MEASUREMENT OF COPOLYMERIZATION REACTIVITY
RATIOS BY NMR

High resolution NMR techniques have been applied successfully to
polymer systems since about early 1960 (1), and, in most cases, the
success of these applications depends primarily on the measurement of
chemical shifts or coupling constants or both. The true significance of
area measurements in NMR has often been minimized or even complete-
ly neglected. It has been well established that areas under bands in
NMR spectra are generally directly proportional to the concentration of
the species giving rise to that band (2). In order that these measure-
ments be quantitative, one usually needs only to invoke the requirement
of similar line shapes in the bands being compared or measured. In this
paper, we wish to illustrate the use of NMR in determining copolymer
composition, and specifically to utilize data in the accurate calculation
of reactivity ratios.

It is well known that a knowledge of reactivity ratios can indicate
structural features simply from considerations of the value of the $r_1 r_2$
product and the individual reactivity ratio values (3). Furthermore, a
knowledge of the reactivity ratios can allow one to calculate the se-
quence distribution in free-radical-derived copolymers, and Harwood and
Ritchey (4) have not only calculated the sequence distribution for sty-
rene–methyl methacrylate but have found quantitative support of this
sequence distribution from NMR measurements on the α-methyl resonance
in the copolymer.

One of the three general methods used for the calculation of monomer
reactivity ratios, the Fineman and Ross method (3,5) has generally
proved to be the most useful, and it has been employed in this work. In
most copolymerization reactions, the composition is primarily determined
by propagation since initiation and termination reactions occur far less
frequently than do propagation reactions. Thus, under steady-state con-
ditions, the consumption of monomers is given by

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left(\frac{r_1[M_1]/[M_2] + 1}{([M_1]/[M_2])\, 2r_2} \right) \tag{1}$$

where M_1 and M_2 refer to monomer concentrations of monomer 1 and 2,
and r_1 and r_2 are the monomer reactivity ratios as they are conventional-
ly defined. If one assumes that at very low conversions $d[M_1]/d[M_2]$
is equal to m_1/m_2, where m_1 and m_2 refer to polymer composition in
mole fractions, then, with the definitions of $f = m_1/m_2$, and $F = M_1/M_2$,
eq. (1) can easily be arranged to

$$(F/f) (f - 1) = r_1 (F^2/f) - r_2 \qquad (2)$$

Thus a plot of the lefthand side of eq. (2) versus F^2/f yields a linear plot with the slope equal to r_1 and the intercept to $-r_2$.

Experimental

Polymer Preparation. The copolymers used in this study were prepared in the suspension system at 70°C. in nitrogen-purged 8-oz. bottles tumbling in a water bath. The general recipe employed is given in Table I. Yields in most cases were restricted to less than 2% by using short time periods (10–20 min.). The resulting polymers were washed several times with methanol to remove excess monomer and dried under reduced pressure at 50°C.

TABLE I

Polymer Recipe

Material	Wt., g.
Mixed monomers, 10–90% AN	50
Water, distilled	100
t-Butyl peroxy pivalate	0.075
t-Dodecyl mercaptan	0.05
Poly(vinyl pyrrolidone), dispersant	0.1

Polymer Analyses. The standard Kjeldahl analysis was essentially that employed, the only exception being that the sample was introduced in 100-mg. tin cups. This was found to be very helpful. The indicator was a mixture of bromcresol green and methyl red. The precision of the Kjeldahl analytical data is easily seen in Figures 2 and 3.

