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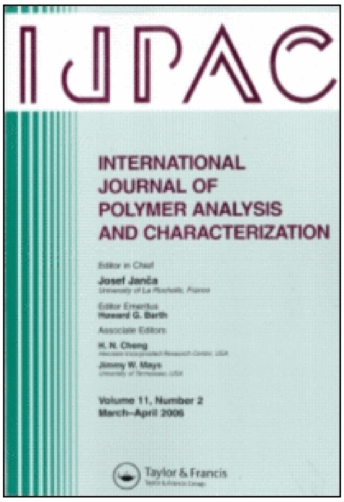

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NMR Sequence Analysis for Copolymers Made at High Conversions

H. N. Cheng[a]
[a] Hercules Incorporated Research Center, Wilmington, Delaware

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NMR Sequence Analysis for Copolymers Made at High Conversions

H. N. CHENG*

Hercules Incorporated Research Center, 500 Hercules Road, Wilmington, Delaware 19808-1599[†]

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Two analytical methodologies have been devised to treat the NMR sequence data of copolymers that are made at high conversions. The first approach is a computer simulation method whereby the copolymerization is simulated through a Monte Carlo process, and the copolymer sequences obtained are compared with the observed NMR data. In the second approach, the NMR triad data are directly analyzed through the first-order Markovian statistics with provision made for conversion. A simplex algorithm is used to optimize the parameters. The procedure has been automated. Examples are shown to illustrate the use of these approaches.

Keywords: Computer simulation, Markovian model, Monte Carlo, NMR, sequence distribution, simplex algorithm, triads

INTRODUCTION

Many copolymers are made industrially in batch processes at high conversions. When the microstructures of these polymers are studied by NMR, care needs to be exercised. For example, if the comonomer reactivity ratios of the comonomers are different, the composition of the instantaneous copolymers formed may change as a function of conversion.[1] The resulting compositional heterogeneity may strongly influence the observed copolymer sequence intensities.

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*Corresponding author.

[†] Hercules Research Center Contribution Number 2287.

Although this problem is well recognized, there have been only a few papers addressing this issue. The most frequent treatment is to derive the comonomer reactivity ratios from low-conversion copolymers and then use the integrated copolymerization expressions to predict high-conversion copolymer sequences. This is the approach first taken by Ito and Yamashita in a series of papers for styrene/methyl methacrylate,[2] vinyl chloride/vinyl acetate,[3] and vinyl chloride/vinylidene chloride [4] copolymers. More recently, similar (and more refined) approaches have been used, for example, for styrene/acrylonitrile and styrene/maleic anhydride copolymers by Hill *et al.*[5] styrene/ethyl methacrylate by Tacx *et al.*,[6] styrene/methyl acrylate by Doremaele *et al.*, and methyl methacrylate/methyl acrylate copolymers by Lopez-Gonzales *et al.*[8]

A different approach has been employed by Johnson *et al.*[9] for styrene/ethyl acrylate copolymers. Using different reactivity ratios, they calculated the predicted NMR triad values. (Only three of the triads were used in their work). They then visually compared the observed and the predicted triads, and chose the reactivity ratios producing the least deviations as the best values for the system.

In view of the commercial importance of polymers made at high conversions, it would be useful to have relatively simple methods to analyze the NMR data of such polymers. In this work, two analytical methodologies have been formulated that are based on the classical terminal copolymerization theory (first-order Markovian statistical model) [10–12] with provisions made for the effects of conversion. The methods have been computerized and found to be useful for many copolymer systems.

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RESULTS AND DISCUSSION

The problem may be approached from two perspectives.[13] One may start from a first-order Markovian model, simulate the copolymerization, and predict the NMR sequence information (spectral simulation approach). Alternately, one may start with the observed NMR data and analyze the data to derive information on comonomer reactivities and Markovian probabilities (analytical approach). Both approaches will be described below.

