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Improvement in the determination of triad distributions in ethylene–propylene copolymers by ^{13}C nuclear magnetic resonance

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A quantitative ^{13}C nuclear magnetic resonance analysis of an ethylene–propylene copolymer produced on a modern high-field instrument produces a spectrum with eight discrete groups of peaks. Assignment of these peaks provides eight simultaneous equations to describe the six triad distribution numbers. We have demonstrated the advantages of solving directly this over-determined set of equations. We have observed that the relative uncertainty in the different triad numbers is approximately constant, and have used this observation to discuss the uncertainties in individual triad numbers as a function of their concentration.

(Keywords: ethylene–propylene copolymer; sequence distributions; nuclear magnetic resonance)

INTRODUCTION

During the last two decades ^{13}C n.m.r. spectroscopy has become a valuable and indispensable analytical tool among polymer chemists. For example, the determination of *n*-ad distribution numbers is frequently a prerequisite in the characterization of copolymers. Randall[1], in his review article from 1989, discusses in great detail how to extract triad concentrations from ^{13}C n.m.r. spectra of ethylene-based copolymers. Generally speaking, triad distribution numbers of copolymers are determined by the relative intensities (areas) of well defined regions in the ^{13}C n.m.r. spectrum. The inherent uncertainties in the determination of triad concentrations are dependent on how well these regions are separated and to what accuracy these integrated regions can be determined. If no significant overlap of peak areas occurs, the uncertainty in the intensity of the region is mainly determined by the quality of the spectrum, i.e. the signal-to-noise ratio. This ratio can be improved by increasing the total number of transients. However, increasing the number of scans extends the experimental time, a factor that one would normally like to keep to a minimum. Thus, a compromise between a short experimental time and the desire for a high-quality spectrum (low uncertainty of a measured integral region) must be encountered. Surprisingly, few—if any—have critically discussed the inherent uncertainty in *n*-ad distribution numbers derived from n.m.r. integral measurements.

With this in mind, we will discuss in more detail the inherent uncertainties in n.m.r. integral measurements and the consequent propagation of errors in derived copolymer parameters such as *n*-ad concentrations. Our discussion will be limited to polypropylene/polyethylene (PP/PE) copolymers. Part of the work will be devoted to the question of how to estimate the expected uncertainty of triad concentrations of a PP/PE copolymer without having to perform the actual n.m.r. experiment.

EXPERIMENTAL

The PP/PE copolymer was dissolved in *o*-dichlorobenzene (ODCB) (approximately 10 wt% of polymer in solution). The spectra were run at 130°C on a Varian XVR 300 n.m.r. spectrometer operating at 75 MHz ^{13}C resonance frequency. A pulse angle of approximately 30° and an acquisition time of 3 s were applied. A repetition time of 10 s ensured quantitative sampling of the free induction decay (f.i.d.). The carbon signals were sampled under ^{1}H decoupling using the WALTZ decoupling pulse sequence to remove any coupling between proton and carbon nuclei. Full nuclear Overhauser effect (NOE) was obtained. A sweep width of 20 kHz was used and the f.i.d. was stored in a double precision mode. A total of 500 transients were sampled, corresponding to a total experimental time of approximately 1 h. Fourier transformation was performed on the final signals after applying a line broadening of 3 Hz. The final spectra were baseline corrected using a second-order polynomial. The areas (intensities) of the regions of interest were measured by digital integration. Six replicas of

