad (9)$$

and

$$n(M_2,n_j)=P_{22}^{n_j-1}(1-P_{22})+P_{22}^{n_j-1}P_{21} \quad (10)$$

The number average sequence length of M_1 runs, $\bar{N}_1$, is:

$$N_1=\sum_{n_i=1}^{\infty}n_iP_{11}^{n_i-1}P_{12}=\frac{1-P_{11}}{P_{11}}\sum_{n_i=1}^{\infty}n_iP_{11}^{n_i} \quad (11)$$

which reduces to [16]:

$$\bar{N}_1=\frac{1}{1-P_{11}}=\frac{1}{P_{12}} \quad (12)$$

Similarly,

$$\bar{N}_2=\frac{P_{21}}{P_{22}}\sum_{n_j=1}^{\infty}n_jP_{22}^{n_j}=\frac{1}{1-P_{22}}=\frac{1}{P_{21}} \quad (13)$$

Equations (4), (7) and (12) yield:

$$\frac{N_{11}+\frac{N_{12}}{2}}{\frac{N_{12}}{2}}=\frac{N_{212}+N_{211}+N_{111}}{N_{212}+\frac{N_{112}}{2}}=r_1\frac{[M_1]}{[M_2]}+1 \quad (14)$$

Similarly, from equations (5), (8) and (13):

$$\frac{N_{22}+\frac{N_{12}}{2}}{\frac{N_{12}}{2}}=\frac{N_{121}+N_{221}+N_{222}}{N_{212}+\frac{N_{112}}{2}}=\frac{\frac{[M_1]}{[M_2]}+r_2}{\frac{[M_1]}{[M_2]}}. \quad (15)$$

Equations (14) and (15) relate the comonomer feed composition and the diad or triad sequence distribution of the corresponding copolymer to values of r_1 and r_2.

They result from combinations of well-known principles[14].

Tetrad sequences are not used in the n.m.r. analysis of binary copolymers of vinyl monomers, although they are valuable when methylene signals can be interpreted, as in copolymers of vinylidene monomers. Vinyl copolymer data are usefully reported in terms of pentad sequences centred on either or both monomers. The foregoing reasoning can be extended directly to yield analogues of equations (14) and (15) in terms of pentad frequencies. It is less awkward, however, to use bond fraction concepts with pentad data. This variation is explained and illustrated in the Results section.

This article focusses particularly on expedients for estimating reactivity ratios from n.m.r. spectra in which the sequence distribution of only one of the comonomers has been resolved.

Table 1 Vinylidene chloride (M_1)-vinyl acetate copolymers

Code[a]	1	2	3	4	5
Feed composition $[M_1]/[M_2]$	1/1.04	1/1.56	1/2.45	1/4.26	1/8.09
Diad distribution (mol fractions)					
N_{11}	0.75	0.67	0.55	0.38	0.21
N_{12}	0.24	0.32	0.42	0.56	0.64
N_{22}	0.00	0.01	0.04	0.05	0.14
$\bar{N}_1$ (equation (4))	7.25	5.19	3.62	2.36	1.66
r_1 (equation (14))	6.5	6.5	6.4	5.8	5.3
$\bar{N}_2$ (equation (5))	1.0	1.06	1.19	1.18	1.44
r_2 (equation (15))	0.0	0.04	0.08	0.04	0.05

[a] Code and data from reference 17

Table 2 Ethylene sulphide (M_1)-propylene sulphide copolymers

Code[a]	2	4
Conversion (%)	12.6	18.8
Feed mole ratio $[M_1]/[M_2]$	1/5.67	1/3
Diad distribution (mol fractions)		
N_{22}	0.503	0.376
N_{12}	0.420	0.473
N_{11}	0.079	0.151
$\bar{N}_1$ (equation (4))	1.38	1.64
r_1 (equation (15))	2.15	1.92
$\bar{N}_2$ (equation (5))	3.40	2.59
r_2 (equation (16))	0.42	0.53