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Computer Simulation Approach

The first approach being proposed here is an amplification of the method used by Johnson *et al.*[9] Previously a family of computer programs (called PODIS) has been developed for the simulation of chemical composition distribution (CCD) curves and NMR data.[14] One program, PODIS3 in particular, has been designed for copolymerizations carried out under batch conditions. The scheme can be depicted below:

reaction	reactivity	polymer		bookkeeping	output	predicted
probability	→	chain	→	procedures	→	CCD or
model	ratios	generation				NMR results

Thus, for two comonomers with reactivity ratios r_1 and r_2, the program generates an ensemble of polymer chains using a Monte Carlo process where the first-order Markovian probabilities (P_{ij}) are given by the conventional expressions,

$$P_{21} = \frac{1}{1 + r_2 / x} \qquad P_{12} = \frac{1}{1 + r_1 x}$$

and x = the ratio of comonomer concentrations $= f_1/f_2$. At the outset of copolymerization, the comonomer concentrations are the same as the initial comonomer feed concentrations, $f_1 = f_1^0, f_2 = f_2^0$ and $x = x^0$ (where the subscript 0 indicates the feed value). If $r_1 \neq r_2$, as the polymerization proceeds, f_1 and f_2 change at different rates and the value x is adjusted accordingly as a function of conversion. In the bookkeeping procedure, the polymer chains are examined for composition and sequences. These are compiled and sorted. The output consists of the predicted copolymer composition, sequence distribution, and CCD curve.

Although designed for simulation, the program PODIS3 may be employed to analyze NMR data. To use this approach, one first takes the known information about the polymer system (*e.g.*, comonomer feed ratio, conversion, and reactivity ratios) and simulates polymerization. One then systematically varies the values of r_1 and r_2 and registers the changes in the intensities of the triad sequences. The calculated and the observed triad intensities are compared and the best r_1 and r_2 values are then chosen.

As an example, the triad distribution of a styrene(S)/ethyl acrylate (A) copolymer[15] made via emulsion polymerization is given in Table I. The sample chosen was 98% converted; thus, polymerization in the water phase

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TABLE I Simulations of Styrene (S) / Ethyl Acrylate (A) Copolymerization Through Program PODIS3*

Triad	I_{obsd}	$I_{calc}1$	$I_{calc}2$	$I_{calc}3$	$I_{calc}4$	$I_{calc}5$	$I_{calc}6$	$I_{calc}7$	$I_{calc}8$	$I_{calc}9$	$I_{calc}10$
AAA	52.0	50.8	50.4	51.0	50.4	50.2	49.8	49.5	49.3	48.9	48.7
AAS	22.4	20.6	20.8	20.5	22.1	22.3	23.0	23.3	23.4	23.5	24.6
SAS	5.6	7.8	8.0	7.6	6.8	6.8	6.4	6.6	6.6	6.0	6.1
ASA	15.7	16.0	16.4	15.6	15.5	15.8	15.8	16.2	16.4	16.3	16.6
SSA	3.8	4.2	3.9	4.5	4.5	4.3	4.4	3.9	3.8	3.9	3.6
SSS	0.5	0.6	0.6	0.7	0.7	0.6	0.6	0.5	0.5	0.5	0.5
$r_A$used		0.17	0.17	0.17	0.22	0.22	0.25	0.25	0.25	0.30	0.30
$r_s$used		0.92	0.80	1.00	1.00	0.92	0.92	0.80	0.77	0.77	0.70
Mean dev.†		1.0	0.9	0.8	0.7	0.6	0.7	0.8	0.9	0.9	1.2

*Results from program PODIS3, simulating the copolymer as reported in [15]. Initial feed concentration = f_A^0/f_S^0 = 80/20; conversion = 98%.

†Mean deviation between the observed and the calculated triads.

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would be negligible. Djekhaba and Guillot[15] have reported $r_A = 0.17$, and $r_S = 0.92$. By varying the $\{r_i\}$ values, the triad sequences can be readily simulated with program PODIS3 (Table I). It appears that the best result for this sample occurs at $r_A = 0.22$, $r_S = 0.92$. With these reactivity ratios, the predicted CCD can be readily obtained (Fig. 1).

Computer-Assisted Analytical Approach

Whereas the computer simulation/visual fitting approach is instructive, it can become rather tedious and time-consuming. In some cases, it also lacks accuracy. An alternative is to directly analyze the experimental NMR triad data and, through computer fitting, obtain the optimal r_1 and r_2 values.