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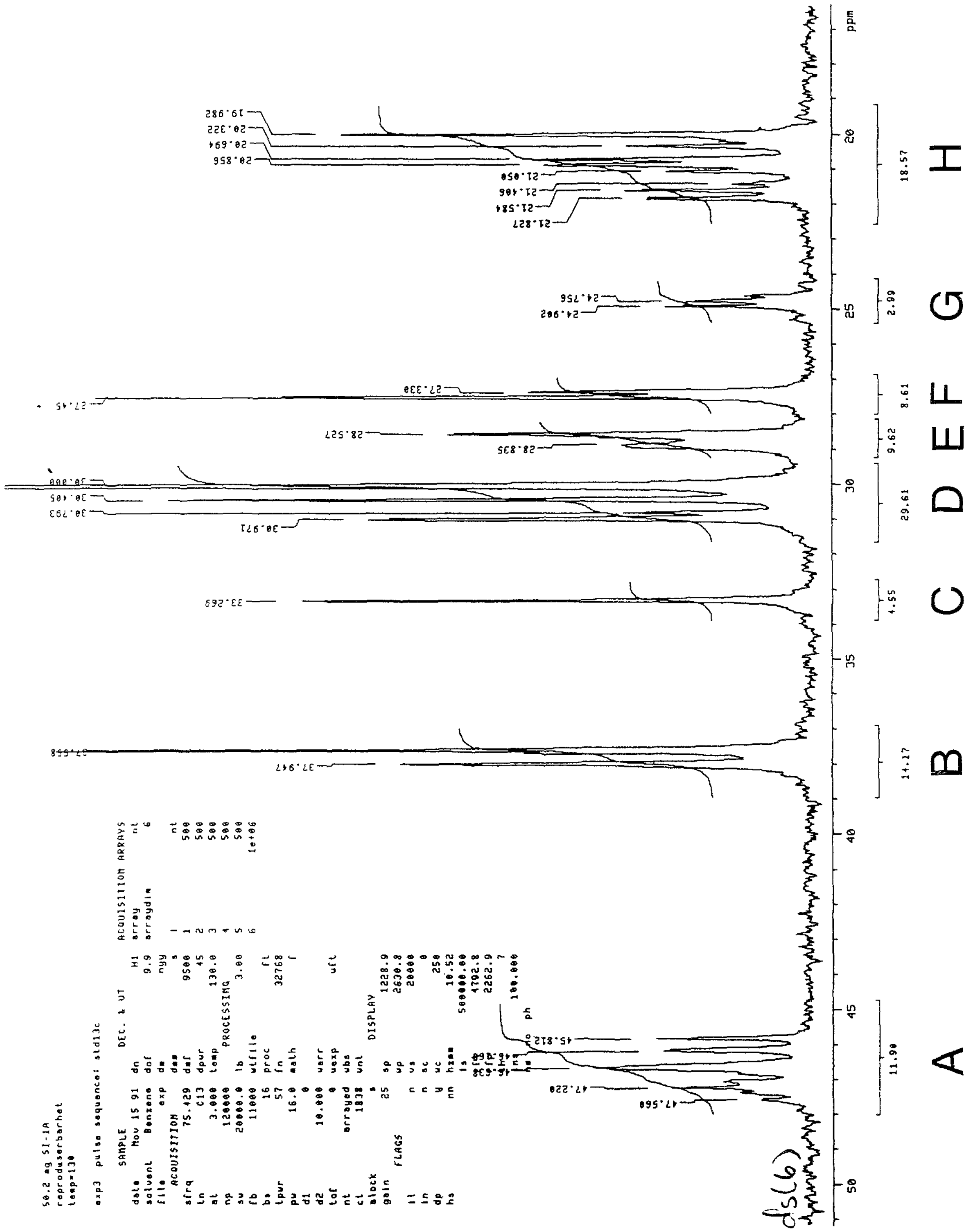

Figure 1 ^{13}C n.m.r. spectrum of a PE/PP copolymer the same sample were measured under the same conditions as previously described.

DERIVED COPOLYMER PARAMETERS FROM N.M.R. INTENSITIES

A typical ^{13}C n.m.r. spectrum of a PP/PE copolymer is shown in *Figure 1*, where the eight integral regions of interest (A–H) are depicted. These eight integral regions result in eight equations available to extract the six triad concentrations: These equations are presented below[1]:

$$T_A = k[\mathrm{PPP} + \tfrac{1}{2}(\mathrm{PPE} + \mathrm{EPP})] \tag{1}$$

$$T_B = k[\mathrm{PEP} + \tfrac{1}{2}(\mathrm{PEE} + \mathrm{EEP}) + \mathrm{EPE} + \tfrac{1}{2}(\mathrm{PPE} + \mathrm{EPP})] \tag{2}$$

$$T_C = k(\mathrm{EPE}) \tag{3}$$

$$T_D = k[2(\mathrm{EEE}) + (\mathrm{PPE} + \mathrm{EPP}) + \tfrac{1}{2}(\mathrm{PEE} + \mathrm{EEP})] \tag{4}$$