[a] Code and data from reference 18

RESULTS

Complete anlyses of sequence distributions

Yamashita and co-workers[17] have reported diad distributions from 60 MHz proton n.m.r. analyses of vinylidene chloride–vinyl acetate copolymers. We have omitted their high conversion data, since the simple copolymer equation is being used in this context in its differential form. The data and calculated values of mean sequence lengths and reactivity ratios are listed in *Table 1*. The average values of r_1 and r_2 in this estimation are 6.1 and 0.04 respectively. The cited authors quote corresponding figures of 6.7 and 0.05. The two sets of reactivity ratios agree closely. This is a straightforward application of the concepts summarized above. Each copolymerization experiment yields values for both r_1 and r_2. It is not surprising that the best coincidence of reactivity ratios from n.m.r. estimates, with those calculated by other methods, is obtained from spectra in which both comonomers are present in significant proportions.

Similarly, Corno and co-workers[18] give diad distributions from ^{13}C n.m.r. analyses of anionically polymerized copolymers of ethylene sulphide and propylene sulphide. Much of the data deals with high conversion experiments but the lowest conversion data are used in *Table 2* to produce mean values of $r_1 = 2.0$ and $r_2 = 0.5$. The authors quote respective figures of 2.1 and 0.5 from a computer-assisted technique which minimized the residual squared deviations between calculated and experimental diad and triad fractions at high conversions. The agreement between their data and our calculations is good. (The same authors[18] also report results for the copolymerization of ethylene sulphide and isobutene sulphide. These data were not used here because they seem to contain an error. In particular, the composition of one copolymer is reported to be the same as that of its commonomer feed, but this is impossible with the reactivity ratios quoted by Corno *et al.* if the simple copolymer model applies to this system.)

Fischer *et al.*[12] and Moritani and Iwasaki[13] have used variations of this method to estimate reactivity ratios from complete n.m.r. analyses of the diad distributions in binary copolymers.

We turn now to a consideration of expedients which can be used to estimate reactivity ratios from analyses in which the n.m.r. spectra cannot be interpreted to yield the distribution of sequences of both monomers. This is not an uncommon situation because n.m.r. spectra reflect configurational variations and inversions of head-to-tail monomer placements as well as comonomer sequences and it is often difficult to sort out all these chemical shift differences.

Incomplete anlyses of sequence distributions

Suzuki and co-workers[19] give results of 220 MHz proton n.m.r. analyses of butadiene acrylonitrile polymers. The triad values reported are for acrylonitrile (M_1) centred sequences only and it is necessary for our purposes to supplement these data with the measured acrylonitrile content of the copolymers, as obtained from elementary analysis. (The last datum would not be needed if the relative areas of the triad peaks centred on both monomers were recorded.) If the fractions of all monomer 1 centred triads (which are 212, 211 and 111) are denoted as $f_{212}, f_{211}, f_{111}$ and the mol fraction of this monomer in the copolymer is n_1, then the foregoing equations for $\bar{N}_1$ and $\bar{N}_2$ are transformed in a straightforward manner into:

$$\bar{N}_1 = \frac{n_1}{\left(f_{212} + \frac{f_{112}}{2}\right) n_1} = \frac{1}{f_{212} + \frac{f_{112}}{2}} \qquad (4a)$$

$$\bar{N}_2 = \frac{1 - n_1}{\left(f_{212} + \frac{f_{112}}{2}\right) n_1} \qquad (5a)$$

Table 3 Triad distribution data for acrylonitrile (M_1)-butadiene (M_2) copolymers

Code[a]	Feed composition $[M_1]/[M_2]$	Polymer composition n_1[b]	f_{212}	f_{211}	f_{111}[c]	$\bar{N}_1$	$\bar{N}_2$	r_1	r_2
A-8	9/1	0.585	0.48	0.43	0.10	1.52	1.07	0.06	0.63
A-9	2.3/1	0.486	0.77	0.23	0	1.13	1.19	0.06	0.44
A-10	1/1	0.423	0.90	0.11	0	1.05	1.42	0.05	0.42
A-11	1/9	0.167	1.00	0	0	1.00	4.99	0	0.44