Methodology

The method is depicted schematically in Figure 2. At the lower part of the figure, one starts with the NMR spectrum from which the triad intensities are calculated from integrations of the appropriate resonances. A suitable

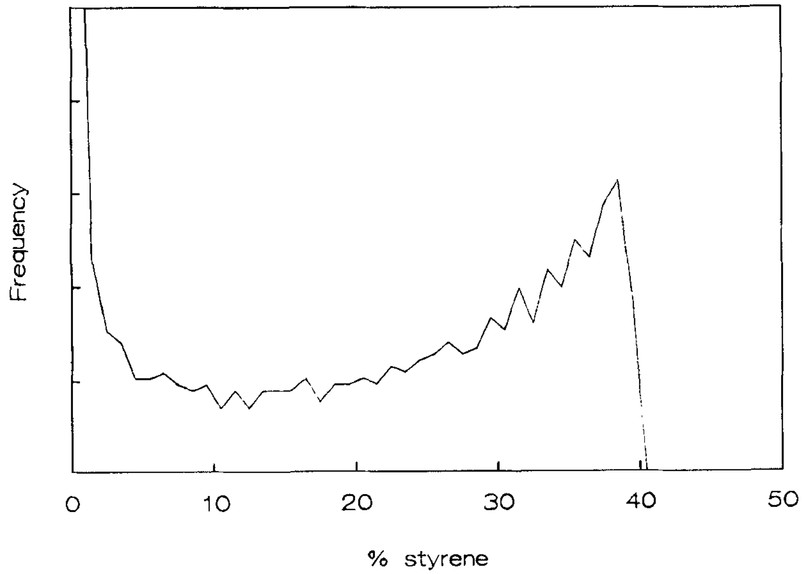

FIGURE 1 Predicted CCD of styrene/ethyl acrylate copolymer. The parameters used are: $r_A = 0.22$, $r_S = 0.92$; $f_A^0/f_S^0 = 80/20$; conversion = 98%. The molecular weight is arbitrarily set high (degree of polymerization = 35,000) to minimize statistical heterogeneity.

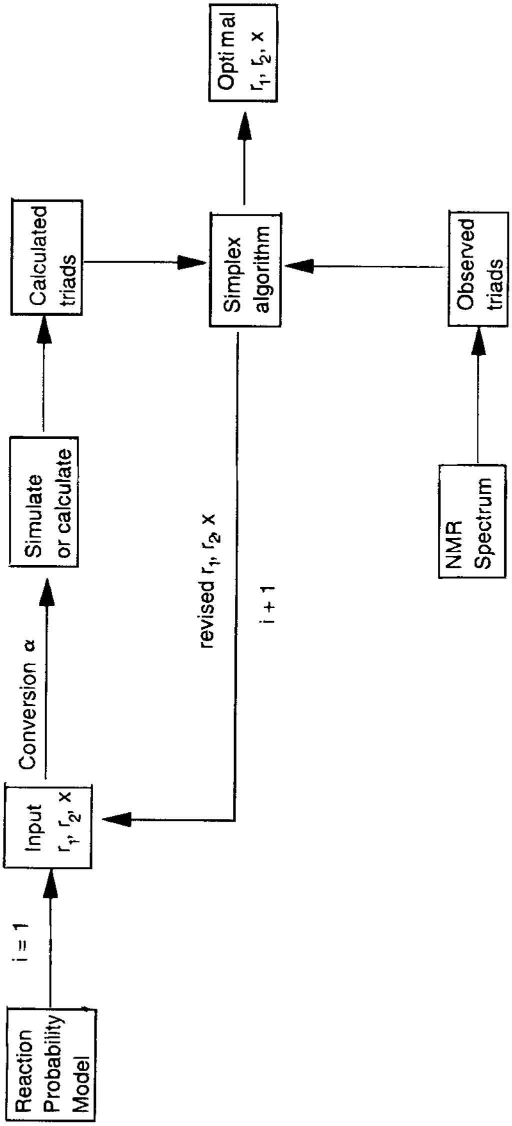

FIGURE 2 Scheme for program NMRCONV.