$$T_E = k(\mathrm{PPP}) \tag{5}$$

$$T_F = k(\mathrm{PEE} + \mathrm{EEP}) \tag{6}$$

$$T_G = k(\mathrm{PEP}) \tag{7}$$

$$T_H = k[\mathrm{PPP} + (\mathrm{PPE} + \mathrm{EPP}) + \mathrm{EPE}] \tag{8}$$

The constant k is a normalization constant. Randall[1] has emphasized that, in cases where there is a possible overlap of spectral regions (in particular between regions, D, E and F), a systematic error might arise in the derived triad concentrations. In this case equations (4)–(6) are combined into one single region TDEF, equation (9):

$$T_{DEF} = T_D + T_E + T_F = k[2\mathrm{EEE} + (\mathrm{PPE} + \mathrm{EPP}) + \tfrac{3}{2}(\mathrm{PEE} + \mathrm{EEP}) + \mathrm{PPP}] \tag{9}$$

Equations (1), (2), (3), (7), (8) and (9) can be solved to give unique triad concentrations. The results are summarized in equations (10)–(15):

$$k(\mathrm{EEE}) = \tfrac{1}{2}(T_{DEF} + T_A + T_C + 3T_G - T_B - 2T_H) \tag{10}$$

$$k(\mathrm{PEE} + \mathrm{EEP}) = T_H + \tfrac{1}{2}T_B - T_A - 2T_G \tag{11}$$

$$k(\mathrm{PEP}) = T_G \tag{12}$$

$$k(\mathrm{EPE}) = T_C \tag{13}$$

$$k(\mathrm{EPP} + \mathrm{PPE}) = \tfrac{1}{2}(2T_H + T_B - 2T_A - 4T_C) \tag{14}$$

$$k(\mathrm{PPP}) = \tfrac{1}{2}(3\mathrm{T}_A + 2\mathrm{T}_C - \tfrac{1}{2}\mathrm{T}_B - \mathrm{T}_H) \tag{15}$$

Our experience is that spectral overlap of regions D, E and F is rare at 75 MHz ^{13}C resonance frequency. Thus, a better approach would be to solve the over-determined set of equations (1)–(8). This will be discussed in the next section.

Table 1 Observed integral regions on a PP/PE copolymer of six replica measurements of the same sample

Experiment	A	B	C	D	E	F	G	H
1	12.18	14.50	4.73	29.41	9.57	8.58	2.75	18.28
2	12.11	14.71	4.60	29.71	9.58	7.95	2.55	18.79
3	12.71	14.10	3.95	29.53	9.42	8.47	2.36	19.47
4	12.44	14.27	4.29	30.11	9.13	7.96	2.23	19.57
5	12.01	14.18	4.42	30.07	9.47	8.46	2.78	18.62
6	11.90	14.17	4.55	29.61	9.62	8.61	2.99	18.57
AVR	12.23	14.32	4.42	29.74	9.47	8.34	2.61	18.88
STDV	0.30	0.24	0.28	0.29	0.18	0.30	0.28	0.52

RESULTS AND DISCUSSION

The eight integral regions A–H measured on six replica ^{13}C n.m.r. spectra of the same PP/PE copolymer are shown in *Table 1* together with the average integral values (AVR) and corresponding standard deviations (STDV).

The data in *Table 1* indicate that the observed uncertainty (standard deviation) of an integral is constant (except for the data in the last column) and independent of the absolute value of the integral. This observation is in agreement with numerous other experimental results obtained on analogous copolymer samples studied in our laboratory, and we make the general statement that the absolute uncertainty of an n.m.r. integral is constant and independent of the absolute intensity of the integral region. One should keep in mind, however, that this constant is dependent on the experimental parameters used in running an n.m.r. spectrum. When changing the repetition time, pulse angle, number of transients or the polymer concentration, this 'absolute' uncertainty will change accordingly. However, under identical experimental conditions this uncertainty will be constant. This observation is of great value and will be adopted beneficially when trying to estimate the uncertainty of triad concentrations, or any polymer parameter derived from these integral regions, by computer simulation. This idea will be discussed in the next section. The triad concentrations can be determined by solving equations (1)–(8) analytically, without reducing the number of equations, by a linear least-squares analysis. Such an approach is rather appealing because it will yield a good test of the internal consistency of the data. These results are given by equations (16)–(21):

