Sequence and Composition of an Amino Ethylene-Ethylene Sulfonate Copolymer by Carbon-13 Nuclear Magnetic Resonance

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Synopsis

^{13}C NMR spectra of a series of aminoethylene-ethylenesulfonate copolymers of varying composition have been taken. It has been found that the methylene groups of the copolymer are clear indicators of amine–amine, sulfonate–sulfonate, and amine–sulfonate sequence diads. Combinations of peak areas with composition data from elemental analysis allows quantitative determination of diad frequencies. Once elemental analysis data for several copolymer compositions have been obtained ratios of peak areas may be used to determine unknown polymer compositions with excellent sensitivity.

INTRODUCTION

Interest in our laboratories in water-soluble polymers with reactive functional groups has led to the synthesis of a series of aminoethylene-ethylenesulfonate copolymers.[1] The reaction sequence for synthesis of these copolymers is as follows:
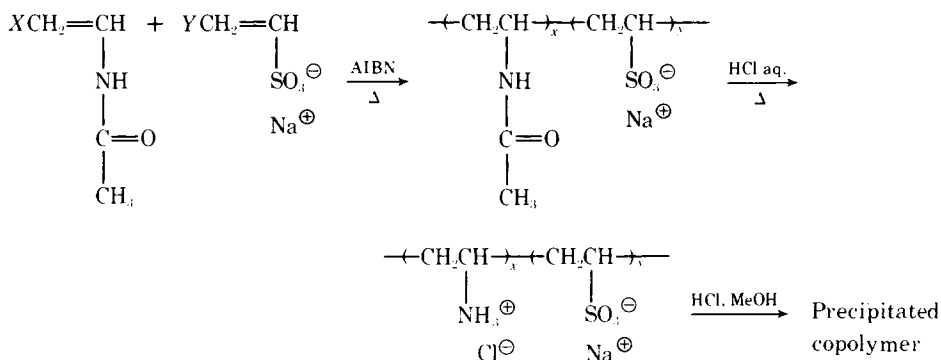
Since it was possible that the sequencing of the reactive amine groups would influence their reactivity, determination of sequence for this copolymer was desirable. Also, due to possible differences in incorporation of aminoethylene and ethylenesulfonate into the polymer, a check of final composition was also necessary.

EXPERIMENTAL

Polymer samples were prepared as follows:

(1) To a 4 dram (approximately 16 ml) vial with a screw cap the following were added: 1.0 ml H_2O, 0.5 ml NaOH 18 M, 0.5 ml D_2O, 0.1 ml dioxane (internal reference), and 1.0 g polymer.

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(2) The vial was then capped and allowed to stir on a hot-plate stirrer with surface temperature 60°–80° until a clear amber solution was obtained—usually about 15 min.

(3) Final pH was then checked. In all cases final pH was found to be 13.0 ± 0.3. pH of 13.0 was employed to insure all amino groups were in the unprotonated form. Spectra were recorded on a Varian XL-100 Spectrometer at 25.2 MHz using pulsed NMR with Fourier transform.

The following instrument settings were used: spectral width, 5000 Hz; acquisition time, 0.400–0.800 sec; pulse width, 16 μsec; sensitivity enhancement, 0.400–0.800 sec; true spectral width, 5120; and Hz/point, 1.25–2.50. The ppm scale was defined by setting the dioxane solvent peak at 67.4 ppm.

RESULTS AND DISCUSSION

Spectra for the homopolymers, poly(aminoethylene)[2] and poly(sodium ethylenesulfonate) are shown in Figures 1(a) and 1(b). Spectra for copolymers of 53%, 54%, 60%, and 66% amine units are given in Figures 1(c)–1(f).

Peak Assignments

The spectrum of polyaminoethylene given in Figure 1(a) shows two major peaks: one at 46.0 ppm and one at 45.0 ppm. It would be difficult to predict from this spectrum alone which would be the $—CHNH_2—$ peak and which would be the $—CH_2—$ peak. Consideration of the copolymer spectra in Figures 1(c)–1(f), however (see below), allows for assignment of the methine $—CHNH_2—$ peak as 46.0 ppm and the methylene peak as 45.0 ppm. Minor peaks in the 20–30 ppm and 40–50 ppm ranges due to catalyst (AIBN) fragments which have been incorporated into the copolymer end groups are also visible.