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copolymerization model is then presumed (usually Bernoullian or first-order Markovian). To start the iteration, one first enters the expected values of the reactivity ratios (r_1, r_2), or makes guesses of them. The predicted triad intensities at a given conversion may be obtained in two ways. One may use the integrated copolymerization equations[1] and numerically evaluate the equations. One may also use computer simulation whereby an ensemble of polymer chains is produced and triad intensities obtained by counting all the sequences. In either case, the calculated triad data are compared with the observed data through a simplex algorithm, which systematically varies the parameters (r_1, r_2) to minimize the deviations between the observed and the calculated triads. If the quality of the NMR data is high, after a number of iterations the values of r_1 or r_2 would have been optimized.

For convenience, the entire procedure has been computerized. The resulting program (called NMRCONV) was written in QuickBasic. In its present form, the calculation of the triads was made through Monte Carlo simulations of polymerization and bookkeeping procedure to extract the copolymer composition and triad information. Although the computational time is longer in this way, this approach permits more flexible programming in more complex models (*e.g.*, multistate or second-order Markovian) or more complex polymerization processes (*e.g.*, sequential feed or multistage reactions) in the future.

In the use of program NMRCONV, the following data need to be entered: 1) at least one data set of complete NMR triads (six intensity values), 2) conversion (α) for each data set. As parameters, one may use comonomer reactivity ratios (r_1, r_2) and also comonomer feed ratio ($x^0 = f_1^0/f_2^0$). However, if one has some prior knowledge about the copolymer system, one may hold one (or more) of the parameters fixed during the fitting procedure.

As an example of this approach, the NMR triad data of styrene/butyl acrylate copolymers reported by Llauro *et al.*[16] have been fitted with the program NMRCONV. In this case, the comonomer feed concentrations have been kept constant ($x^0 = 0.235$). The NMR triad data at five conversions are reproduced in Table II. Through program NMRCONV it is clear that the optimal reactivity ratios are: $r_1 = 0.64$, $r_2 = 0.18$.

The fact that the agreement in the observed and the calculated data is good across a large range of conversions (5–87%) indicates that the first-order Markovian model is indeed a good description of this copolymer system.

TABLE II Analysis of Styrene (S)/Butyl Acrylate (B) Data by Program NMRCONV

Sequence	I_{obsd}	I_{calc}	*dev.*
SET 1 α = 5 %			
SSS	1.5	1.0	0.5
SSB	12.2	10.7	1.5
BSB	29.1	29.9	–0.8
SBS	21.8	21.4	0.4
BBS	25.8	27.8	–2.0
BBB	9.7	9.2	0.5
SET 2 α = 32.5 %			
SSS	0	0.6	–0.6
SSB	8.6	8.0	0.6
BSB	30.5	30.2	0.3
SBS	19.5	19.2	0.3
BBS	29.9	30.0	–0.1
BBB	11.6	11.9	–0.3
SET 3 α = 63 %			
SSS	0	0.4	–0.4
SSB	7	5.7	1.3
BSB	24.8	27.1	–2.3
SBS	12.6	14.5	–1.9
BBS	31.4	30.8	0.6
BBB	24.2	21.4	2.8
SET 4 α = 79 %			
SSS	0	0.5	–0.5
SSB	4.5	4.7	–0.2
BSB	23	23.0	0
SBS	12.3	11.5	0.8
BBS	27.6	27.6	0
BBB	32.6	32.7	–0.1
SET 5 α = 87.5%			
SSS	0	.3	–0.3
SSB	4.2	4.4	–0.2
BSB	19.2	20.8	–1.6
SBS	9.2	10.6	–1.4
BBS	25.7	24.8	0.9
BBB	41.7	39.1	2.6

Observed data taken from.[16]
Mean dev. (all data) = 0.9
Optimal Parameters:
reactivity ratios: $r_S = 0.639$ $r_B = 0.177$
feed S and B conc.: $f_S^0 = 0.224$ $f_B^0 = 0.776$

Different Modes of Operation

In the literature, a fair amount of information has been reported giving the NMR results as a function of conversion. Some papers gave very detailed NMR data, including all six triads, and sometimes even higher sequences.