$$k(\mathrm{EEE}) = \mathrm{a}_{11}\mathrm{T}_A + \mathrm{a}_{12}\mathrm{T}_B + \mathrm{a}_{13}\mathrm{T}_C + \mathrm{a}_{14}\mathrm{T}_D + \mathrm{a}_{15}\mathrm{T}_E + a_{16}T_F + a_{17}T_G + a_{18}T_H \tag{16}$$

$$k(\mathrm{PEE} + \mathrm{EEP}) = a_{21}T_A + a_{22}T_B + a_{23}T_C + a_{24}T_D + a_{25}T_E + a_{26}T_F + a_{27}T_G + a_{28}T_H \tag{17}$$

$$k(\mathrm{PEP}) = a_{31}T_A + a_{32}T_B + a_{33}T_C + a_{34}T_D + a_{35}T_E + a_{36}T_F + a_{37}T_G + a_{38}T_H \tag{18}$$

$$k(\mathrm{EPE}) = a_{41}T_A + a_{42}T_B + a_{43}T_C + a_{44}T_D + a_{45}T_E + a_{46}T_F + a_{47}T_G + a_{48}T_H \tag{19}$$

$$k(\mathrm{EPP} + \mathrm{PPE}) = a_{51}T_A + a_{52}T_B + a_{53}T_C + a_{54}T_D + a_{55}T_E + a_{56}T_F + a_{57}T_G + a_{58}T_H \tag{20}$$

Table 2 Calculated coefficients a_{ij} (equations (16)–(21)) derived by solving equations (1)–(8)

i	1	2	3	4	5	6	7	8
1	−0.1627	−0.1386	0.4880	0.5000	0.5120	−0.1807	0.1386	−0.3494
2	0.0241	0.1687	−0.0723	0.0000	0.0723	0.9157	−0.1687	−0.0964
3	0.0482	0.3373	−0.1446	0.0000	0.1446	−0.1687	0.6627	−0.1928
4	−0.2651	0.1446	0.7952	0.0000	0.2048	−0.0723	0.1446	0.0602
5	0.3133	0.1928	−0.9398	0.0000	−1.0602	−0.0964	−0.1928	0.7470
6	0.2651	−0.1446	0.2048	0.0000	0.7952	0.0723	0.1446	−0.0602

$$k(\mathrm{PPP}) = a_{61}T_{\mathrm{A}} + a_{62}T_{\mathrm{B}} + a_{63}T_{\mathrm{C}} + a_{64}T_{\mathrm{D}} + a_{65}T_{\mathrm{E}} + a_{66}T_{\mathrm{F}} + a_{67}T_{\mathrm{G}} + a_{68}T_{\mathrm{H}} \qquad (21)$$

The coefficients a_{ij} are presented in *Table 2*.

Thus, triad concentrations can be solved by two different approaches as summarized by the two sets of equations (10)–(15) and (16)–(21). In the discussion that follows we simply denote these solutions 'A' (equations (10)–(15)) and 'B' (equations (16)–(21)). The derived concentrations are calculated from the integral regions A to H for each of the six replicas shown in *Table 1*. The average values and corresponding standard deviations are summarized in Table 3.

Table 3 Average n-ad concentrations as determined from the data presented in *Table 1* by use of equations (10)–(15) ('A') and equations (16)–(21) ('B'). The numbers in parentheses represent standard deviations. The averages of the 'A' and 'B' solutions are given in the last column

Triads	'A'	'B'	('A'+'B')/2
(EEE)	0.247 (0.024)	0.251 (0.008)	0.249
(PEE+EEP)	0.214 (0.021)	0.209 (0.006)	0.211
(PEP)	0.065 (0.007)	0.070 (0.006)	0.067
(EPE)	0.110 (0.007)	0.110 (0.007)	0.110
(PPE+EPP)	0.123 (0.018)	0.128 (0.023)	0.126
(PPP)	0.242 (0.007)	0.233 (0.004)	0.237

Except for the (PPE + EPP) concentration the standard deviation of the triad concentrations determined by method 'B' is smaller than the corresponding standard deviation by method 'A'. A statistical comparison (Z-test) between the two sets of mean concentrations tells us that there is no significant difference between the 'A' and 'B' solutions based on a 0.01 significance level, and indicates that method 'B' is to be recommended over 'A' when calculating triad concentrations. It is not possible to make such a general statement at this stage. However, this question will be discussed more thoroughly in the next section.