The spectrum of poly(sodium ethylenesulfonate) given in Figure 1(b) shows two major peaks which are easily assigned as the methine $—CHSO_3—$ peak at 55.2 ppm and the methylene peak(s) at 30.5–35.5 ppm. The minor peaks in this spectrum are not identified. Since this unpurified homopolymer is only a model compound used in peak assignment in the amine-sulfonate copolymers, investigation of these peaks was not pursued further.

The spectra of the copolymers of varying amine-sulfonate composition are given in Figures 1(c)–1(f). Assignment of the methine $—CHNH_2—$ and $—CHSO_3—$ carbon peaks as 46.0 and 55.2 ppm can be made from the spectra of polyaminoethylene [Fig. 1(a)] and poly(sodium ethylenesulfonate) [Fig. 1(b)]. Assignment of the other three peaks can be made in terms of methylene groups for the three possible sequence diads:
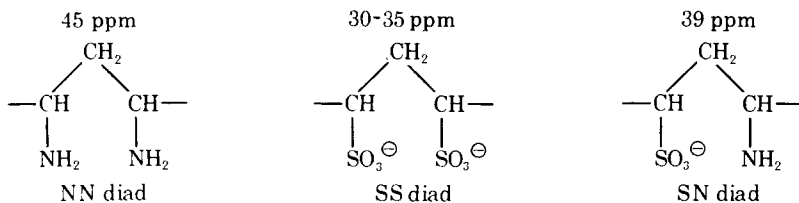
These assignments also seem clear from the methylene signals of the homopolymers as seen in the spectra given in Figures 1(a) and 1(b).
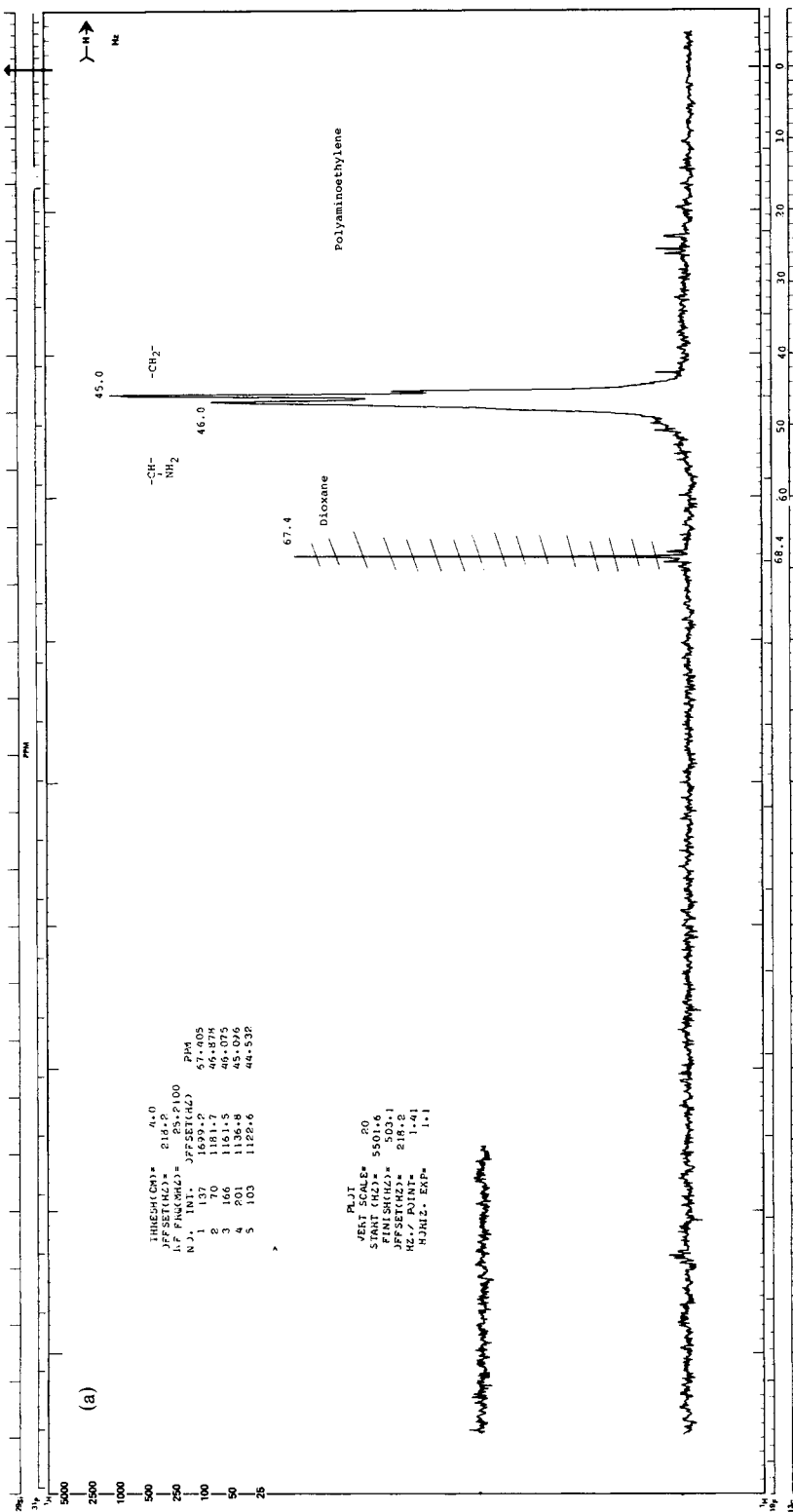
Fig. 1. ^{13}C NMR spectra of polyaminoethylene, polyethylenesulfonate, and four amino ethylene-ethylenesulfonate copolymers of varying composition in H$_2$O-D$_2$O, pH 13.0, proton decoupled with dioxane as internal standard.