[a] Code and data from reference 19
[b] From elementary analysis
[c] The mol fractions recorded here are fractions of the total n.m.r. peak areas of triads centred on monomer 1 (acrylonitrile)

The data and results of our calculations are given in *Table 3*. The average values of r_1 and r_2 are 0.04 and 0.48, respectively. The corresponding reactivity ratios given by Suzuki and co-workers[19] agree well at 0.05 and 0.35.

The data in the last example comprised the comonomer feed composition, the distribution of triad sequences centred on one of the monomers and the overall copolymer composition. The copolymer composition was obtained by elementary analysis in this case, but it can often be estimated from the n.m.r. spectrum which was used to determine the sequence distribution of one of the monomers.

Suzuki *et al.*[19] also present data for the relative frequencies of monomer 2 centred pentads. This system is quite highly alternating ($r_1 r_2 = 0.02$) and it seems reasonable to assume that the entire composition of the copolymer has been covered by assignments of monomer 2 centred pentads. That is to say, with the cited reactivity ratios pentads in which the units are all or mostly monomer 1 will be rare and can be neglected. If we assume that the monomer 2 centred pentad distribution provides a good approximation to the composition of the entire polymer then this distribution can be used to estimate r_1 and r_2 without reference to the polymer chemical composition which had to be invoked to supplement the partial triad information in *Table 3*. The circumstances in which such assumptions are useful are examined in the following section of this article.

When pentad distributions are being used the least cumbersome computational method appears to involve bond fraction calculations rather than extensions of the diad and triad equations given above. A bond fraction α_1, is the fraction of M_i bonds which connect two M_i units in the particular sequence. The values of α_i and α_j are obtained by direct inspection. For example, if pentad $M_iM_jM_jM_iM_i$ comprises a mole fraction N_{ijjii} of all M_j centred pentads then the fraction of M_jM_j bonds $= \alpha_j = N_{ijjii}/3$, since there are 3 M_j bonds and 1 M_{jj} bond in this particular sequence. (In this example, also, $\alpha_j = \alpha_i$) It can be shown[20] that:

$$\bar{N}_1 = 1/(1-\alpha_1) \quad (16)$$

$$\bar{N}_2 = 1/(1-\alpha_2) \quad (17)$$

The reactivity ratios can be calculated by combining equations (7), (12) and (16) for r_1 and (8), (13) and (17), for r_2. Inspection of equations (12) and (16) and (13) and (17) reveals that $\alpha_1 = P_{ii}$.

Table 4 shows the pentad data of Suzuki and co-workers[19] and the calculated r_1 and r_2 values, which agree reasonably well with the triad-based values of *Table 3*.

Table 4 Pentad distribution data for acrylonitrile (M_1)—butadiene (M_2) copolymers

Code[a]	A-8	A-9	A-10	A-11
Feed mole ratio $[M_1]/[M_2]$	9/1	2.3/1	1/1	1/9
Polymer composition mol fraction of specified pentads				
22222	0	0	0	0.32
12222	0	0	0.03	0.38
12221	0	0.02	0.02	0
22212	0	0.08	0.15	0.12
22211 / 12212	0.07	0.15	0.17	0.13
12211	0.04	–	–	–
21212	0.55	0.60	0.54	0.05
11212	0.27	0.12	0.03	0
11211	0.07	0.02	0.05	0
α_1	0.13	0.07	0.07	0.03
α_2	0.04	0.11	0.18	0.67
$\bar{N}_1$	1.15	1.08	1.07	1.03
$\bar{N}_2$	1.04	1.13	1.22	3.00
r_1	0.02	0.03	0.07	0.23
r_2	0.36	0.30	0.22	0.22