Nuclear Magnetic Resonance Analysis. The copolymers were all examined in dimethyl sulfoxide-d_6 (DMSO-d_6) in the temperature range 70–90°C. and at a concentration of 10–20% (w/v) copolymer. A fully equipped Varian DP-60 spectrometer was employed and has been described elsewhere (6). One typical spectrum of each of the three copolymer systems studied is shown in Figures 1a, 1b, 1c. The DMSO-d_6
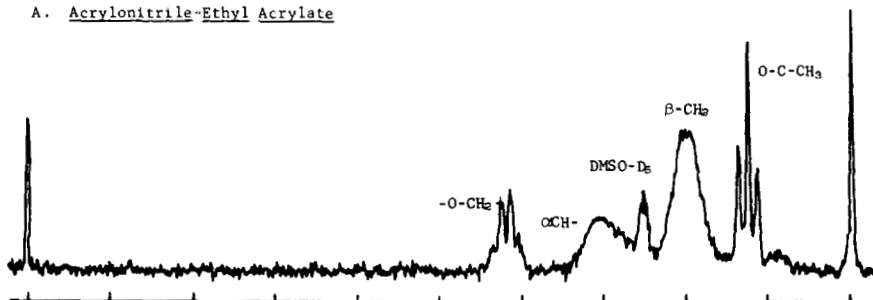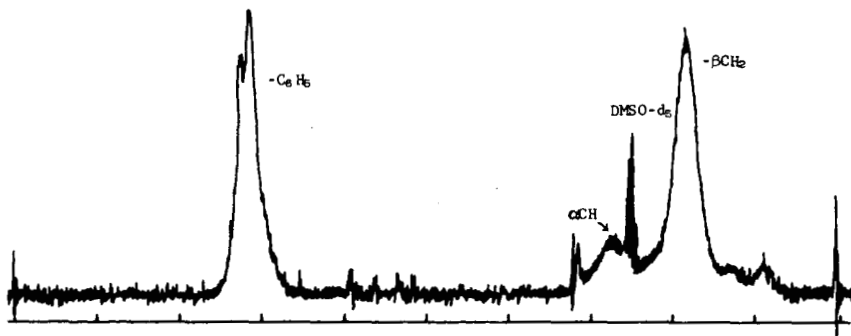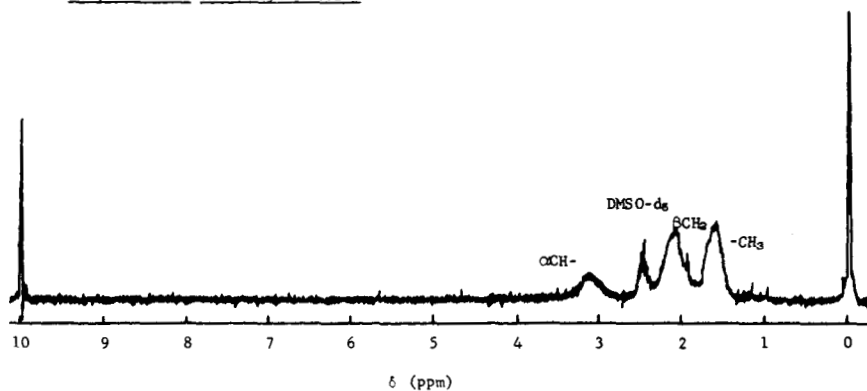
A. Acrylonitrile-Ethyl Acrylate

B. Acrylonitrile-Styrene

C. Acrylonitrile-Methacrylonitrile

Fig. 1. NMR spectra for various copolymers.

shown in each spectrum is present as an isotopic impurity of DMSO-d_6. DMSO-d_6 is very hygroscopic, and, hence, a resonance line due to H_2O

is also observed. Other pertinent line assignments are given.

In order to calculate the composition of a copolymer, it is necessary to integrate the total area of all polymer spectral lines and that of a given peak for which one knows the number of protons in one of the monomer units giving rise to said peak. In the ethyl acrylate—acrylonitrile (EA—AN) system, the lowest field peak in the spectrum (Fig. 1a) is due to the OCH_2 group. It was on the basis of this line that the copolymer composition was determined. In the styrene—acrylonitrile (S—AN) system, the peak appearing at lowest field (Fig. 1b) is due to the protons in the phenyl rings, and these were utilized in determining the composition of this copolymer system. Finally, in the acrylonitrile—methacrylonitrile (AN—MAN) system (Fig. 1c), the composition was based on the backbone methyl in MAN.

Discussion

Acrylonitrile—Ethyl Acrylate. Shown in Table II are the copolymer compositions derived from the NMR spectral measurements, along with the charge compositions, and, in all cases, conversion was held to approximately 2% or less. The data is plotted according to the method of Fineman and Ross (5) (AN = M_1 in all cases), as shown in Figure 2 (the circled points are derived from the NMR data and the diamonds from the Kjeldahl analysis data). The actual line was drawn utilizing the method of least squares. The precision of both methods is obviously quite acceptable. However, as one goes to higher nitrile-content copolymers,

TABLE II

Acrylonitrile—Ethyl Acrylate Feed and Copolymer Composition

Sample No.	F, AN/EA mole ratio	f, AN/EA mole ratio in polymer
1	0.210	0.239
2	0.809	1.16
3	1.26	1.42
4	1.89	2.14