Fig. 1. (Continued from previous page.)
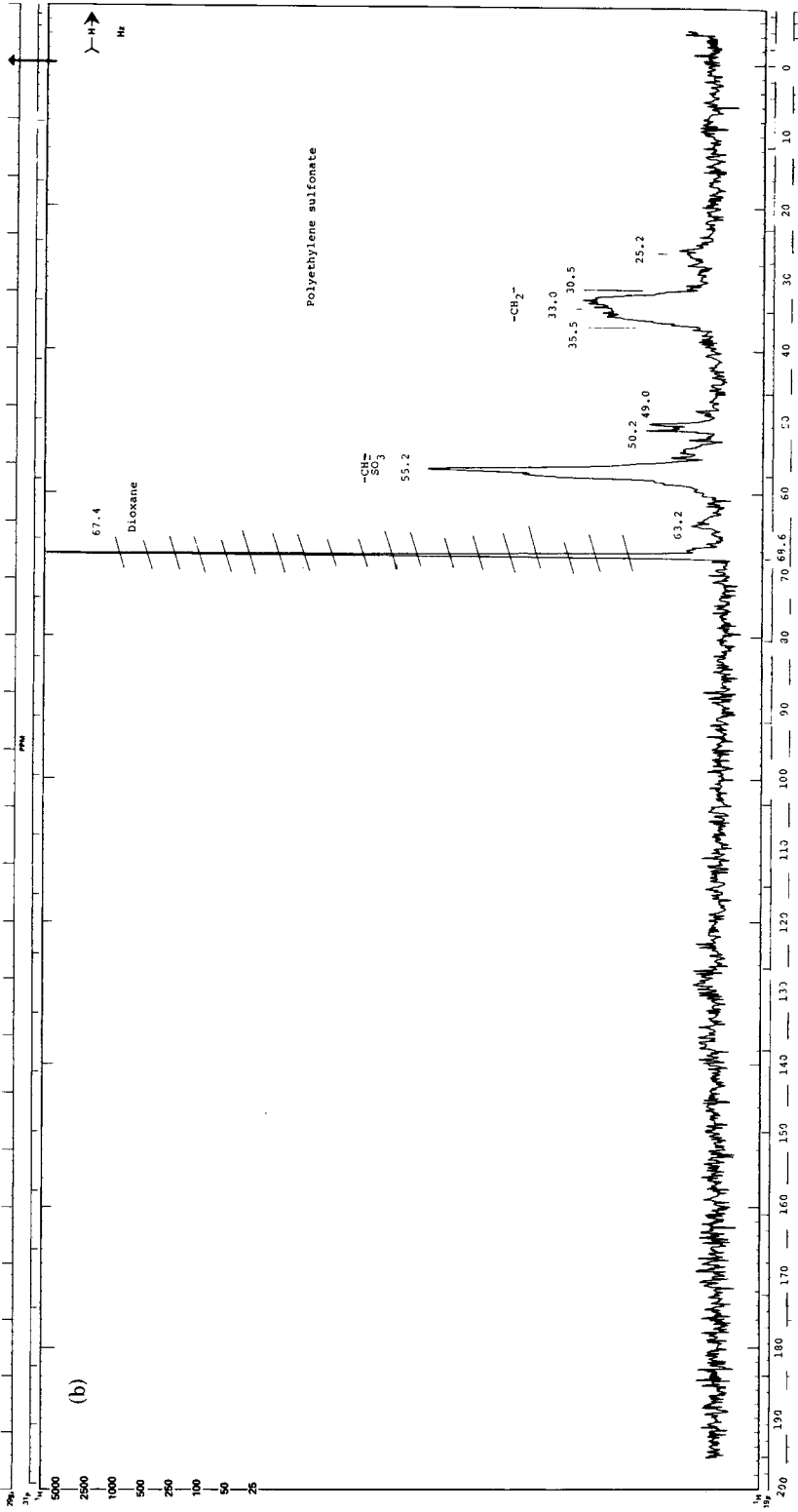
Fig. 1. (Continued from previous pages.)