[a] Code and data from reference 19

Pentad distributions centred on one monomer only were useful in the foregoing example because the copolymer was highly alternating. This expedient cannot be used to determine both reactivity ratios if the reactivities of the two monomers differ appreciably. It may, however, be used to measure the reactivity ratio of the central monomer in the particular pentad distribution. An example is the data of Okada and co-workers[21] on proton n.m.r. of copolymers of methyl methacrylate (M_1) and chloroprene (M_2). These authors list the reactivity ratios as $r_1 = 0.116$ and $r_2 = 6.0$. Other figures in the literature are $r_1 = 0.08$, $r_2 = 6.12$ [22] and $r_1 = 0.18$, $r_2 = 3.9$ [23].

Data are given in this case for the M_1 centred pentads, from signals assigned to the methoxy group of methyl methacrylate. (Actually only 6 peaks were available to characterize the 10 possible M_1 centred pentads. In both *Tables 4* and 5, the existence of fewer n.m.r. peaks than the possible number of M_1 centred sequences necessitates the assumption that the frequency of occurrence is equal for those sequences assigned to the same n.m.r. peak.) The data and an example of the calculations are given in *Table 5*. The estimated values of r_1 average out to $r_1 = 0.08$, which is within the experimental uncertainty of the other values quoted.

Unlike the butadiene/acrylonitrile case, however, a count of only M_1 centred pentads cannot yield a good value for r_2 because so much of the M_2 content of the copolymer is excluded from the measurements as a result

Table 5 Pentad distribution for methyl methacrylate (M_1)—chloroprene copolymers

Code[a]	CM-3	CM-4	CM-5	CM-6	CM-7
Feed mole ratio $[M_1]/[M_2]$	1/1.13	1/0.43	1/0.25	1/0.11	1/0.03
Peaks corresponding to M_1-centred pentads[b] relative areas					
S_1	0.59	0.38	0.14	0.05	0.01
S_2	0.32	0.49	0.45	0.31	0.03
S_3	0.04	0.06	0.13	0.08	0.05
S_4	0.04	0.06	0.17	0.25	0.25
S_5	0	0.02	0.09	0.24	0.25
S_6	0	0	0.02	0.07	0.42
α_1	0.07	0.12	0.27	0.43	0.75
$\bar{N}_1$ (equation (17))	1.08	1.14	1.36	1.76	3.95
r_1	0.09	0.06	0.09	0.08	0.09
$[m_1]/[m_2]$	0.12/1	0.32/1	0.54/1	1.17/1	4/1
$\bar{N}_2$ (equation (18))	9.00	3.56	2.52	1.50	0.99
r_2	7.1	6.0	6.1	4.6	

[a] Code and data from reference 21

[b] $S_1 = N_{22122}$; $S_2 = 2N_{22121} + N_{12121} + 2N_{22112}$; $S_3 = 2N_{12112}$; $S_4 = 2N_{11122} + 2N_{11121}$; $S_5 = N_{21112} + 2N_{11112}$; $S_6 = N_{11111}$

$$\therefore \alpha_1 = \frac{0}{2}S_1 + \frac{2}{16}S_2 + \frac{2}{8}S_3 + \frac{8}{14}S_4 + \frac{8}{12}S_5 + S_6$$

of the differences in monomer reactivity. (The values of r_2 calculated without regard to the foregoing differ by more than an order of magnitude from the correct r_2.) One can, however, combine the n.m.r. sequence distribution with an estimate of the chemical composition of the copolymer from relative areas of appropriate peaks in the same n.m.r. spectrum. This will provide a value of r_2 even in this case since:

$$\frac{\bar{N}_1}{\bar{N}_2} = \frac{[m_1]}{[m_2]} \qquad (18)$$

where $[m_i]$ is the concentration of monomer M_i in the copolymer. Thus, a single copolymerization experiment can provide estimates for both reactivity ratios from n.m.r. analysis of the distribution of pentads centred on one of the monomers and the overall copolymer composition. This expedient has been tried with the data in *Table 5*. It is clear that a fair approximation to the missing reactivity ratio can be provided by this method. Not surprisingly, however, the reliability of the estimate of r_2 decreases with decreasing M_2 content in the feed.