the Kjeldahl analysis may tend to yield results which are on the low side (not shown). Other workers have encountered low nitrile analysis in high nitrile-content copolymers (16). However, in this system, the analyses by both methods yield accurate reactivity ratios. The r_1r_2 product gives an indication of the nature of the polymer (3). When this product is unity, the copolymer is composed primarily of random sequences of the comonomers. If the product is somewhat less than unity,
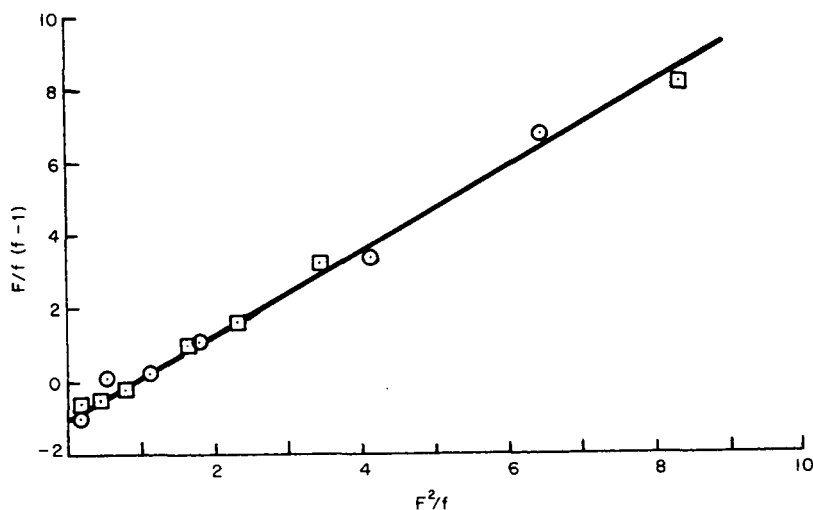
Fig. 2. Acrylonitrile–ethyl acrylate r_1 and r_2 analysis: $r_1 = 1.12$ and $r_2 = 0.93$; O, NMR analysis; □, Kjeldahl analysis.

then block sequences are present. It should be noted that in this system we observe an r_1, r_2 product of 1.04, suggesting that this copolymer is highly random in nature and could be construed as being an almost ideal random copolymer. Our values for r_1 and r_2 are compared with literature values (7,8) in Table III.

TABLE III

Reactivity Ratios of Acrylonitrile–Ethyl Acrylate

	r_1	r_2
This work	1.12	0.93
L. J. Young (7)	0.44	0.95
J. Brandrup (8)	1.17	0.67

   Acrylonitrile–Styrene. Shown in Table IV are the feed and copolymer composition data; these data are plotted in Figure 3. The least squares line was constructed utilizing only the NMR data. Again, it is noted that the precision here is quite acceptable. The reactivity ratios determined are given in Table V, and are compared with those of other work-
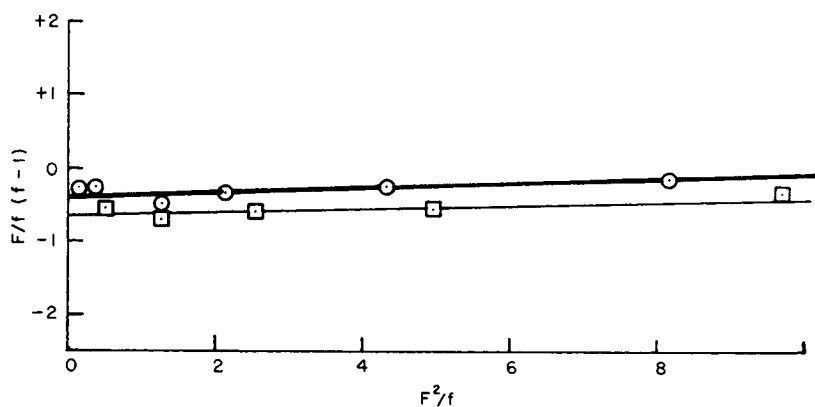
Fig. 3. Acrylonitrile–styrene r_1 and r_2 analysis: $r_1 = 0.057_6$ and $r_2 = 0.39_8$; O, NMR analysis; □, Kjeldahl analysis.

TABLE IV

Acrylonitrile–Styrene Feed and Copolymer Composition

Sample No.	F, AN/S mole ratio	f, AN/S mole ratio in polymer
1	0.218	0.426
2	0.490	0.66
3	0.840	0.627
4	1.31	0.802
5	1.96	0.890
6	2.94	1.05

ers (9–12). It is seen that our results are in reasonable agreement with those previously obtained with this well-studied system. Referring again to Figure 3, it is also noted that the Kjeldahl results, while still displaying reasonably good precision, do tend to be somewhat lower in total nitrile content than those obtained by NMR; r_1 determined from the Kjeldahl data would fall in the range 0.02–0.03. It seems clear, then, that the NMR method appears to provide a more accurate determination of reactivity ratios in nitrile-containing copolymer systems. The fact that the nitrile analyses appear to be somewhat lower by Kjeldahl analysis may be explained on the basis that, in this copolymer system, the r_1r_2 product is considerably less than unity ($\sim$0.02), suggesting that