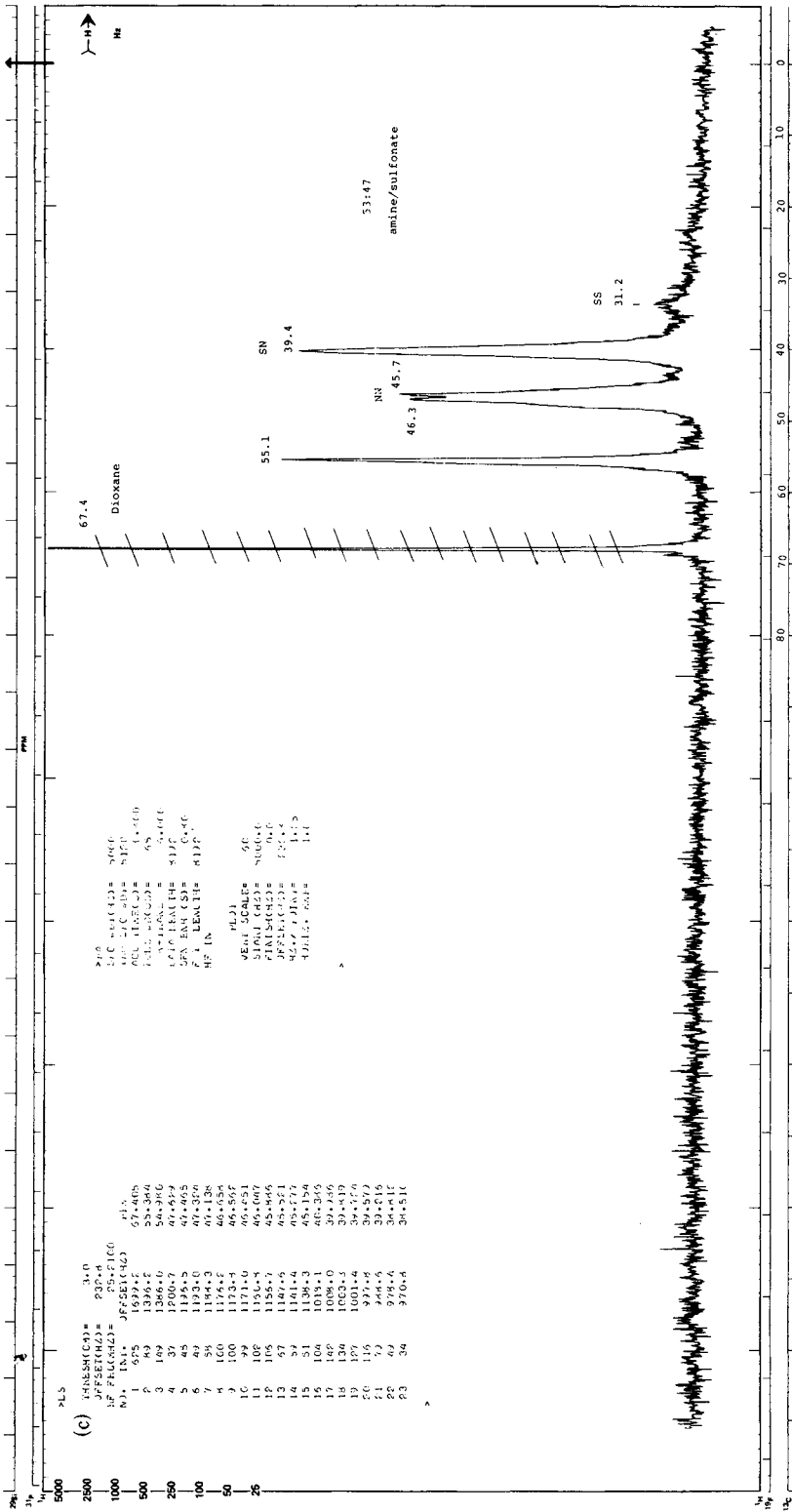Fig. 1. (Continued from previous pages.)