Monto Carlo simulations

In the preceding section, several experimental examples were given for estimations of reactivity ratio values from n.m.r. spectra in which the sequence distributions of both comonomers could not be deduced. It is clear from these few cases that the efficacy of this expedient will depend on the actual values of the reactivity ratios and the overall copolymer composition and that these independent variables interact. It is not possible to derive analytical expressions for the limiting values of r_1, r_2 and the feed composition at which analysis of the sequence distribution of one of the monomers does not yield reliable reactivity ratio estimates. A general picture of the potential of such partial analyses can be obtained, however, from Monte Carlo simulations of binary copolymer compositions.

The input data for the Monte Carlo calculations[24] were monomer feed concentration ratios and reactivity ratios. The calculations generated macromolecules with a predetermined number of monomer units and counted the different pentads. An example is given in *Table 6*. (Note that the computer counts sequences from one end of the simulated copolymer but the two ends of a real macromolecule are indistinguishable in n.m.r. sequence analysis. The program therefore sums the frequencies of pentads which would be identical if the sequence were reversed.)

The next step involves verification that the initial reactivity ratios can be calculated from the Monte Carlo sequences. This is not a completely foregone conclusion because the process is based on probabilities of occurrence of monomers in a finite macromolecule while the copolymerization model itself assumes an infinitely long polymer.

To avoid counting a given monomer unit more than once we note that the total number of M_i units in a polymer equals the number of M_i-centred pentads in that molecule. If there are x M_i-centred pentads in the molecule then the total number of M_iM_i and M_iM_j bonds in the molecule is $2x$. The bond fraction ($M_{ii}/(M_{ii}+M_{ij})$) for the central unit in the pentad is obtained by inspection. The possible values of M_{ii} are 0, 1 and 2 as illustrated respectively in pentads $M_jM_jM_iM_jM_i$, $M_jM_jM_iM_iM_j$ and $M_jM_iM_iM_iM_j$. To obtain the α_i value for the polymer one sums the products of the bond fraction for the central atom in each pentad and the number of such pentads and divides this sum by $2x$. The reactivity ratios follow from equations (16) and (17). This calculation serves to confirm that the Monte Carlo simulation is self consistent and to establish a reasonable size for the macromolecule which the computer generates. *Table 7* compares the results of such verifications of Monte Carlo simulations of copo-

Table 6 Example of monte carlo simulation. First 100 elements of the copolymer which is 10 000 units long: 1212212121211221 221212221212122121212121221212212212121212121211221212 121222122121121212121212212211; Feed mol fraction of monomer 1 = 0.50; Reactivity ratios: r_1 = 0.20; r_2 = 0.20; Reaction probabilities: P_{11} = 0.167; P_{12} = 0.833; P_{21} = 0.833; P_{22} = 0.167; Number of monomer residues: Monomer 1 = 4967; Monomer 2 = 5033; Total number of pentads = 9996; Total number of Monomer 1 centred pentads = 4966; Total number of Monomer 2 centred pentads = 5030

Monomer sequence	Reverse sequence	Fraction of 1 centred pentads	Fraction of 2 centred pentads
22122		0.024	
22121	12122	0.205	
22112	21122	0.046	
22111	11122	0.008	
21121	12112	0.200	
21112		0.017	
12121		0.455	
21111	11112	0.009	
12111	11121	0.035	
11111		0.001	
11211			0.021
11212	21211		0.189
11221	12211		0.047
11222	22211		0.007
12212	21221		0.206
12221			0.020
21212			0.455
12222	22221		0.010
21222	22212		0.044
22222			0.001

Table 7 Verification of Monte Carlo simulations of copolymers[a]