In the last column of *Table 3* we have calculated the mean triad concentrations by the 'A' and 'B' methods. Applying equations (1)–(8) we can calculate the integrals of regions A–H and present these integrals as an eight-dimensional vector $\boldsymbol{T}$:

$$\boldsymbol{T} = (12.14,\ 13.96,\ 4.43,\ 29.50,\ 9.60,\ 8.53,\ 2.72,\ 19.11)$$

where the successive numbers represent the integrals of regions T_{A}, T_{B}, T_{C}, T_{D}, T_{E}, T_{F}, T_{G} and T_{H} respectively. All these integrals lie within the experimental uncertainty of the observed integrals in *Table 2*. The interesting property of these integrals is that they will give identical triad concentrations whether one is using method 'A' or method 'B'. The reason for introducing the vector $\boldsymbol{T}$ is a matter of convenience and will be explained in the next section.

UNCERTAINTY IN TRIAD CONCENTRATIONS DETERMINED BY SIMULATION

We have already seen that, for a particular choice of experimental conditions (pulse angle, repetition time, number of transients, etc.), the uncertainty in the integral of a particular region (A–H) will be constant and independent of the absolute integral of the region itself. An interesting question arises. Knowing the true triad concentrations of a copolymer, would it be possible to predict the expected uncertainty of these concentrations before actually running the n.m.r. experiment?

Assuming a Gaussian error distribution about the mean integral T_i of region i, we could simulate the error distribution function of any triad concentration by method 'A' or method 'B'. This implies that eight integral regions must be varied independently. Let 'σ' be the standard deviation of the integral T_i (i = A–H), which is assumed to be constant and independent of the integral T_i (i = A–H), and equal to 0.30 (see Table 1; $\Sigma T_i = 100$). The possible combinations of the eight error integrals of regions A–H can thus be written by an eight-dimensional integral vector of the form:

$$\boldsymbol{T}^{*} = (g_1,\ g_2,\ g_3,\ g_4,\ g_5,\ g_6,\ g_7,\ g_8)$$

where g_i represents the Gaussian error distribution of integral i.

To determine the distribution of triad concentrations within the range of integrals $\boldsymbol{T}$ given by:

$$\boldsymbol{T}' = \boldsymbol{T} + \boldsymbol{T}^{*}$$

where $\boldsymbol{T}$ is given by:

$$\boldsymbol{T} = (12.14,\ 13.96,\ 4.43,\ 29.50,\ 9.60,\ 8.53,\ 2.72,\ 19.11)$$

1000 $\boldsymbol{T}$ vectors were chosen randomly from the $\boldsymbol{T}^{*}$ distributions. The corresponding 1000 triad concentrations were calculated by method 'A' and method 'B', respectively. The results are presented in *Figure 2*, where only the envelopes of the respective triad frequency distributions are shown. The numerical data are well fitted to Gaussian functions with mean values and standard deviations given in *Table 4*.

Both methods predict the mean value of the triad concentrations with excellent accuracy, method 'B' somewhat better than method 'A'. The calculated uncertainties derived by method 'A' are significantly larger than those derived by method 'B'. The reason for this is probably the inherent 'self-correction' effect when