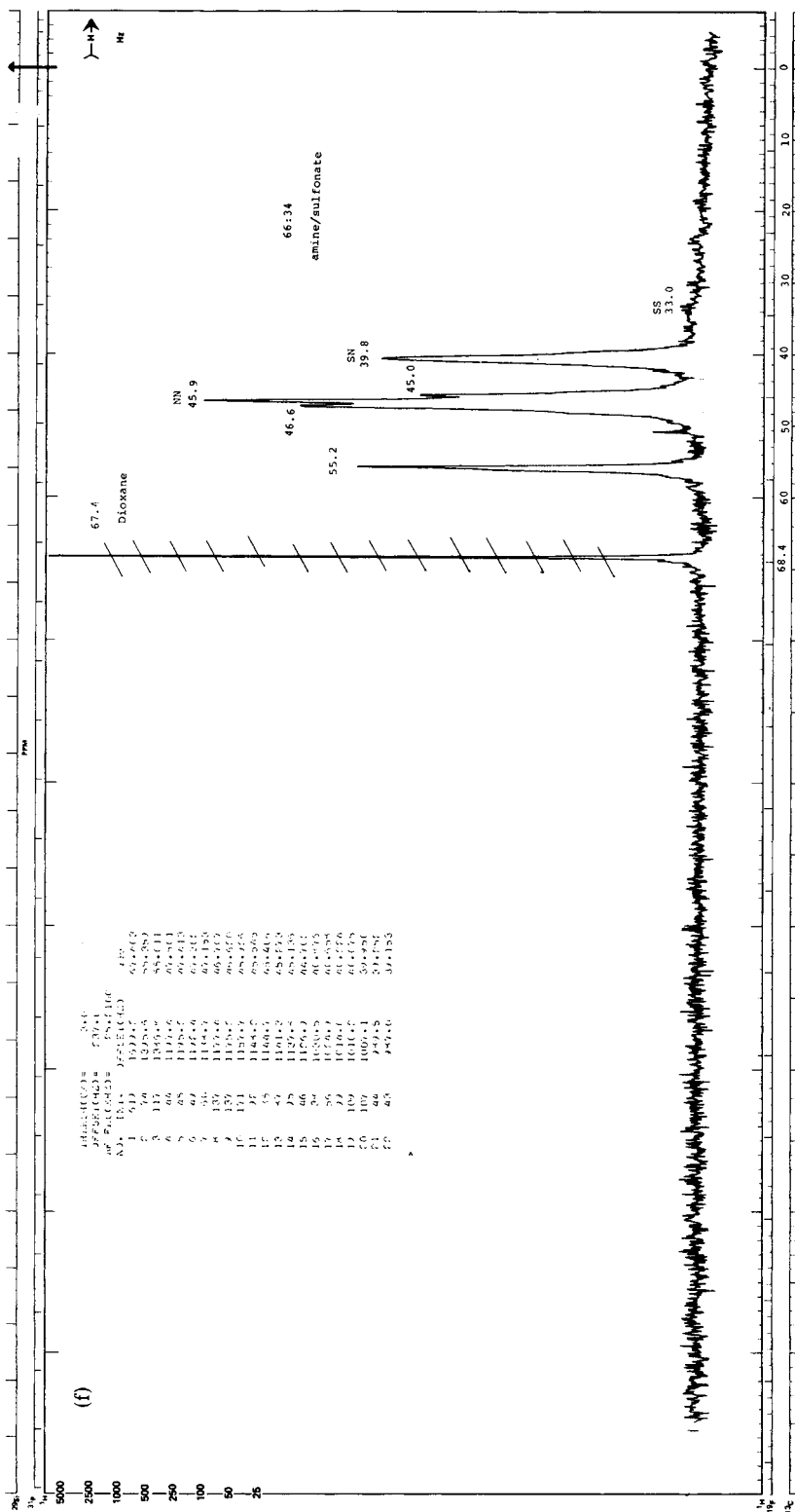Fig. 1. (Continued from previous pages.)