Given reactivity ratios		Copolymer with 10000 units				Copolymer with 1000 units			
r_1	r_2	α_1	α_2	r_1	r_2	α_1	α_2	r_1	r_2
0.20	0.20	0.172	0.183	0.21	0.22	0.163	0.189	0.20	0.23
0.50	0.50	0.332	0.326	0.50	0.48	0.314	0.348	0.46	0.53
0.80	0.80	0.438	0.445	0.78	0.80	0.426	0.465	0.74	0.87

[a] Feed comprised of equimolar mixture of M_1 and M_2 in each case

lymers containing 1000 and 10000 monomer units. The simulation is more reliable the more alternating the copolymer structure ($r_1 < 1, r_2 < 1, r_1 r_2 \to 0$) and the longer the simulated copolymer molecule. Our present purpose is to seek qualitative limits for the estimation of reactivity ratios from partial sequence distribution analyses and Monte Carlo calculations with 1000 comonomer units appear to provide adequate information without excessive use of computer time. The following calculations are based on 1000 unit simulations.

To compare with actual n.m.r. analyses we now assume that only pentad distribution entered on M_1 or on M_2 is available and that this distribution reflects the monomer distribution in the whole polymer. (We are trying to find out here when this assumption will hold.) The calculations then proceed as follows. If we take the pentad sequence $M_jM_jM_iM_iM_i$ as an example the bond fraction $(M_iM_i/(M_iM_i+M_iM_j))$ is 2/3 and $(M_jM_j/(M_jM_j+M_iM_j))$ is 1/2. The contribution to α_i in this case is $2N_{jjiii}/3$ while the α_j contribution is $N_{jjiii}/2$, where the numerator is the corresponding mol fraction of all pentads centred on monomer i. These contributions are summed over all pentads centred on each monomer. It is then possible to calculate r_1 (equations (16), (12) and (7)) and r_2 (equations (17), (13) and (8)) from the monomer feed composition and either one or the other pentad distribution and to compare the calculated values with the initial reactivity ratios which were used to generate the simulated copolymer.

Table 8 compares the reactivity ratios determined from complete sequence distributions of the simulated copolymers with those estimated from pentad distributions centred on one or other comonomer. It is instructive to note first that the reactivity ratios which characterize the 1000 unit simulated copolymer appear to differ significantly in some instances from those used to generate the Monte Carlo probabilities. If this were a copolymer of styrene and methyl methacrylate, say, the molecular weight of the macromolecule would be in the neighbourhood of 100000. The mean composition of all copolymer molecules in a real sample would be characterized by the input reactivity ratios but the composition of a single molecule of finite molecular weight can deviate from these values, as pointed out by Stockmayer[25] and illustrated in some of these examples. Note also that *Table 8* compares reactivity ratios and not copolymer compositions. It will be recalled that the differential form of the simple copolymer[5,11] equation is

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+[M_2]}{[M_1]+r_2[M_2]} \qquad (19)$$

where $d[M_i]$ and $[M_i]$ are corresponding molar concentrations of monomer i in the polymer and comonomer feed, respectively. Since one reactivity ratio occurs in the numerator and the other in the denominator deviations from the true values have less of an effect on copolymer composition than might be expected at first glance. Indeed, even when the most extreme deviations between the input reactivity ratios and those derived from complete pentad distributions in *Table 8* are compared it is seen that the corresponding differences in calculated copolymer compositions are negligible compared to uncertainties in polymer analyses. Proceeding from other considerations, Berger and Kuntz[26] have shown that composition is a much less sensitive parameter than is sequence distribution.

Turning now to the reactivity ratios estimated from M_1-centred or M_2-centred pentad distributions in *Table 8*, it can be seen that the calculated values of r_1 and r_2 are almost always lower than the r_1 and r_2 figures which pertain to the actual simulated macromolecule. The reason for this bias is inherent in the assumption that the M_1- (or M_2-) centred pentads fairly represent the entire copolymer chain. It is also clear that r_1, r_2 determinations from partial sequence distributions are most reliable for the more highly alternating copolymers. Further, it is to be noted (as with the real experimental data of *Table 5*) that M_1-centred pentads yield fair values of r_1 and poor values of r_2, the opposite being true for M_2-centred pentads. It can be concluded that reasonable estimates of the reactivity ratios can be obtained from such partial analyses with fewer experiments than are needed in more conventional methods.