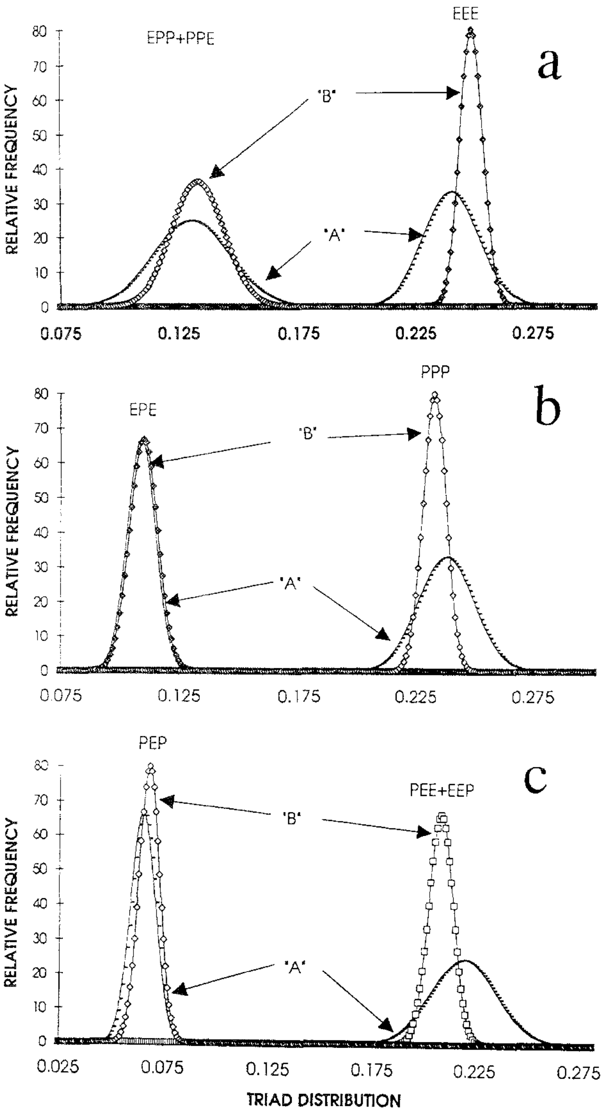

Figure 2 Relative frequency distribution of triads calculated by method 'A' and method 'B' (see text for further details): EPP+PPE and EEE, (b) EPE and PPP, (c) PEP and PEE+EEP

using the over-determined set of equations (method 'B'). One important question remains to be answered. How does the uncertainty of a triad concentration depend on the triad concentration itself? We will limit the discussion by applying only method 'B'.

ABSOLUTE UNCERTAINTY IN TRIAD CONCENTRATION

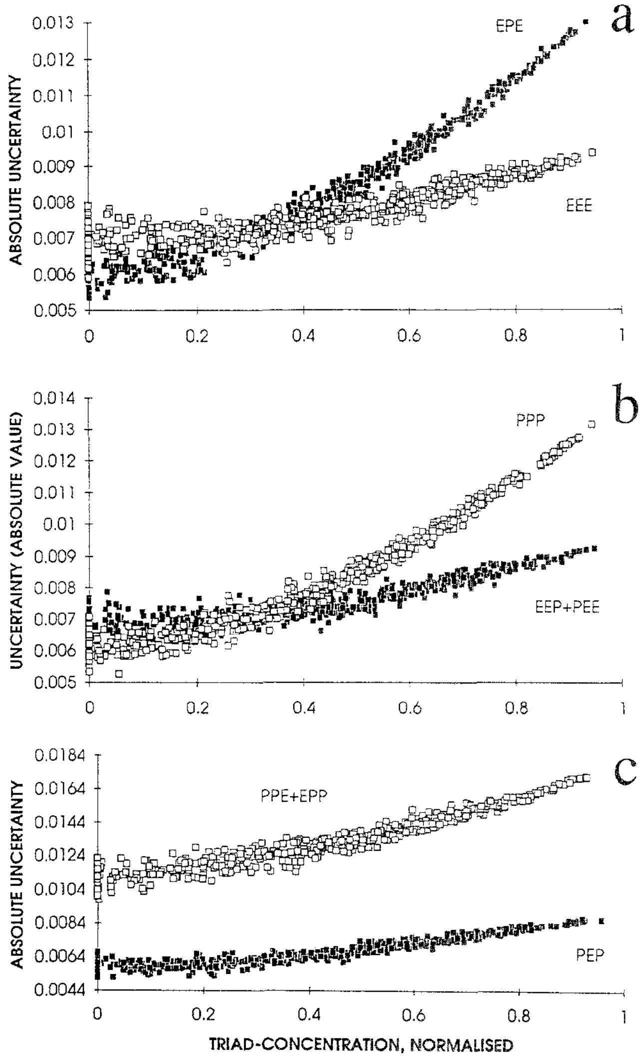

Figure 3 Absolute uncertainty of triad concentration vs. triad concentration: (a) EPE and EEE, (b) PPP and EEP+PEE, (c) PEP and PPE+EPP