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SEQUENCE IN TERMS OF FREQUENCY OF DIADS

If the methylene peak for each of the three diads were completely resolved from all other peaks and if the assumption were made that the nuclear Overhauser effects were the same for each diad methylene (so that peak area were exactly proportional to diad frequency) then diad frequency could simply and directly be measured from the copolymer spectrum. The NN diad methylene signal, however, is not fully resolved from the methine —$CHNH_2$— signal. It is therefore necessary to use overall copolymer composition as determined from elemental analysis in combination with peak area data to obtain diad frequency. Using the relative peak areas of the SN and SS diad methylene groups in combination with overall composition as determined by elemental analysis N:S ratio, frequency of diads for the copolymers of varying composition have been calculated and are given in Table I.

COPOLYMER COMPOSITION FROM PEAK AREAS

Overall copolymer composition may be, and has in this study, been obtained by elemental analysis. This method of determining overall composition, however, is accurate to only ±2% for polymer samples of this type and is subject to error from nitrogen or sulfur containing impurities in any given sample. Simple analysis of the ^{13}C spectrum of the copolymer provides an alternate method for determination of composition which is accurate to ±0.2% of composition and is not nearly as subject to error from nitrogen or sulfur containing impurities.

It can be seen by inspection of the copolymer spectra in Figures 1(c)–1(f) that the area of the SN diad methylene peak at 39 ppm decreases sharply and area of the composite —CHNH— and NN diad methylene peak at 45–46 ppm increases sharply as overall amine units increase from 53% to 66%. The ratio of the area of the 45–46 ppm peak to 39 ppm peak is a very sensitive indicator of overall copolymer composition. The value for this ratio may be calibrated using well purified samples of copolymer that have been carefully analyzed for overall composition by elemental analysis. This ratio can then be plotted against the percent of amine units for the pure copolymers of known composition to provide a composition calibration curve. Any number of data points may be added to this calibration curve. When enough data points from copolymers of various composition, as determined by repeated elemental analysis, have been added such that the curve itself has an uncertainty of <0.1% in terms of overall composition then the curve may be used to determine composition more accurately than by elemental analysis.

TABLE I

Monomer Sequence in a Series of Aminoethylene-Ethylenesulfonate Copolymers Expressed as Frequency of Diads as Determined by ^{13}C NMR

Composition by elemental analysis	Diad frequency as percent of total diads		
	SS	SN	NN
53:47	5.6	82.8	11.6
54:46	6.4	79.2	14.4
60:40	3.9	72.2	23.9
66:34	3.3	61.4	35.3

References

1. D. J. Dawson, K. Otteson, P. Wang, and R. E. Wingard, Jr., unpublished.
2. D. J. Dawson, R. D. Gless, and R. E. Wingard, Jr., *J. Am. Chem. Soc.*, **98,** 5996 (1976).