A final point to be noted is that the random nature of a Monte Carlo chain only 1000 units long can occasionally produce a significant deviation from the average chain as expected from Stockmayer's equations[25]. In *Table 8* symmetry considerations permit us to make comparisons. For example, where $r_1 = r_2 = 0.800$; when M_1 in the feed is 0.25 the value of r_1 calculated from the M_1-centred pentads is expected to be equal to that of r_2 calculated from M_2-centred pentads where M_1 in the feed $(= 1 - M_2)$ is 0.75. The observed values are respectively 0.548 and 0.421, the difference being attributable to the chance differences in the Monte Carlo chains generated in two separate experiments. By contrast much better agreement can be seen in many other symmetry-related pairs, e.g. $r_1 = r_2 = 1.000$ where M_1 is 0.25 and 0.75, r_1 and r_2 respectively are 0.713 and 0.711.

DISCUSSION

Assignment of individual statistical uncertainties to r_1 and r_2 is generally incorrect because the two reactivity ratios are derived from the same data. The example quoted above in connection with *Table 5* and the simulations of *Table 8* show that the present method permits the calculation of one reactivity ratio in some cases when the other is not readily accessible. The

Table 8 Monte Carlo simulations

Input data for copolymer simulation		Mol fraction	Calculated reactivity ratios					
			Results based on complete pentad distribution		Results based on M_1-centred pentads		Results based on M_2-centred pentads	
r_1	r_2	M_1 in feed	r_1	r_2	r_1	r_2	r_1	r_2
0.100	0.100	0.25	0.093	0.112	0.052	0.047	0.043	0.063
0.100	0.100	0.50	0.074	0.091	0.039	0.040	0.033	0.049
0.100	0.100	0.75	0.091	0.118	0.049	0.046	0.040	0.063
0.300	0.300	0.25	0.337	0.334	0.210	0.100	0.106	0.208
0.300	0.300	0.50	0.291	0.277	0.180	0.102	0.096	0.159
0.300	0.300	0.75	0.294	0.324	0.181	0.117	0.095	0.196
0.500	0.500	0.25	0.409	0.451	0.278	0.119	0.094	0.285
0.500	0.500	0.50	0.459	0.535	0.277	0.160	0.147	0.336
0.500	0.500	0.75	0.529	0.485	0.336	0.117	0.132	0.320
0.800	0.800	0.25	0.836	0.895	0.548	0.159	0.166	0.600
0.800	0.800	0.50	0.743	0.869	0.503	0.206	0.172	0.579
0.800	0.800	0.75	0.767	0.655	0.505	0.140	0.151	0.421
1.000	1.000	0.25	1.047	0.780	0.713	0.150	0.207	0.516
1.000	1.000	0.50	0.972	0.957	0.670	0.206	0.201	0.639
1.000	1.000	0.75	0.960	1.058	0.655	0.179	0.147	0.711
1.400	0.800	0.25	1.263	0.781	0.834	0.133	0.237	0.532
1.400	0.800	0.50	1.327	0.732	0.890	0.149	0.269	0.491
1.400	0.800	0.75	1.430	1.000	0.964	0.144	0.193	0.685
1.400	0.650	0.25	1.327	0.657	0.875	0.123	0.267	0.442
1.400	0.650	0.50	1.353	0.643	0.896	0.144	0.290	0.418
1.400	0.650	0.75	1.432	0.770	0.967	0.121	0.191	0.494
3.200	0.300	0.25	3.057	0.260	2.027	0.053	0.646	0.177
3.200	0.300	0.50	3.333	0.200	2.242	0.032	0.520	0.132
3.200	0.300	0.75	2.871	0.290	1.941	0.022	0.223	0.196
2.700	0.100	0.25	3.149	0.086	2.016	0.024	0.851	0.055
2.700	0.100	0.50	2.490	0.135	1.653	0.029	0.457	0.082
2.700	0.100	0.75	3.098	0.068	2.046	0.006	0.265	0.045