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Some reported the intensities of only three of the six possible triads. Others provided only the overall polymer composition. In general, the data available can be approximately classified into four categories:

Category 1. Low Conversions, Different Comonomer Feed Ratios. This is the most commonly found. From the data on the low-conversion polymers, particularly feed concentrations (f_1^0 and f_2^0) and polymer composition (F_1 and F_2), reactivity ratios can be directly calculated via the well-known methods (*e.g.*, Mayo-Lewis,[17] Fineman-Ross,[18] and Kelen-Tudos[19]). Many more refined methods have also been developed.[20] The NMR data from the low-conversion polymers can be likewise analyzed to determine reaction probabilities and reactivity ratios.[21–24] It has been argued [22] that the NMR methods may be better than f_1^0/F_1 methods for the determination of reactivity ratios.

Category 2. Same Comonomer Feed Ratio, Different Conversions. Some data exist in this category. Experimentally, the samples may be generated by either separate polymerizations or by sampling a batch reactor at different times. Examples include styrene/butyl acrylate copolymers,[16] styrene/acrylonitrile copolymers[5] and methyl methacrylate/methyl acrylate copolymers.[8]

Category 3. Variable Comonomer Feed, Different Conversions. This is a more complex situation where both x^0 and α vary. Some examples of data in this category include the vinylidene chloride/vinyl acetate,[3] styrene/methyl methacrylate,[2] styrene/ethyl methacrylate,[6] styrene/methyl acrylate,[7] styrene/acrylonitrile,[5] and styrene/ethyl acrylate[15] copolymers.

Category 4. Variable Comonomer Feed, Almost 100% Conversion. Some industrial polymers fall in this category. To optimize end-use properties, a manufacturer may vary the comonomer feed ratios, and then allow each polymerization to proceed to completion (in order to maximize polymer yield). Some data in the literature also belong to this category. Examples are styrene/ethyl acrylate,[9] styrene/methyl methacrylate,[25] styrene/acrylonitrile,[26] vinyl chloride/vinylidene chloride,[27] and acrylamide/acrylic acid[28] copolymers.

The program NMRCONV has been written to accommodate all four types of data categories. Two versions of the program are available. In the first version, the initial feed ratio (x^0) is considered to be the same for all the datasets. In this case, one can even treat x^0 as a parameter and include it in the fitting procedure. Thus, in this version of the program, it is not necessary to know exactly the initial feed ratio.

In the second version of the program, the input can permit different comonomer feed ratios and different conversions. In this case, it is not possible to treat $\{x_i^0\}$ as parameters in the fitting process. The x_i^0 value for each dataset i is considered accurate by the program.

More Examples

Examples will be given of data in each category. Data in category 2 has been illustrated earlier (Table II). An example of category 1 has been published by Borbely *et al.*[29] concerning the acrylonitrile(A) /methacrylic acid(M) copolymers. Four of their copolymers samples (all made at low conversions) have been arbitrarily chosen for analysis with program NMRCONV. The observed and the calculated data are given in Table III. The agreement is good, with $r_M = 2.78$, $r_A = 0.20$. These values compare favorably with the reported values[29]: $r_M = 3.14$, $r_A = 0.163$.

The second example is taken from a paper by Doremaele *et al.*[7] on styrene(S) / methyl acrylate(M) copolymers. They reported the NMR data of several copolymers at variable monomer feeds and at different conversions (Category 3). The calculated results (via program NMRCONV) are given in Table IV together with the observed data. The fit is satisfactory with $r_S = 0.81$, $r_M = 0.16$. These values compare well with the reactivity ratios obtained at low conversions[7]: $r_S = 0.73$, $r_M = 0.19$.

In the last example, analysis has been made of two commercial vinyl chloride(1)/vinylidene chloride(2) copolymers.[27] In these cases, the copolymers are presumed to be 100% converted. Calculation with program NMRCONV gives surprisingly good results (Table V). However, the reactivity ratios for the two samples are not the same:

sample B1:	$r_1 = 0.14$,	$r_2 = 2.72$
sample B2:	$r_1 = 0.16$,	$r_2 = 5.44$

Note that this calculation assumes that the only source of compositional heterogeneity is conversion. Also, batch polymerization is assumed. It is not known that for these two samples either of these assumptions is valid. The different values of r_2 perhaps suggest that the two polymers have been made via slightly different processes.