TABLE V

Reactivity Ratios of Acrylonitrile–Styrene

	r_1	r_2
This work	0.058	0.40
Lewis et al. (9)	0.04	0.41
Simha and Wall (10)	0.05	0.37
Fordyce (11)	0.03	0.52
Goldfinger and Steidlitz (12)	0.02	0.45

the styrene units here are present in large blocks. The spectra also indicate this, due to the presence of a second resonance line appearing in the phenyl region. It has been suggested (13) that styrene sequences of four or five monomer units or more must be present in order to observe this second phenyl resonance line. Since the acrylonitrile is present in low concentration, this may cause the Kjeldahl analysis to be less accurate; or it may be due to sequence distribution (4) effects. It has been observed (14) in another system that, at constant composition and molecular weight, changing the sequence distribution markedly affects the copolymer solubility. NMR does not seem to have this nitrile analysis limitation, since NMR composition analysis is not dependent on the degradation properties of a polymer.
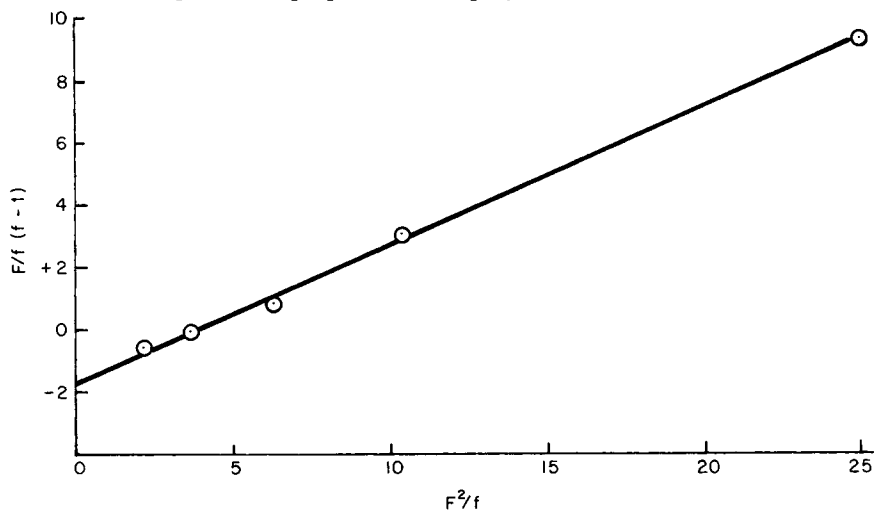

Fig. 4. Acrylonitrile–methacrylonitrile r_1 and r_2 analysis: $r_1 = 0.43$ and $r_2 = 1.69$.

TABLE VI

Acrylonitrile–Methacrylonitrile Feed and Copolymer Composition

Sample No.	F, AN/MAN mole ratio	f, AN/MAN mole ratio in polymer
1	1.26	0.676
2	1.89	0.971
3	2.95	1.38
4	5.06	2.46
5	11.4	5.18

Acrylonitrile–Methacrylonitrile. Shown in Table VI are the composition data from which the plot in Figure 4 was constructed. The precision observed here was quite good, and the calculated reactivity ratios are given in Table VII. The r_1r_2 product is 0.73, which suggests that the methacrylonitrile tends to be present in blocks. Also given in Table VI is the only literature value (15) found for this system. While the discrepancy here appears quite large, it is not surprising, for the measurement of composition of this system by conventional techniques should prove to be exceedingly difficult.

TABLE VII

Reactivity Ratios of Acrylonitrile–Methacrylonitrile

	r_1	r_2
This work	0.43	1.69
Berry et al. (15)	0.32	2.68

Summary

We have attempted here to demonstrate the utility of polymer compositional analysis by application of NMR. More specifically, we have applied it to three copolymers of acrylonitrile: ethyl acrylate, styrene, and methacrylonitrile. We have shown in the first case that the reactivity ratios do agree with those obtained by the classical Kjeldahl method of analysis. In the second case, the Kjeldahl analysis gives results lower than those obtained by NMR. In the latter case, we demonstrate the same ease of obtaining the reactivity ratios for the copolymer in which both monomers contain nitriles, whereas this would be exceedingly diffi-

cult to do by conventional analyses. Furthermore, we suggest that in the ethyl acrylate—acrylonitrile system, both the classical and NMR analyses give agreeing results due to the random nature of the copolymer. In the styrene—acrylonitrile case, this is not true because the acrylonitrile tends to be present in very short sequences, and, traditionally, conventional methods of analysis for nitrile-containing polymers have given low results or have been difficult; this may be due to sequence distribution effects. Finally, we would like to suggest that, in the future, NMR will be utilized to a considerably greater extent in determining various parameters which can be obtained from compositional data in heteropolymer systems.

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