So far we have discussed the uncertainty of the different triad concentrations for a specific choice of these concentrations. To determine how the absolute uncertainty in a specific triad concentration depends on the triad concentration itself, we can calculate this uncertainty by applying the traditional method of error analysis. The (normalized) concentration of a triad distribution (i), expressed by the integrals T_i and the coefficients a_{ij} (*Table 2*), can be written by equation (22):

$$(i) = \frac{\sum_j a_{ij} T_j}{\sum_m \sum_j a_{mj} T_j} \qquad (22)$$

The term (i) on the left-hand side of equations (22) is a shorthand notation for the specific triad concentration, $i = 1$ (EEE), $i = 2$ (PEE + EEP), $i = 3$ (PEP), $i = 4$ (EPE), $i = 5$ (EPP + PPE), $i = 6$ (PPP). The uncertainty (standard deviation) in each of the eight integrals T_i is the same and equal to σ_0. Using the principle of 'error of propagation' the standard deviation of (i) can be written:

$$\sigma(i) = \sigma_0 \left[\sum_j \left(\frac{\partial(i)}{\partial T_j} \right)^2 \right]^{1/2} \qquad (23)$$

Inserting equation (22) into equation (23), an analytical expression for the uncertainty (standard deviation, $\sigma(i)$)

Table 4 Mean values and standard deviations of triad concentrations determined by simulation. For further details, see text

(Triads	'A'	'B'	True value
(EEE)	0.240 (0.012)	0.249 (0.005)	0.250
(PEE+EEP)	0.219 (0.016)	0.208 (0.006)	0.210
(PEP)	0.065 (0.006)	0.068 (0.005)	0.067
(EPE)	0.109 (0.006)	0.110 (0.006)	0.110
(PPE+EPP)	0.130 (0.016)	0.133 (0.011)	0.126
(PPP)	0.238 (0.012)	0.233 (0.005)	0.237

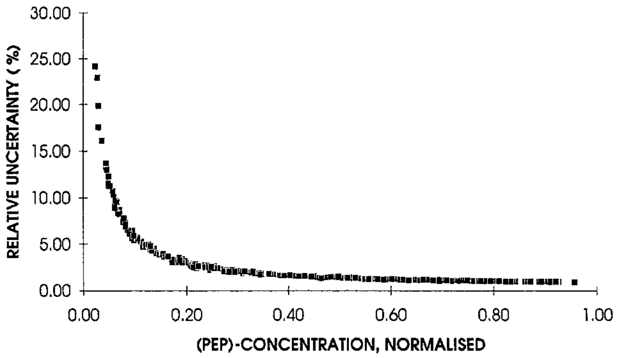

Figure 4 Relative uncertainty of triad concentration PEP

of the triad concentration (i) can be derived, equation (24):

$$\frac{\sigma(i)}{(i)} = \sigma_0 \left[\frac{\sum_j {a_{ji}}^2}{\left(\sum_j a_{ij} T_j\right)^2} + \frac{\sum_j \left(\sum_j a_{ij}\right)^2}{\left[\sum_j T_j \left(\sum_m a_{mj}\right)\right]^2} \right]^{1/2} \tag{24}$$

The integrals T_A to T_H have been varied randomly to produce 1000 combinations of normalized triad distribution concentrations. The derived standard deviation for each triad concentration is shown in *Figure 3*. One characteristic property of these plots is the broad range of σ (i) values for small (i). These observations simply tell us that the uncertainty related to a specific value of the triad concentration (i) is affected by the relative distribution of the five residual triad concentrations. As can be seen on *Figure 3*, the uncertainty in a triad concentration increases with increasing concentration. However, the relative uncertainty decreases, as demonstrated in *Figure 4* for $i = 3$ (PEP).

CONCLUSION

From the results obtained in this work we conclude that method 'B' using the over-determined set of eight equations would be the method of choice if triad concentrations are to be derived from n.m.r. integral measurements. This conclusion implicitly assumes that no overlap of integral regions exists in the n.m.r. spectrum which thus might lead to systematic errors in the derived triad concentrations as discussed by Randall[1]. Such an overlap of peaks has not been observed by us using a high-field spectrometer. The experimental n.m.r. data obtained on one copolymer sample made it possible to calculate the uncertainty of any normalized triad concentration. The results show that the uncertainty in a triad concentration is affected by the relative distribution of the other triad concentrations. This effect is larger for smaller values of (i).

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