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TABLE III Analysis of Acrylonitrile (A)/Methacrylic Acid(M) Copolymers by Program NMRCONV

Sequence	set 1		set 2		set 3		set 4	
	I_{obsd}	I_{calc}	I_{obsd}	I_{calc}	I_{obsd}	I_{calc}	I_{obsd}	I_{calc}
AAA	0	0.1	3.8	1.6	60.2	62.5	77.3	74.5
AAM	1.4	1.4	14.9	10.5	22.8	21.7	12.0	15.4
MAM	9.5	9.5	17.2	18.3	2.5	1.9	0	0.9
AMA	1.5	1.3	10.8	8.0	12.0	11.6	9.6	8.1
MMA	13.6	17.9	29.7	31.0	2.4	2.3	1.2	1.1
MMM	73.9	70.0	23.6	30.5	0.1	0.1	0.1	0.0
	α	7.4%		5.5%		4.5%		5.5%
	x^0	0.0299		0.1136		2.0675		3.4248

Observed data from.[29]
Mean dev. (all data) = 1.7
Optimal Parameters: reactivity ratios: $r_A = 2.778$ $r_M = 0.202$

Knowing the reactivity ratios, one can simulate the CCD curve using program PODIS3. For illustration, the calculated CCD for vinyl chloride/vinylidene chloride copolymer sample B2 is given in Figure 3.

Critique of the Approach

The advantages of the present approach (program NMRCONV) are given as follows: 1) the method in its computerized form is relatively easy to use; 2) it permits direct fitting of the high-conversion NMR data to obtain

TABLE IV Analysis of Styrene (S)/Methyl Acrylate (M) Copolymers by Program NMRCONV

Sequence	set 1		set 2		set 3		set 4	
	I_{obsd}	I_{calc}	I_{obsd}	I_{calc}	I_{obsd}	I_{calc}	I_{obsd}	I_{calc}
SSS6.9	4.9	9.1	9.2	68.6	58.6	53.5	52.4	
SSM	22.2	20.2	26.8	27.6	19.4	23.8	27.5	26.8
MSM	24.0	24.5	21.1	21.0	0	2.6	0	3.3
SMS	24.1	25.4	31.0	28.7	11.2	14.1	17.1	16.1
MMS	18.1	18.3	12.0	12.2	0.8	0.9	1.9	1.4
MMM	4.8	6.6	0	1.3	0	0	0	0
	α	92%		14.3%		99%		9.7%
	x^0	0.85		0.85		5.7		4.78

Observed data from.[7]
Mean dev. (all data) = 1.6
Optimal Parameters: reactivity ratios: $r_S = 0.806$ $r_M = 0.160$

TABLE V Analysis of Vinyl Chloride/Vinylidene Chloride Copolymers by Program NMRCONV

Sequence	*Sample B1*		*Sample B2*	
	I_{obsd}	I_{calc}	I_{obsd}	I_{calc}
111	16.2	16.3	36.0	36.9
112	9.9	9.2	13.0	13.1
212	14.9	16.3	9.3	8.6
121	8.6	8.8	6.7	6.8
221	24.8	24.2	16.8	16.6
222	25.7	25.1	18.2	18.0
Mean dev.		0.6		0.3
α	99.9%		99.99%	
f_1^0	0.419		0.584	
f_2^0	0.581		0.416	
Reactivity ratios:				
r_1		0.141		0.157
r_2		2.721		5.443

Observed data from.[27] 1 = vinyl chloride, 2 = vinylidene chloride.