0.400	0.900	0.25	0.398	0.983	0.250	0.180	0.085	0.643
0.400	0.900	0.50	0.458	0.857	0.299	0.230	0.124	0.559
0.400	0.900	0.75	0.413	0.918	0.258	0.233	0.113	0.607
0.700	0.300	0.25	0.913	0.343	0.553	0.097	0.289	0.218
0.700	0.300	0.50	0.643	0.299	0.394	0.090	0.193	0.181
0.700	0.300	0.75	0.755	0.344	0.488	0.088	0.163	0.208
0.100	0.400	0.25	0.080	0.437	0.046	0.142	0.023	0.259
0.100	0.400	0.50	0.088	0.417	0.049	0.160	0.036	0.244
0.100	0.400	0.75	0.109	0.432	0.061	0.153	0.044	0.258
0.200	0.300	0.25	0.166	0.281	0.098	0.094	0.056	0.170
0.200	0.300	0.50	0.155	0.281	0.088	0.106	0.060	0.163
0.200	0.300	0.75	0.215	0.367	0.130	0.142	0.076	0.216
0.400	0.500	0.25	0.398	0.479	0.260	0.130	0.112	0.302
0.400	0.500	0.50	0.405	0.516	0.266	0.171	0.116	0.315
0.400	0.500	0.75	0.386	0.554	0.247	0.155	0.104	0.351
0.700	0.800	0.25	0.821	0.814	0.564	0.152	0.152	0.537
0.700	0.800	0.50	0.677	0.818	0.427	0.204	0.188	0.547
0.700	0.800	0.75	0.713	0.629	0.476	0.150	0.139	0.377
1.300	0.700	0.25	1.416	0.727	0.939	0.134	0.291	0.496
1.300	0.700	0.50	1.369	0.710	0.948	0.136	0.251	0.486
1.300	0.700	0.75	1.441	0.691	0.974	0.102	0.188	0.449
1.400	0.600	0.25	1.385	0.679	0.909	0.117	0.268	0.464
1.400	0.600	0.50	1.252	0.669	0.818	0.142	0.284	0.463
1.400	0.600	0.75	1.372	0.929	0.922	0.122	0.187	0.656
1.800	0.200	0.25	1.534	0.232	0.963	0.064	0.447	0.150
1.800	0.200	0.50	1.707	0.163	1.091	0.036	0.411	0.111
1.800	0.200	0.75	1.839	0.183	1.203	0.024	0.231	0.110

uncertainties in the two reactivity ratios are, however, not necessarily uncoupled by this method since errors in peak assignments or peak areas may be reflected in the estimations of mol fractions of all sequences.

Conventional curve-fitting derivations of reactivity ratios from direct or gas chromatographic analyses of copolymer compositions and monomer feed compositions require the production of more than a few different copolymers. Some of the uncertainties in data in the literature result, in fact, from the use of rather too few data points because the copolymerization experiments can easily become prohibitively tedious or expensive.

As shown above, a single copolymerization can yield estimates of both reactivity ratios if the sequence distribution of the polymer can be analysed completely, or if M_i centreed sequences and composition are measured. The uncertainty of the calculated r_i values is of course reduced as the number of data points is increased. For many applications, however, one or two copolymerizations may suffice for the purposes for which the reactivity ratios are used.

The most formidable task in the application of the technique described is the actual assignment of peaks to the various possible sequences and the compensation, if

necessary, for stereoregular differences in the copolymer[27]. Once this is done, however, it provides a test of the applicability of a copolymerization model to the data as well as estimates of the parameters which are used with the particular model.

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