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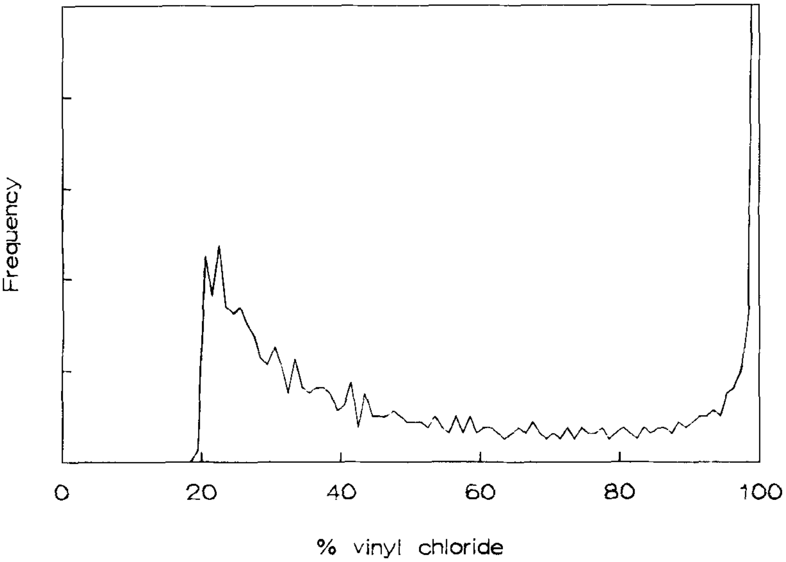

FIGURE 3 Calculated CCD of vinyl chloride/vinylidene chloride copolymer sample B2.

copolymerization parameters; 3) data on low-conversion copolymers are not needed. 4) the program is flexible. With suitable changes in the Monte Carlo algorithm, one can allow for process variations or other statistical models in the simulations.

Although this approach is user-friendly, it does have its limitations. The following observations may be useful to a prospective user.

1. In all cases, it is assumed that the NMR assignments are correct and the triads are accurately determined. Furthermore, the conversion is known. If these assumptions are not valid, the method may not produce the right answers.
2. In version 1 of the program, it is possible to treat r_1, r_2, and x^0 as parameters. However, the fitting is faster (and more accurate) if some prior information on comonomer feed ratio (x^0) is available. For example, one may consult the polymerization records for the comonomer feeds. Alternately, one may make suitable measurements and derive x^0. For data belonging to *Category 4* (*i.e.,* almost complete conversion), one may equate the initial feed concentrations (f_1^0 , f_2^0) to the copolymer composition (F_1, F_2).
3. Sometimes x^0 is not available. Version 1 of the program can treat it as a parameter (together with r_1 and r_2) and carry out the fitting procedure. However, in this case one needs accurate NMR data (and/or a large number of data sets) in order to obtain reliable results.
4. For commercial samples where no record of polymerization is available, accurate results are more difficult to obtain. One may need more analytical data to guide the NMR analysis. One possibility is to combine fractionation with NMR (*vide infra*). Another possibility is to determine the CCD of the copolymer by some means. In turn, the CCD of the copolymer may provide clues as to the polymerization process used (*e.g.,* continuous or batch process). For example, if the polymer exhibits a narrow compositional distribution, the data can be simply analyzed by the Bernoullian or Markovian models in their conventional forms. If the polymer has a broad CCD curve and appears to exhibit conversion heterogeneity, then further analysis of the polymer is needed.
5. Although the emphasis in this work is conversion heterogeneity, other kinds of compositional heterogeneity exist (*e.g.,* statistical, multi-state, or process).[14] For a polymer of unknown origin, it is often desirable to fractionate the polymer and obtain the NMR data of the polymer fractions. For

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example, the NMR/fractionation result may provide some clues as to the nature of the compositional heterogeneity. Furthermore, the NMR/fractionation data may be analyzed through some of the methodologies previously reported for heterogeneous polymers.[30–33]

CONCLUSION

In this paper two methodologies are presented that can be used to treat the NMR data of copolymers made at high (and low) conversions. The computer-assisted analytical approach (program NMRCONV) provides a means to analyze the NMR data directly to give the reactivity ratios. The computer simulation approach (program PODIS3) can be used either to determine, or to confirm, the reactivity ratios. In addition, it provides the calculated CCD curve. The two approaches are complementary and (where appropriate) can be used together to maximize the information content of the NMR data.

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